Part Three

Energy Balances

Chapter 7

Energy and Energy Balances

Energy is expensive. We have not yet learned how to use efficiently the seemingly endless supply of "free" energy provided by the sun, winds, and tides; nuclear power generation is feasible, but the need for safe disposal of radioactive wastes from nuclear reactors is a serious unresolved problem; and there are not nearly enough waterfalls and dams to provide sufficient hydroelectric power to meet the world's energy needs. This leaves us with fuel combustion—burning a combustible gas, oil, or solid fuel, and using the energy released as a source of thermal or (indirectly) electrical energy.

Process industries have always recognized that wasting energy leads to reduced profits, but throughout most of this century the cost of energy was often an insignificant part of the overall process cost, and gross operational inefficiencies were tolerated. In the 1970s, a sharp increase in the price of natural gas and petroleum raised the cost of energy severalfold and intensified the need to eliminate unnecessary energy consumption. If a plant uses more energy than its competitors, its product could be priced out of the marketplace.

As an engineer designing a process, one of your principal jobs would be to account carefully for the energy that flows into and out of each process unit and to determine the overall energy requirement for the process. You would do this by writing **energy balances** on the process, in much the same way that you write material balances to account for the mass flows to and from the process and its units. Typical problems that may be solved using energy balances include the following:

1. How much power (energy/time) is required to pump 1250 m^3/h of water from a storage vessel to a process unit? (The answer determines the size of the required pump motor.)
2. How much energy is required to convert 2000 kg of water at 30°C to steam at 180°C?
3. A hydrocarbon mixture is distilled, producing a liquid and a vapor stream, each with a known or calculable flow rate and composition. The energy input to the distillation column is provided by condensing saturated steam at a pressure of 15 bar. At what rate must steam be supplied to process 2000 mol/h of the feed mixture?
4. A highly exothermic chemical reaction $A \rightarrow B$ takes place in a continuous reactor. If a 75% conversion of A is to be achieved, at what rate must energy be transferred from the reactor to keep the contents at a constant temperature?
5. How much coal must be burned each day to produce enough energy to generate the steam to run the turbines to produce enough electricity to meet the daily power requirements of a city of 500,000 people?
6. A chemical process consists of four reactors, 25 pumps, and a number of compressors, distillation columns, mixing tanks, evaporators, filter presses, and other materials handling and separation units. Each individual unit either requires or releases energy.

(a) How can the process operation be designed to minimize the total energy requirement? (For example, can the energy released by an energy-emitting process unit be transferred to an energy-absorbing process unit?)

(b) What is the total energy requirement for the process as it is finally designed, and how much will it cost to provide this energy? (The answer could determine whether or not the process is economically feasible.)

In this chapter we show how energy balances are formulated and applied. Section 7.1 defines the types of energy a process system can possess and the ways in which energy can be transferred to and from a system. Section 7.2 reviews the procedure for calculating the kinetic energy and gravitational potential energy of a process stream. Sections 7.3 and 7.4 derive the general energy balance equation for closed (batch) systems and open (semibatch and continuous) systems, and various applications of these equations are illustrated in Sections 7.5 through 7.7.

7.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to do the following:

- List and define in your own words the three components of the total energy of a process system and the two forms of energy transfer between a system and its surroundings. State the conditions under which heat and work are positive. Convert an energy or power (energy/time) expressed in any unit (e.g., J, dyne·cm, Btu, ft·lb_f/h, kW, hp) to its equivalent in any other dimensionally consistent units.
- Calculate the kinetic energy of a body of mass m moving with velocity u or the rate of transport of kinetic energy by a stream moving with mass flow rate $\dot{m}$ and velocity u. Calculate the gravitational potential energy of a body of mass m at elevation z or the rate of transport of gravitational potential energy by a stream moving with mass flow rate $\dot{m}$ at elevation z, where z is height above a reference plane at which potential energy is defined to equal zero.
- Define the terms **closed process system, open process system, isothermal process,** and **adiabatic process.** Write the first law of thermodynamics (the energy balance equation) for a closed process system and state the conditions under which each of the five terms in the balance can be neglected. Given a description of a closed process system, simplify the energy balance and solve it for whichever term is not specified in the process description.
- Define the terms **flow work, shaft work, specific internal energy, specific volume,** and **specific enthalpy.** Write the energy balance for an open process system in terms of enthalpy and shaft work and state the conditions under which each of the five terms can be neglected. Given a description of an open process system, simplify the energy balance and solve it for whichever term is not specified in the process description.
- State why the actual values of $\hat{U}$ and $\hat{H}$ can never be known for a given species in a specified **state** (temperature, pressure, and phase) and define the concept of a **reference state.** Explain in your own terms the statement, "The specific enthalpy of CO(g) at 100°C and 0.5 atm relative to CO(g) at 500°C and 1 atm is −12,141 J/mol." (Your explanation should involve a process in which carbon monoxide gas goes from one state to another.)
- Explain why the reference state used to generate a table of specific internal energies or enthalpies is irrelevant if one is only interested in calculating ΔU or ΔH for a process. (The term "state property" should appear in your explanation.)
- Given a process in which a specified mass m of a species goes from one state to another and tabulated values of $\hat{U}$ or $\hat{H}$ for the species at the initial and final states are available, calculate ΔU or ΔH. Given values of $\hat{V}$ at each state, calculate ΔH from the previously calculated ΔU or vice versa. Carry out the corresponding calculations to determine $\Delta \dot{U}$ and $\Delta \dot{H}$ for a stream with mass flow rate $\dot{m}$ going from one state to another.

- Use the saturated and superheated steam tables (Tables B.5, B.6, and B.7) to determine (a) whether water at a specified temperature and pressure is liquid, saturated vapor, or superheated vapor; (b) the specific volume, specific internal energy, and specific enthalpy of liquid water or steam at a specified temperature and pressure; (c) the vapor pressure of water at a specified temperature; (d) the boiling point of water at a specified pressure; and (e) the dew point of superheated steam at a specified pressure.
- Explain the significance of the specific internal energies and enthalpies tabulated in the steam tables (B.5, B.6, and B.7), remembering that we can never know the true values of either variable in a given state. Given any process in which a specified mass (or mass flow rate) of water changes from one state to another, use the steam tables to calculate ΔU (or $\Delta\dot{U}$) and/or ΔH (or $\Delta\dot{H}$).
- Given a description of any nonreactive process for which tabulated specific internal energies or specific enthalpies are available at all input and output states for all process species, (a) draw and completely label a flowchart, including Q and W (or $\dot{Q}$ and $\dot{W}_s$ for an open system) if their values are either specified or called for in a problem statement; (b) perform a degree-of-freedom analysis; and (c) write the necessary equations (including the appropriately simplified energy balance) to determine all requested variables.
- Starting with the open system balance equation, derive the steady-state mechanical energy balance equation (Equation 7.7-2) for an incompressible fluid and simplify the equation further to derive the Bernoulli equation. List all the assumptions made in the derivation of the latter equation.
- Given fluid conditions (pressure, flow rate, velocity, elevation) at the inlet and outlet of an open system and values of friction loss and shaft work within the system, substitute known quantities into the mechanical energy balance (or the Bernoulli equation if friction loss and shaft work can be neglected) and solve the equation for whichever variable is unknown.

7.1 FORMS OF ENERGY: THE FIRST LAW OF THERMODYNAMICS

The total energy of a system has three components:

1. **Kinetic energy:** Energy due to the translational motion of the system as a whole relative to some frame of reference (usually the earth's surface) or to rotation of the system about some axis. In this text, we will deal only with translational kinetic energy.
2. **Potential energy:** Energy due to the position of the system in a potential field (such as a gravitational or electromagnetic field). In this text, we will deal only with gravitational potential energy.
3. **Internal energy:** All energy possessed by a system other than kinetic and potential energy, such as energy due to the motion of molecules relative to the center of mass of the system, to the rotational and vibrational motion and the electromagnetic interactions of the molecules, and to the motion and interactions of the atomic and subatomic constituents of the molecules.

Suppose a process system is **closed,** meaning that no mass is transferred across its boundaries while the process is taking place. Energy may be transferred between such a system and its surroundings in two ways:

1. As **heat,** or energy that flows as a result of temperature difference between a system and its surroundings. The direction of flow is always from a higher temperature to a lower one. *Heat is defined as positive when it is transferred to the system from the surroundings.*
2. As **work,** or energy that flows in response to any driving force other than a temperature difference, such as a force, a torque, or a voltage. For example, if a gas in a cylinder expands and moves a piston against a restraining force, the gas does work on the piston (energy is transferred as work from the gas to its surroundings, which include the piston). *In this*

text, work is defined as positive when it is done by the system on the surroundings. (*Note:* The opposite sign convention is sometimes used. The choice is arbitrary, as long as it is used consistently; however, to avoid confusion when reading thermodynamics references, you should be sure which convention has been adopted.)

The terms “work” and “heat” refer only to energy that is being transferred: you can speak of the heat or work added to a system or given off by a system, but it is meaningless to speak of the heat or work possessed by or contained within a system.

Energy, like work, has units of force times distance: for example, joules (N·m), ergs (dyne·cm), and ft·lb_f. It is also common to use energy units defined in terms of the amount of heat that must be transferred to a specified mass of water to raise the temperature of the water by a specified temperature interval at a constant pressure of 1 atm. The most common of these units are tabulated here.

Unit	Symbol	Mass of Water	Temperature Interval
Kilogram-calorie or kilocalorie	kcal	1 kg	15°C to 16°C
Gram-calorie or calorie	cal	1 g	15°C to 16°C
British thermal unit	Btu	1 lb_m	60°F to 61°F

Conversion between these and other energy units may be performed using the conversion factors in the table on the inside front cover.

The principle that underlies all energy balances is the law of conservation of energy, which states that energy can neither be created nor destroyed. This law is also called the **first law of thermodynamics.** In its most general form, the first law states that the rate at which energy (kinetic + potential + internal) is carried into a system by the input streams, plus the rate at which it enters as heat, minus the rate at which it is transported out of the system by the output streams, minus the rate at which it leaves as work, equals the rate of accumulation of energy in the system. (That is, accumulation = input − output, as would be expected.)

Instead of presenting the equation in its most general form at this point, we will build up to it in stages. The next section reviews how to evaluate the kinetic and potential energies of an object and shows how the calculation can readily be extended to determine the rates at which kinetic and potential energies are transported by a flowing stream. Section 7.3 presents an integrated form of the transient balance equation that describes the behavior of a system between an initial state and a final state. This form of the equation is particularly useful for analyzing batch process systems. In Section 7.4 the first law is developed for a continuous steady-state process.

Most process systems are conveniently analyzed using one of the two forms of the energy balance equation presented in Sections 7.3 and 7.4. To perform energy balance calculations on other types of processes, such as semibatch processes or continuous processes that are being started up or shut down, the full transient energy balance equation is required. This equation is discussed in an introductory fashion in Chapter 11. A more thorough treatment of the full equation is deferred to thermodynamics courses and texts.

TEST YOURSELF (Answers, p. 659)

1. What forms of energy may a system possess? In what forms may energy be transferred to and from a closed system?
2. Why is it meaningless to speak of the heat possessed by a system?
3. Suppose the initial energy of a system (internal + kinetic + potential) is E_i, the final energy is E_f, an amount of energy Q is transferred from the environment to the system as heat, and an amount W is transferred from the system to the environment as work. According to the first law of thermodynamics, how must E_i, E_f, Q, and W be related?

7.2 KINETIC AND POTENTIAL ENERGY

The kinetic energy, E_k(J), of an object of mass m(kg) moving with velocity u(m/s) relative to the surface of the earth is

$$E_\text{k} = \tfrac{1}{2}mu^2 \qquad \textbf{(7.2-1a)}$$

If a fluid enters a system with a mass flow rate $\dot{m}$(kg/s) and uniform velocity u(m/s), then

$$\dot{E}_\text{k} = \tfrac{1}{2}\dot{m}u^2 \qquad \textbf{(7.2-1b)}$$

$\dot{E}_\text{k}$(J/s) may be thought of as the rate at which kinetic energy is transported into the system by the fluid.

EXAMPLE 7.2-1 *Kinetic Energy Transported by a Flowing Stream*

Water flows into a process unit through a 2-cm ID pipe at a rate of 2.00 m^3/h. Calculate $\dot{E}_\text{k}$ for this stream in joules/second.

SOLUTION First calculate the linear velocity (which equals the volumetric flow rate divided by the cross-sectional area of the pipe) and the mass flow rate of the fluid:

$$u = \begin{array}{c|c|c|c} 2.00\ \text{m}^3 & 100^2\ \text{cm}^2 & & 1\ \text{h} \\ \hline \text{h} & 1^2\ \text{m}^2 & \pi(1)^2\ \text{cm}^2 & 3600\ \text{s} \end{array} = 1.77\ \text{m/s}$$

$$\dot{m} = \begin{array}{c|c|c} 2.00\ \text{m}^3 & 1000\ \text{kg} & 1\ \text{h} \\ \hline \text{h} & \text{m}^3 & 3600\ \text{s} \end{array} = 0.556\ \text{kg/s}$$

Then, from Equation 7.2-1b

$$\dot{E}_\text{k} = \begin{array}{c|c|c} 0.556\ \text{kg/s} & (1.77)^2\ \text{m}^2 & 1\ \text{N} \\ \hline 2 & \text{s}^2 & 1\ \text{kg}\cdot\text{m/s}^2 \end{array} = 0.870\ \text{N}\cdot\text{m/s} = \boxed{0.870\ \text{J/s}}$$

The gravitational potential energy of an object of mass m is

$$E_\text{p} = mgz \qquad \textbf{(7.2-2a)}$$

where g is the acceleration of gravity and z is the height of the object above a reference plane at which E_p is arbitrarily defined to be zero. If a fluid enters a system with a mass flow rate $\dot{m}$ and an elevation z relative to the potential energy reference plane, then

$$\dot{E}_\text{p} = \dot{m}gz \qquad \textbf{(7.2-2b)}$$

$\dot{E}_\text{p}$(J/s) may be thought of as the rate at which gravitational potential energy is transported into the system by the fluid. Since we are normally interested in the *change* in potential energy when a body or fluid moves from one elevation to another $[\dot{E}_{\text{p}2} - \dot{E}_{\text{p}1} = \dot{m}g(z_2 - z_1)]$, the elevation chosen as the reference plane does not matter.

EXAMPLE 7.2-2 *Potential Energy Increase of a Flowing Fluid*

Equipment
Encyclopedia
pump

Crude oil is pumped at a rate of 15.0 kg/s from a point 220 meters below the earth's surface to a point 20 meters above ground level. Calculate the attendant rate of increase of potential energy.

SOLUTION Let subscripts 1 and 2 denote the first and second points, respectively:

$$
\begin{aligned}
\Delta\dot{E}_\text{p} &= \dot{E}_\text{p2} - \dot{E}_\text{p1} = \dot{m}g(z_2 - z_1) \\
&= \begin{array}{c|c|c|c} 15.0\ \text{kg} & 9.81\ \text{m} & 1\ \text{N} & [20 - (-220)]\ \text{m} \\ \hline \text{s} & \text{s}^2 & 1\ \text{kg}\cdot\text{m/s}^2 & \end{array} \\
&= 35{,}300\ \text{N}\cdot\text{m/s} = \boxed{35{,}300\ \text{J/s}}
\end{aligned}
$$

The answer could also have been expressed as 35,300 W or 35.3 kW. A pump would have to deliver at least this much power to raise the oil at the given rate.

TEST YOURSELF (Answers, p. 659)

A gas flows through a long pipe of constant diameter. The outlet of the pipe is higher than the inlet, and the pressure of the gas at the outlet is less than the inlet pressure. The gas temperature is constant throughout the pipe and the system is at steady state.

1. How do the mass flow rates at the inlet and outlet compare? The densities? The volumetric flow rates? (Assume ideal gas behavior.)
2. Is the change in potential energy of the gas from inlet to outlet positive, negative, or zero? What about the change in kinetic energy?

7.3 ENERGY BALANCES ON CLOSED SYSTEMS

A system is termed **open** or **closed** according to whether or not mass crosses the system boundary during the period of time covered by the energy balance. A batch process system is, by definition, closed, and semibatch and continuous systems are open.

An integral energy balance may be derived for a closed system between two instants of time. Since energy can neither be created nor destroyed, the generation and consumption terms of the general balance (4.2-1) drop out, leaving

$$\text{accumulation} = \text{input} - \text{output} \tag{7.3-1}$$

In deriving the integral mass balance for a closed system in Section 4.2c we eliminated the input and output terms, since by definition no mass crosses the boundaries of a closed system. It is possible, however, for energy to be transferred across the boundaries as heat or work, so that the right side of Equation 7.3-1 may not be eliminated automatically. As with mass balances, however, the accumulation term equals the final value of the balanced quantity (in this case, the system energy) minus the initial value of this quantity. Equation 7.3-1 may therefore be written

$$\begin{matrix}\text{final system} \\ \text{energy}\end{matrix} - \begin{matrix}\text{initial system} \\ \text{energy}\end{matrix} = \begin{matrix}\text{net energy transferred to} \\ \text{the system (in} - \text{out)}\end{matrix} \tag{7.3-2}$$

Now

$$
\begin{aligned}
\text{initial system energy} &= U_\text{i} + E_\text{ki} + E_\text{pi} \\
\text{final system energy} &= U_\text{f} + E_\text{kf} + E_\text{pf} \\
\text{energy transferred} &= Q - W
\end{aligned}
$$

where the subscripts i and f refer to the initial and final states of the system and U, E_k, E_p, Q, and W represent internal energy, kinetic energy, potential energy, heat transferred to the system from its surroundings, and work done by the system on its surroundings. Equation 7.3-2 then becomes

$$(U_\text{f} - U_\text{i}) + (E_\text{kf} - E_\text{ki}) + (E_\text{pf} - E_\text{pi}) = Q - W \tag{7.3-3}$$

or, if the symbol Δ is used to signify (final − initial),

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q - W} \tag{7.3-4}$$

Equation 7.3-4 is the basic form of the first law of thermodynamics for a closed system. When applying this equation to a given process, you should be aware of the following points:

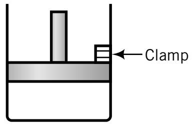
1. The internal energy of a system depends almost entirely on the chemical composition, state of aggregation (solid, liquid, or gas), and temperature of the system materials. It is independent of pressure for ideal gases and nearly independent of pressure for liquids and solids. *If no temperature changes, phase changes, or chemical reactions occur in a closed system and if pressure changes are less than a few atmospheres, then* $\Delta U \approx 0$.
2. *If a system is not accelerating, then* $\Delta E_k = 0$. *If a system is not rising or falling, then* $\Delta E_p = 0$.
3. *If a system and its surroundings are at the same temperature or the system is perfectly insulated, then* $Q = 0$. The process is then termed **adiabatic.**
4. Work done on or by a closed system is accomplished by movement of the system boundary against a resisting force or the passage of an electrical current or radiation across the system boundary. Examples of the first type of work are motion of a piston or rotation of a shaft that projects through the system boundary. *If there are no moving parts or electrical currents or radiation at the system boundary, then* $W = 0$.

TEST YOURSELF (Answers, p. 659)

1. What do the terms closed system and open system mean? What is an adiabatic process?
2. If 250 J is added to a system as heat, what is the value of Q in the energy balance equation? If 250 J of work is done to the system, what is the value of W?
3. If a closed system has an internal energy of 100 kcal at the beginning of a process and 50 kcal at the end, what is ΔU?
4. Under what circumstances might U be considered independent of pressure for a pure substance?

EXAMPLE 7.3-1 Energy Balance on a Closed System

A gas is contained in a cylinder fitted with a movable piston.



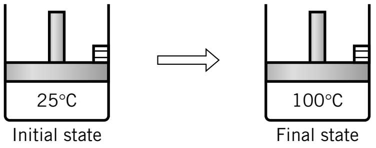
The initial gas temperature is 25°C.

The cylinder is placed in boiling water with the piston held in a fixed position. Heat in the amount of 2.00 kcal is transferred to the gas, which equilibrates at 100°C (and a higher pressure). The piston is then released, and the gas does 100 J of work in moving the piston to its new equilibrium position. The final gas temperature is 100°C.

Write the energy balance equation for each of the two stages of this process, and in each case solve for the unknown energy term in the equation. In solving this problem, consider the gas in the cylinder to be the system, neglect the change in potential energy of the gas as the piston moves vertically, and assume the gas behaves ideally. Express all energies in joules.

SOLUTION

1.



$$\Delta U + \Delta E_\mathrm{k} + \Delta E_\mathrm{p} = Q - W \quad \text{(Equation 7.3-4)}$$

$$\Bigg\Downarrow \begin{array}{rl} \Delta E_\mathrm{k} = 0 & \text{(the system is stationary)} \\ \Delta E_\mathrm{p} = 0 & \text{(no vertical displacement)} \\ W = 0 & \text{(no moving boundaries)} \end{array}$$

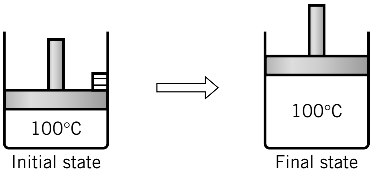
$$\Delta U = Q$$

$$\Big\Downarrow Q = 2.00 \text{ kcal}$$

$$\Delta U = \begin{array}{c|c|c} 2.00 \text{ kcal} & 10^3 \text{ cal} & 1 \text{ J} \\ \hline & \text{kcal} & 0.23901 \text{ cal} \end{array} = \boxed{8370 \text{ J} = \Delta U}$$

The gas thus gains 8370 J of internal energy in going from 25 to 100°C.

2.



$$\Delta U + \Delta E_\mathrm{k} + \Delta E_\mathrm{p} = Q - W$$

$$\Bigg\Downarrow \begin{array}{rl} \Delta E_\mathrm{k} = 0 & \text{(the system is stationary at the initial and final states)} \\ \Delta E_\mathrm{p} = 0 & \text{(assumed negligible by hypothesis)} \\ \Delta U = 0 & (U \text{ depends only on } T \text{ for an ideal gas, and } T \text{ does not change)} \end{array}$$

$$0 = Q - W$$

$$\Big\Downarrow W = +100 \text{ J} \quad \text{(Why is it positive?)}$$

$$\boxed{Q = 100 \text{ J}}$$

Thus an additional 100 J of heat is transferred to the gas as it expands and reequilibrates at 100°C.

7.4 ENERGY BALANCES ON OPEN SYSTEMS AT STEADY STATE

An open process system by definition has mass crossing its boundaries as the process occurs. Work must be done on such a system to push mass in, and work is done on the surroundings by mass that emerges. Both work terms must be included in the energy balance.

In Section 7.4a we outline the calculation of the work (or more precisely, the rate of energy transferred as work) required to move fluid through a continuous process system, and in Section 7.4b we review the concepts of intensive and extensive variables introduced in Chapter 6 and introduce the concept of specific properties of a substance. Section 7.4c uses the results of the two preceding sections to derive the energy balance for an open system at steady state.

7.4a Flow Work and Shaft Work

The net rate of work done by an open system on its surroundings may be written as

$$\dot{W} = \dot{W}_\mathrm{s} + \dot{W}_\mathrm{fl} \tag{7.4-1}$$

where

$\dot{W}_\mathrm{s}$ = **shaft work,** or rate of work done by the process fluid on a moving part within the system (e.g., a pump rotor)

$\dot{W}_\mathrm{fl}$ = **flow work,** or rate of work done by the fluid at the system outlet minus the rate of work done on the fluid at the system inlet

To derive an expression for $\dot{W}_{\text{fl}}$, we initially consider the single-inlet–single-outlet system shown here.

Fluid at a pressure $P_{\text{in}}(\text{N/m}^2)$ enters a pipe at a volumetric flow rate $\dot{V}_{\text{in}}(\text{m}^3/\text{s})$ and exits at a pressure $P_{\text{out}}(\text{N/m}^2)$ and volumetric flow rate $\dot{V}_{\text{out}}(\text{m}^3/\text{s})$. The fluid that enters the system has work done on it by the fluid just behind it at a rate

$$\dot{W}_{\text{in}}(\text{N}\cdot\text{m/s}) = P_{\text{in}}(\text{N/m}^2)\dot{V}_{\text{in}}(\text{m}^3/\text{s}) \tag{7.4-2}$$

while the fluid leaving the system performs work on the surroundings at a rate

$$\dot{W}_{\text{out}} = P_{\text{out}}\dot{V}_{\text{out}} \tag{7.4-3}$$

The net rate at which work is done by the system at the inlet and outlet is therefore

$$\dot{W}_{\text{fl}} = P_{\text{out}}\dot{V}_{\text{out}} - P_{\text{in}}\dot{V}_{\text{in}} \tag{7.4-4}$$

If several input and output streams enter and leave the system, the $P\dot{V}$ products for each stream must be summed to determine $\dot{W}_{\text{fl}}$.

TEST YOURSELF (Answers, p. 659)

An incompressible liquid flows through a straight horizontal pipe. Friction of the fluid within the pipe causes a small amount of heat to be transferred from the fluid; to compensate, flow work must be done on the fluid to move it through the system (so that $\dot{W}_{\text{fl}}$ is less than zero).

1. How are $\dot{V}_{\text{in}}$ and $\dot{V}_{\text{out}}$ related, where $\dot{V}$ is the volumetric flow rate of the liquid? (Remember, the fluid is incompressible.)
2. How must the pressures P_{in} and P_{out} be related? ($P_{\text{in}} > P_{\text{out}}$, $P_{\text{in}} = P_{\text{out}}$, or $P_{\text{in}} < P_{\text{out}}$?)

7.4b Specific Properties and Enthalpy

As we observed in Section 6.2, the properties of a process material are either extensive (proportional to the quantity of the material) or intensive (independent of the quantity). Mass, number of moles, and volume (or mass flow rate, molar flow rate, and volumetric flow rate for a continuous stream), and kinetic energy, potential energy, and internal energy (or the rates of transport of these quantities by a continuous stream) are extensive properties, while temperature, pressure, and density are intensive.

A **specific property** is an intensive quantity obtained by dividing an extensive property (or its flow rate) by the total amount (or flow rate) of the process material. Thus, if the volume of a fluid is 200 cm^3 and the mass of the fluid is 200 g, the **specific volume** of the fluid is 1 cm^3/g. Similarly, if the mass flow rate of a stream is 100 kg/min and the volumetric flow rate is 150 L/min, the specific volume of the stream material is $(150\text{ L/min}/100\text{ kg/min}) = 1.5$ L/kg; if the rate at which kinetic energy is transported by this stream is 300 J/min, then the **specific kinetic energy** of the stream material is $(300\text{ J/min})/(100\text{ kg/min}) = 3$ J/kg. *We will use the symbol ˆ to denote a specific property:* $\hat{V}$ will denote specific volume, $\hat{U}$ specific internal energy, and so on.

If the temperature and pressure of a process material are such that the specific internal energy of the material is $\hat{U}$(J/kg), then a mass m(kg) of this material has a total internal energy

$$U(\text{J}) = m(\text{kg})\hat{U}(\text{J/kg}) \tag{7.4-5}$$

Similarly, a continuous stream of this material with a mass flow rate $\dot{m}$(kg/s) transports internal energy at a rate

$$\dot{U}(\text{J/s}) = \dot{m}(\text{kg/s})\hat{U}(\text{J/kg}) \tag{7.4-6}$$

A property that occurs in the energy balance equation for open systems (Section 7.4c) is the **specific enthalpy,** defined as

$$\hat{H} \equiv \hat{U} + P\hat{V} \tag{7.4-7}$$

where P is total pressure and $\hat{U}$ and $\hat{V}$ are specific internal energy and specific volume. The gas constants tabulated on the inside back cover provide a convenient source for the conversion factors needed to evaluate $\hat{H}$ from Equation 7.4-7, as the following example shows.

EXAMPLE 7.4-1 *Calculation of Enthalpy*

The specific internal energy of helium at 300 K and 1 atm is 3800 J/mol, and the specific molar volume at the same temperature and pressure is 24.63 L/mol. Calculate the specific enthalpy of helium at this temperature and pressure, and the rate at which enthalpy is transported by a stream of helium at 300 K and 1 atm with a molar flow rate of 250 kmol/h.

SOLUTION

$$\hat{H} = \hat{U} + P\hat{V} = 3800 \text{ J/mol} + (1 \text{ atm})(24.63 \text{ L/mol})$$

To convert the second term to joules we need the factor J/(L·atm). From the gas constant table on the inside back cover,

$$0.08206 \text{ L·atm/(mol·K)} = 8.314 \text{ J/(mol·K)}$$

Dividing the right side by the left side yields the desired factor:

$$\frac{8.314 \text{ J/mol·K}}{0.08206 \text{ L·atm/(mol·K)}} = 101.3 \text{ J/(L·atm)}$$

Therefore,

$$\hat{H} = 3800 \text{ J/mol} + \frac{24.63 \text{ L·atm}}{\text{mol}}\left|\frac{101.3 \text{ J}}{1 \text{ L·atm}}\right. = \boxed{6295 \text{ J/mol}}$$

If $\dot{n} = 250$ kmol/h

$$\dot{H} = \dot{n}\hat{H} = \frac{250 \text{ kmol}}{\text{h}}\left|\frac{10^3 \text{ mol}}{\text{kmol}}\right|\frac{6295 \text{ J}}{\text{mol}} = \boxed{1.57 \times 10^9 \text{ J/h}}$$

The enthalpy function is important in the analysis of open systems, as we will show in the next section. It can also be shown, however, that *if a closed system expands (or contracts) against a constant external pressure, ΔE_k and ΔE_p are negligible, and the only work done by or on the system is the work of the expansion, then the energy balance equation reduces to $Q = \Delta H$.* A proof of this statement is required in Problem 7.15.

TEST YOURSELF (Answers, p. 659)

The specific internal energy of a fluid is 200 cal/g.

1. What is the internal energy of 30 g of this fluid?
2. If the fluid leaves a system at a flow rate of 5 g/min, at what rate does it transport internal energy out of the system?
3. What would you need to know to calculate the specific enthalpy of this fluid?

7.4c The Steady-State Open-System Energy Balance

The first law of thermodynamics for an open system at steady state has the form

$$\text{input} = \text{output} \qquad \textbf{(7.4-8)}$$

(Why do the accumulation, generation, and consumption terms of the general balance equation vanish?) "Input" here signifies the total rate of transport of kinetic energy, potential energy, and internal energy by all process input streams plus the rate at which energy is transferred in as heat, and "output" is the total rate of energy transport by the output streams plus the rate at which energy is transferred out as work.

If $\dot{E}_j$ denotes the total rate of energy transport by the jth input or output stream of a process, and $\dot{Q}$ and $\dot{W}$ are again defined as the rates of flow of heat into and work out of the process, then Equation 7.4-8 may be written

$$\dot{Q} + \sum_{\substack{\text{input}\\ \text{streams}}} \dot{E}_j = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{E}_j + \dot{W}$$

$$\Big\Downarrow$$

$$\sum_{\substack{\text{output}\\ \text{streams}}} \dot{E}_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{E}_j = \dot{Q} - \dot{W} \tag{7.4-9}$$

If $\dot{m}_j$, $\dot{E}_{\mathrm{k}j}$, $\dot{E}_{\mathrm{p}j}$, and $\dot{U}_j$ are the flow rates of mass, kinetic energy, potential energy, and internal energy for the jth process stream, then the total rate at which energy is transported into or out of the system by this stream is

$$\dot{E}_j = \dot{U}_j + \dot{E}_{\mathrm{k}j} + \dot{E}_{\mathrm{p}j}$$

$$\Bigg\Downarrow \begin{aligned} \dot{U}_j &= \dot{m}_j \hat{U}_j \\ \dot{E}_{\mathrm{k}j} &= \dot{m}_j u_j^2/2 \\ \dot{E}_{\mathrm{p}j} &= \dot{m}_j g z_j \end{aligned}$$

$$\dot{E}_j = \dot{m}_j \left(\hat{U}_j + \frac{u_j^2}{2} + g z_j \right) \tag{7.4-10}$$

where u_j is the velocity of the jth stream and z_j is the height of this stream relative to a reference plane at which $E_{\mathrm{p}} = 0$.

The total work $\dot{W}$ done by the system on its surroundings equals the shaft work $\dot{W}_{\mathrm{s}}$ plus the flow work $\dot{W}_{\mathrm{fl}}$ (Equation 7.4-1). If $\dot{V}_j$ is the volumetric flow rate of the jth stream and P_j is the pressure of this stream as it crosses the system boundary, then as was shown in Section 7.4a,

$$\dot{W}_{\mathrm{fl}} = \sum_{\substack{\text{output}\\ \text{streams}}} P_j \dot{V}_j - \sum_{\substack{\text{input}\\ \text{streams}}} P_j \dot{V}_j$$

$$\Big\Downarrow \; \dot{V}_j = \dot{m}_j \hat{V}_j$$

$$\dot{W} = \dot{W}_{\mathrm{s}} + \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j P_j \hat{V}_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j P_j \hat{V}_j \tag{7.4-11}$$

Substituting the expression for $\dot{E}_j$ of Equation 7.4-10 and that for $\dot{W}$ of Equation 7.4-11 into Equation 7.4-9 and bringing the $P\hat{V}$ terms to the left side yields

$$\sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + g z_j \right] - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j \left[\hat{U}_j + P_j \hat{V}_j + \frac{u_j^2}{2} + g z_j \right] = \dot{Q} - \dot{W}_{\mathrm{s}} \tag{7.4-12}$$

Equation 7.4-12 could be used for all steady-state open system energy balance problems. As a rule, however, the term $\hat{U}_j + P_j \hat{V}_j$ is combined and written as $\hat{H}_j$, the variable previously defined as the specific enthalpy. In terms of this variable, Equation 7.4-12 becomes

$$\sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + g z_j \right) - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j \left(\hat{H}_j + \frac{u_j^2}{2} + g z_j \right) = \dot{Q} - \dot{W}_{\mathrm{s}} \tag{7.4-13}$$

Finally, let us use the symbol Δ to denote total output minus total input, so that

$$\Delta \dot{H} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j \hat{H}_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j \hat{H}_j \tag{7.4-14a}$$

$$\Delta \dot{E}_{\mathrm{k}} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j u_j^2/2 - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j u_j^2/2 \tag{7.4-14b}$$

$$\Delta \dot{E}_{\mathrm{p}} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j g z_j \tag{7.4-14c}$$

In terms of these quantities, Equation 7.4-13 becomes

$$\boxed{\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p = \dot{Q} - \dot{W}_s} \quad \textbf{(7.4-15)}$$

Equation 7.4-15 states that the net rate at which energy is transferred to a system as heat and/or shaft work ($\dot{Q} - \dot{W}_s$) equals the difference between the rates at which the quantity (enthalpy + kinetic energy + potential energy) is transported into and out of the system ($\Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$). We will use this equation as the starting point for most energy balance calculations on open systems at steady state.

Notice that if a process has a single input stream and a single output stream and there is no accumulation of mass in the system (so that $\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = \dot{m}$), the expression for $\Delta\dot{H}$ of Equation 7.4-14a simplifies to

$$\Delta\dot{H} = \dot{m}(\hat{H}_{\text{out}} - \hat{H}_{\text{in}}) = \dot{m}\Delta\hat{H} \quad \textbf{(7.4-16)}$$

Also notice that if a specific variable has the same value for all input and output streams, the corresponding term of Equation 7.4-15 drops out. For example, if $\hat{H}_j$ is the same for all streams, then from Equation 7.4-14a

$$\Delta\dot{H} = \hat{H}\left[\sum_{\substack{\text{output}\\\text{streams}}} \dot{m}_j - \sum_{\substack{\text{input}\\\text{streams}}} \dot{m}_j\right] \quad \textbf{(7.4-17)}$$

But from a total mass balance the quantity in brackets (which is simply total mass in minus total mass out) equals zero, and hence $\Delta\dot{H} = 0$, as claimed.

TEST YOURSELF (Answers, p. 659)

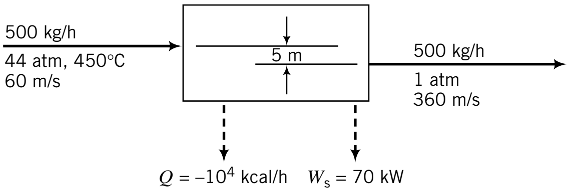
How would you simplify Equation 7.4-15 in each of the following cases?

1. There are no moving parts in the system.
2. The system and its surroundings are at the same temperature.
3. The linear velocities of all streams are the same.
4. All streams enter and leave the process at a single height.

EXAMPLE 7.4-2 Energy Balance on a Turbine

Five hundred kilograms per hour of steam drives a turbine. The steam enters the turbine at 44 atm and 450°C at a linear velocity of 60 m/s and leaves at a point 5 m below the turbine inlet at atmospheric pressure and a velocity of 360 m/s. The turbine delivers shaft work at a rate of 70 kW, and the heat loss from the turbine is estimated to be 10^4 kcal/h. Calculate the specific enthalpy change associated with the process.

SOLUTION



From Equation 7.4-15

$$\Delta\dot{H} = \dot{Q} - \dot{W}_s - \Delta\dot{E}_k - \Delta\dot{E}_p$$

Normally, heat, work, and kinetic and potential energy terms are determined in different units. To evaluate $\Delta\dot{H}$, we will convert each term to kW (kJ/s) using conversion factors given on the inside front cover, first noting that $\dot{m} = (500 \text{ kg/h}/3600 \text{ s/h}) = 0.139$ kg/s.

$$\Delta\dot{E}_k = \frac{\dot{m}}{2}(u_2^2 - u_1^2) = \frac{0.139 \text{ kg/s}}{2}\left|\frac{1 \text{ N}}{1 \text{ kg·m/s}^2}\right|\frac{(360^2 - 60^2)\text{ m}^2}{\text{s}^2}\left|\frac{1 \text{ W}}{1 \text{ N·m/s}}\right|\frac{1 \text{ kW}}{10^3 \text{ W}}$$

$$= 8.75 \text{ kW}$$

$$\Delta \dot{E}_{\text{p}} = \dot{m}g(z_2 - z_1) = \begin{array}{c|c|c|c} 0.139 \text{ kg/s} & 9.81 \text{ N} & (-5) \text{ m} & 1 \text{ kW} \\ \hline & \text{kg} & & 10^3 \text{ N}\cdot\text{m/s} \end{array} = -6.81 \times 10^{-3} \text{ kW}$$

$$\dot{Q} = \begin{array}{c|c|c|c} -10^4 \text{ kcal} & 1 \text{ J} & 1 \text{ h} & 1 \text{ kW} \\ \hline \text{h} & 0.239 \times 10^{-3} \text{ kcal} & 3600 \text{ s} & 10^3 \text{ J/s} \end{array} = -11.6 \text{ kW}$$

$$\dot{W}_{\text{s}} = 70 \text{ kW}$$

$$\Downarrow$$

$$\Delta \dot{H} = \dot{Q} - \dot{W}_{\text{s}} - \Delta \dot{E}_{\text{k}} - \Delta \dot{E}_{\text{p}} = -90.3 \text{ kW}$$

But

$$\Delta \dot{H} = \dot{m}(\hat{H}_2 - \hat{H}_1) \quad \text{(from Equation 7.4-16)}$$

$$\Downarrow$$

$$\begin{aligned} \hat{H}_2 - \hat{H}_1 &= \Delta \dot{H} / \dot{m} \\ &= \frac{-90.3 \text{ kJ/s}}{0.139 \text{ kg/s}} = \boxed{-650 \text{ kJ/kg}} \end{aligned}$$

7.5 TABLES OF THERMODYNAMIC DATA

7.5a Reference States and State Properties

It is not possible to know the absolute value of $\hat{U}$ or $\hat{H}$ for a process material, but you can determine the *change* in $\hat{U}(\Delta\hat{U})$ or in $\hat{H}(\Delta\hat{H})$ corresponding to a specified change of state (temperature, pressure, and phase). This may be done, for example, by bringing a known mass m of a substance through the specified change of state in such a way that all terms of the energy balance except ΔU (i.e., heat, work, and changes in potential and kinetic energies) are known. Once $\Delta\hat{U}(= \Delta U/m)$ has been determined, $\Delta\hat{H}$ for the same change in state can be calculated as $\Delta\hat{U} + \Delta P\hat{V}$.

A convenient way to tabulate measured changes in $\hat{U}$ or $\hat{H}$ is to choose a temperature, pressure, and state of aggregation as a **reference state,** and to list $\Delta\hat{U}$ or $\Delta\hat{H}$ for changes from this state to a series of other states. Suppose, for example, that the enthalpy changes for carbon monoxide going from a reference state of 0°C and 1 atm to two other states are measured, with the following results:

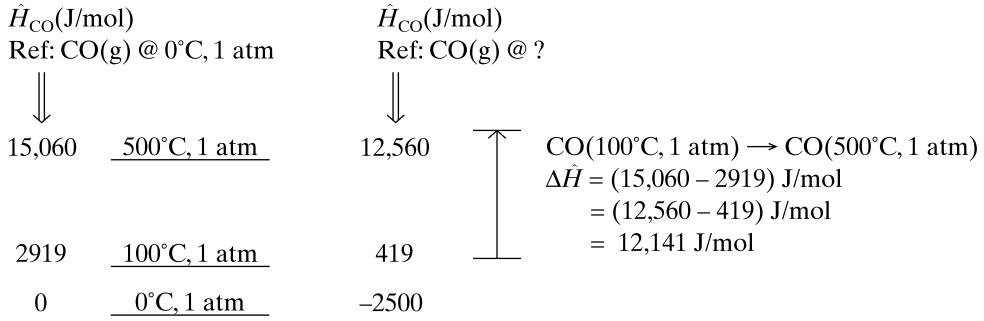
$$\begin{aligned} &\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 100°C, 1 atm)}: && \Delta\hat{H}_1 = 2919 \text{ J/mol} \\ &\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 500°C, 1 atm)}: && \Delta\hat{H}_2 = 15{,}060 \text{ J/mol} \end{aligned}$$

Since $\hat{H}$ cannot be known absolutely, for convenience we may assign a value $\hat{H}_0 = 0$ to the reference state; then $\Delta\hat{H}_1 = \hat{H}_1 - 0 = \hat{H}_1$, $\Delta\hat{H}_2 = \hat{H}_2$, and so on. A table may then be constructed for CO at 1 atm:

T(°C)	$\hat{H}$(J/mol)
0	0
100	2919
500	15,060

Note that the value 2919 J/mol for $\hat{H}$ at 100°C does *not* mean that the absolute value of the specific enthalpy of CO at 100°C and 1 atm is 2919 J/mol—we cannot know the absolute value of $\hat{H}$—but rather means that the *change* in $\hat{H}$ when CO goes from the reference state to 100°C and 1 atm is 2919 J/mol. We then say *the specific enthalpy of CO at 100°C and 1 atm relative to CO at 0°C and 1 atm is 2919 J/mol.*

Some enthalpy tables give the reference states on which the listed values of $\hat{H}$ are based and others do not; however, you do not have to know the reference state to calculate $\Delta\hat{H}$ for the transition from one tabulated state to another. If $\hat{H}_1$ is the specific enthalpy at state 1 and $\hat{H}_2$ is that at state 2, then $\Delta\hat{H}$ for the transition from state 1 to state 2 equals $\hat{H}_2 - \hat{H}_1$, regardless of the reference state on which $\hat{H}_1$ and $\hat{H}_2$ are based. (*Caution:* If two different tables are used, be sure $\hat{H}_1$ and $\hat{H}_2$ are based on the same reference state.) For example, $\Delta\hat{H}$ for CO going from 100 to 500°C at 1 atm is (15,060 − 2919) J/mol = 12,141 J/mol. If another reference state had been used to generate the specific enthalpies of CO at 100°C and 500°C, $\hat{H}_1$ and $\hat{H}_2$ would have different values but $\hat{H}_2 - \hat{H}_1$ would still be 12,141 J/mol. (See diagram below.)



This convenient result is a consequence of the fact that $\hat{H}$, like $\hat{U}$, is a **state property,** or a property of a system component whose value depends only on the state of the system (temperature, pressure, phase, and composition) and not on how the system reached that state.[1] We will have more to say about this concept in Chapter Eight.

EXAMPLE 7.5-1 *Use of Tabulated Enthalpy Data*

The following entries are taken from a data table for saturated methyl chloride:

State	T(°F)	P(psia)	$\hat{V}$(ft^3/lb$_m$)	$\hat{H}$(Btu/lb$_m$)
Liquid	−40	6.878	0.01553	0.000
Vapor	0	18.90	4.969	196.23
Vapor	50	51.99	1.920	202.28

1. What reference state was used to generate the given enthalpies?
2. Calculate $\Delta\hat{H}$ and $\Delta\hat{U}$ for the transition of saturated methyl chloride vapor from 50°F to 0°F.
3. What assumption did you make in solving question 2 regarding the effect of pressure on specific enthalpy?

SOLUTION

1. Liquid at −40°F and 6.878 psia (the state at which $\hat{H} = 0$). You do not need this information to solve part 2.
2. $\Delta\hat{H} = \hat{H}(0°\text{F}) - \hat{H}(50°\text{F}) = (196.23 - 202.28) = -6.05\ \text{Btu/lb}_\text{m}$

$$\Delta\hat{U} = \Delta\hat{H} - \Delta P\hat{V} = \Delta\hat{H} - (P_\text{final}\hat{V}_\text{final} - P_\text{initial}\hat{V}_\text{initial})$$

$$= -6.05\ \text{Btu/lb}_\text{m} - \frac{[(18.90)(4.969) - (51.99)(1.920)]\ \text{ft}^3\cdot\text{psia/lb}_\text{m}}{} \left| \frac{1.987\ \text{Btu}}{10.73\ \text{ft}^3\cdot\text{psia}} \right.$$

$$= \boxed{-4.96\ \text{Btu/lb}_\text{m}}$$

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[1] We will not prove our claim that $\hat{U}$ and $\hat{H}$ satisfy this condition. All references on thermodynamics discuss this point in detail.

The value of the conversion factor Btu/(ft^3·psia) was obtained from the table of gas constants in back of the book. (Verify it!)

3. $\hat{H}$ was assumed independent of P.

Tables of enthalpies and other state properties of many substances may be found in tables B5-B9 of this text and *Perry's Chemical Engineers' Handbook*[2] on pp. 2-206 through 2-316.

TEST YOURSELF (Answers, p. 659)

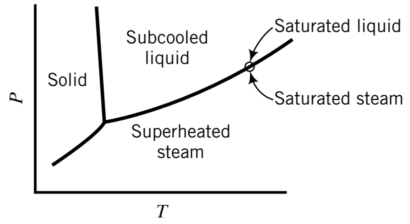
1. What is a state property?
2. The enthalpy of a vapor A relative to liquid A at 0°C and 1 atm is 5000 J/kg at 0°C and 1 atm, and 7500 J/kg at 30°C and 1 atm.
   (a) What is $\hat{H}$ of A(l) at 0°C and 1 atm?
   (b) What is the approximate value of $\hat{H}$ for A(v) at 0°C and 5 atm?
   (c) What is $\Delta\hat{H}$ for the process

$$\text{A(v, 30°C, 1 atm)} \rightarrow \text{A(v, 0°C, 1 atm)}$$

Does the answer depend on the reference state used to generate the table of enthalpies? Why not?

7.5b Steam Tables

Recall the phase diagram for water (Figure 6.1-1a, p. 239), which has the following appearance:



Pure water may coexist as liquid and vapor only at temperature–pressure pairs that fall on the vapor–liquid equilibrium (VLE) curve. At points above the VLE curve (but to the right of the solid–liquid equilibrium curve), water is a **subcooled liquid.** At points on the VLE curve, water may be **saturated liquid** or **saturated steam** (vapor) or a mixture of both. At points below the VLE curve, water is **superheated steam.**

For many years, compilations of physical properties of liquid water, saturated steam, and superheated steam issued in **steam tables** have been standard references for mechanical and chemical engineers involved with steam cycles for electrical power generation. Steam tables are contained in Tables B.5–B.7 of this text. We recommend that you look at these tables as we describe what you can find in them.

Table B.5 lists properties of saturated liquid water and saturated steam at temperatures from 0.01°C (the triple point temperature) to 102°C. The following properties can be determined for each tabulated temperature (and for intermediate temperatures by interpolation):

- ***Column 2.*** The pressure, P(bar), corresponding to the given temperature on the VLE curve—by definition, the vapor pressure of water at the given temperature. Instead of looking up a given temperature and finding the pressure, you could look up a given pressure in the second column and find the corresponding boiling point temperature in the first column.

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[2] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook,* 7th Edition, McGraw-Hill, New York, 1997.

- ***Columns 3 and 4.*** The specific volumes, $\hat{V}$(m^3/kg), of liquid water and saturated steam at the given temperature. The inverses of these quantities are the densities (kg/m^3) of liquid water and steam.
- ***Columns 5 and 6.*** The specific internal energies, $\hat{U}$(kJ/kg), of saturated liquid water and saturated steam at the given temperature *relative to a reference state of liquid water at the triple point.* (Remember, we can never know the absolute value of internal energy or enthalpy, but only how these quantities change when the substance goes from one state to another—in this case, from the reference state to the states listed in the table.)
- ***Columns 7–9.*** The specific enthalpies, $\hat{H}$(kJ/kg), of saturated liquid water (Column 7) and saturated steam (Column 9), and the difference between these quantities, known as the *heat of vaporization* (Column 8). The reference point for the tabulated values of $\hat{H}$ is again liquid water at the triple point.

Table B.6 lists the same properties as Table B.5, except that pressure is the first column and temperature the second and the table covers a much broader range of temperatures and pressures. Tables B.5 and B.6 are commonly referred to as the *saturated steam tables.*

Table B.7—which is referred to as the *superheated steam table*—lists $\hat{V}$, $\hat{U}$, and $\hat{H}$ of water (the latter two properties relative to liquid water at the triple point) at *any* temperature and pressure, not just at points on the VLE curve. If you are given a temperature and a pressure, you can locate the properties of water at the intersection of the column corresponding to the given temperature and the row corresponding to the given pressure. If the intersection falls within the closed region on the table bounded by the vertical line to the left of the 50°C column, the horizontal line below the 221.2 bar row, and the zigzag hypotenuse, the water is a liquid; outside this region, it is a superheated vapor.

When you look up a pressure in the first column of Table B.7, you will find just below it in parentheses the boiling point temperature and in Columns 2 and 3 the properties of saturated liquid water and saturated steam at that pressure. If you are at a point in the superheated steam region, you can move all the way to the left to determine the saturation temperature at the same pressure, or the *dew point* of the superheated steam.

The next example illustrates the use of these tables to obtain physical property data for water.

EXAMPLE 7.5-2 ***The Steam Tables***

1. Determine the vapor pressure, specific internal energy, and specific enthalpy of saturated steam at 133.5°C.
2. Show that water at 400°C and 10 bar is superheated steam and determine its specific volume, specific internal energy, and specific enthalpy relative to liquid water at the triple point, and its dew point.
3. Show that $\hat{U}$ and $\hat{H}$ for superheated steam depend strongly on temperature and relatively slightly on pressure.

SOLUTION Verify the results to be given.

1. Table B.5 does not go up to 133.5°C, so we turn to Table B.6. For saturated steam at the given temperature (Column 2),

$$\boxed{p^* = 3.0 \text{ bar}, \hat{V} = 0.606 \text{ m}^3/\text{kg}, \hat{U} = 2543.0 \text{ kJ/kg}, \hat{H} = 2724.7 \text{ kJ/kg}}$$

2. From Table B.7, [$T = 400$°C, $P = 10$ bar] falls outside the closed region, showing that water is superheated steam at this temperature and pressure. The table also shows that at this condition,

$$\boxed{\hat{H} = 3264 \text{ kJ/kg}, \hat{U} = 2958 \text{ kJ/kg}, \hat{V} = 0.307 \text{ m}^3/\text{kg}, T_{\text{dp}} = 179.9\text{°C}}$$

3. Look at the properties of water at 400°C and 450°C, both at a pressure of 10 bar. You will see that both $\hat{U}$ and $\hat{H}$ change by about 3% when water goes from the first temperature to the second one (3264 kJ/kg → 3371 kJ/kg for $\hat{H}$, 2958 kJ/kg → 3041 kJ/kg for $\hat{U}$).

   Now consider the properties at 10 bar and 20 bar, both at a temperature of 400°C. Even though the pressure has doubled, the values of $\hat{U}$ and $\hat{H}$ change by much less than 1%. Similar results would be obtained for liquid water. The conclusion is that when you need a value of $\hat{U}$ or $\hat{H}$ for water (or for any other species) at a given T and P, you must look it up at the correct temperature—interpolating if necessary—but you don't have to find it at the exact pressure.

The next example illustrates the use of the steam tables to solve energy balance problems.

EXAMPLE 7.5-3 *Energy Balance on a Steam Turbine*

Steam at 10 bar absolute with 190°C of superheat is fed to a turbine at a rate $\dot{m} = 2000$ kg/h. The turbine operation is adiabatic, and the effluent is saturated steam at 1 bar. Calculate the work output of the turbine in kilowatts, neglecting kinetic and potential energy changes.

SOLUTION The energy balance for this steady-state open system is

$$\dot{W}_s = -\Delta\dot{H} = -\dot{m}(\hat{H}_{\text{out}} - \hat{H}_{\text{in}})$$

(Why was the heat term dropped?)

Inlet Steam

Table B.7 indicates that steam at 10 bar is saturated at 180°C (*verify*), so that the inlet steam temperature is 180°C + 190°C = 370°C. Interpolating in the same table,

$$\hat{H}_{\text{in}}(10\text{ bar}, 370°\text{C}) = 3201\text{ kJ/kg}$$

Outlet Steam

From either Table B.6 or B.7, you can find that the enthalpy of saturated steam at 1 bar is

$$\hat{H}_{\text{out}}(1\text{ bar, saturated}) = 2675\text{ kJ/kg}$$

Energy Balance

$$\dot{W}_s = -\Delta\dot{H} = -\begin{array}{r|r|r} 2000\text{ kg} & (2675 - 3201)\text{ kJ} & 1\text{ h} \\ \hline \text{h} & \text{kg} & 3600\text{ s} \end{array}$$

$$= 292\text{ kJ/s} = \boxed{292\text{ kW}}$$

The turbine thus delivers 292 kW of work to its surroundings.

The superheated steam table, Table B.7, lists values for both liquid water and steam. If you wish to determine $\hat{H}$ for liquid water at a temperature T and pressure P that cannot easily be found in this table, you may calculate it in the following manner: (1) look up $\hat{U}$ and $\hat{V}$ for *saturated* liquid at the specified temperature in Table B.5; (2) assume these values are independent of pressure, and calculate $\hat{H}(P,T) = \hat{U} + P\hat{V}$. Furthermore, if the pressure is not excessive (say, less than 10 bar) or *if it is unknown,* neglect the $P\hat{V}$ correction and use the saturated liquid enthalpy $\hat{H}(T)$ given in Table B.5.

7.6 ENERGY BALANCE PROCEDURES

A properly drawn and labeled flowchart is essential for the efficient solution of energy balance problems. When labeling the flowchart, be sure to include all of the information you will need to determine the specific enthalpy of each stream component, including known temperatures and pressures. In addition, show states of aggregation of process materials when they are not obvious: do not simply write H_2O, for example, but rather $H_2O(s)$, $H_2O(l)$, or $H_2O(v)$, according to whether water is present as a solid, a liquid, or a vapor.

In the rest of this chapter, we will consider only species (such as water) for which tabulated internal energies or enthalpies are available. In Chapters 8 and 9 we will show how to choose reference states and calculate the required values of $\hat{U}$ and $\hat{H}$ when tabulated values cannot be found.

EXAMPLE 7.6-1 *Energy Balance on a One-Component Process*

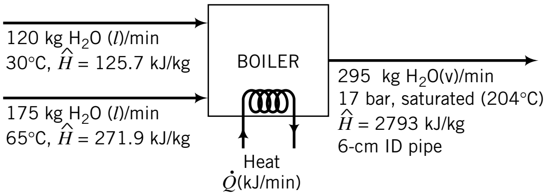
Equipment Encyclopedia
boiler

Two streams of water are mixed to form the feed to a boiler. Process data are as follows:

Feed stream 1	120 kg/min @ 30°C
Feed stream 2	175 kg/min @ 65°C
Boiler pressure	17 bar (absolute)

The exiting steam emerges from the boiler through a 6-cm ID pipe. Calculate the required heat input to the boiler in kilojoules per minute if the emerging steam is saturated at the boiler pressure. Neglect the kinetic energies of the liquid inlet streams.

SOLUTION



1. ***A first step in solving problems of this sort is to determine (if possible) the flow rates of all stream components using material balances.*** In this case, it is a trivial matter to write and solve a mass balance on water to determine that the flow rate of the emerging steam is 295 kg/min.
2. ***Next, determine the specific enthalpies of each stream component.*** Tables B.5 and B.6 were used to determine $\hat{H}$ for liquid water at 30°C and 65°C and for saturated steam at 17 bar. The latter entry in the table also furnished the temperature of the saturated steam corresponding to this pressure (204°C). Note that the entries for liquid water correspond to pressures that may or may not equal the actual pressures of the inlet streams (which we do not know); we assume, however, that the enthalpy of liquid water is approximately independent of pressure and use the tabulated values.
3. ***The final step is to write the appropriate form of the energy balance and solve it for the desired quantity.*** For this open process system,

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Big\Downarrow \begin{array}{ll} \dot{W}_s = 0 & \text{(no moving parts)} \\ \Delta\dot{E}_p = 0 & \text{(generally assumed unless displacements through} \\ & \text{large heights are involved)} \end{array}$$

$$\dot{Q} = \Delta\dot{H} + \Delta\dot{E}_k$$

Evaluate $\Delta\dot{H}$

From Equation 7.4-14a,

$$\Delta\dot{H} = \sum_{\text{outlet}} \dot{m}_i\hat{H}_i - \sum_{\text{inlet}} \dot{m}_i\hat{H}_i$$

$$= \frac{295\text{ kg}}{\text{min}}\Big|\frac{2793\text{ kJ}}{\text{kg}} - \frac{120\text{ kg}}{\text{min}}\Big|\frac{125.7\text{ kJ}}{\text{kg}} - \frac{175\text{ kg}}{\text{min}}\Big|\frac{271.9\text{ kJ}}{\text{kg}}$$

$$= 7.61 \times 10^5 \text{ kJ/min}$$

Evaluate $\Delta \dot{E}_k$

From Table B.6, the specific volume of saturated steam at 17 bar is 0.1166 m^3/kg, and the cross-sectional area of the 6-cm ID pipe is

$$A = \pi R^2 = \frac{3.1416 \mid (3.00)^2\ \text{cm}^2 \mid 1\ \text{m}^2}{\quad \mid \quad \mid 10^4\ \text{cm}^2} = 2.83 \times 10^{-3}\ \text{m}^2$$

The steam velocity is

$$\begin{aligned} u(\text{m/s}) &= \dot{V}(\text{m}^3/\text{s})/A(\text{m}^2) \\ &= \frac{295\ \text{kg} \mid 1\ \text{min} \mid 0.1166\ \text{m}^3 \mid}{\text{min} \mid 60\ \text{s} \mid \text{kg} \mid 2.83 \times 10^{-3}\ \text{m}^2} \\ &= 202\ \text{m/s} \end{aligned}$$

Then, since the kinetic energies of the inlet streams are assumed negligible,

$$\begin{aligned} \Delta \dot{E}_k \approx (\dot{E}_k)_{\text{outlet stream}} &= \dot{m}u^2/2 \\ &= \frac{295\ \text{kg/min} \mid (202)^2\text{m}^2 \mid 1\ \text{N} \mid 1\ \text{kJ}}{2 \mid \text{s}^2 \mid 1\ \text{kg}\cdot\text{m/s}^2 \mid 10^3\ \text{N}\cdot\text{m}} = 6.02 \times 10^3\ \text{kJ/min} \end{aligned}$$

Finally,

$$\begin{aligned} \dot{Q} &= \Delta \dot{H} + \Delta \dot{E}_k \\ &= [7.61 \times 10^5 + 6.02 \times 10^3]\ \text{kJ/min} \\ &= \boxed{7.67 \times 10^5\ \text{kJ/min}} \end{aligned}$$

Observe that the kinetic energy change is only a small fraction—roughly 0.8%—of the total energy requirement for the process. This is a typical result, and it is not uncommon to neglect kinetic and potential energy changes (at least as a first approximation) relative to enthalpy changes for processes that involve phase changes, chemical reactions, or large temperature changes.

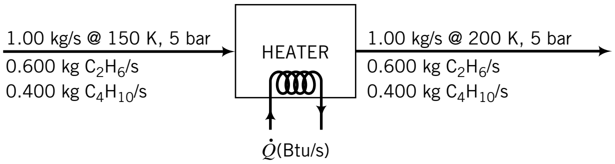
When process streams contain several components, the specific enthalpies of each component must be determined separately and substituted in the energy balance equation when $\Delta \dot{H}$ is evaluated. *For mixtures of near-ideal gases or of liquids with similar molecular structures* (e.g., mixtures of paraffins), *you may assume that $\hat{H}$ for a mixture component is the same as $\hat{H}$ for the pure substance at the same temperature and pressure.* Procedures to follow for solutions of gases or solids in liquids and for mixtures of dissimilar liquids are outlined in Chapter 8.

EXAMPLE 7.6-2 Energy Balance on a Two-Component Process

A liquid stream containing 60.0 wt% ethane and 40.0% *n*-butane is to be heated from 150 K to 200 K at a pressure of 5 bar. Calculate the required heat input per kilogram of the mixture, neglecting potential and kinetic energy changes, using tabulated enthalpy data for C_2H_6 and C_4H_{10} and assuming that mixture component enthalpies are those of the pure species at the same temperature.

SOLUTION ***Basis: 1 kg/s Mixture***

The enthalpies of *n*-butane at 150 K and 5 bar and at 200 K and 5 bar are given on p. 2-223 of *Perry's Chemical Engineers' Handbook* (see footnote 2), and those of ethane at the same conditions are given on p. 2-234 of the *Handbook*. The tabulated enthalpy values are shown in the energy balance.



No material balances are necessary since there is only one input stream and one output stream and no chemical reactions, so we may proceed directly to the energy balance:

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Bigg\Downarrow \begin{array}{l} \dot{W}_s = 0 \quad \text{(no moving parts)} \\ \Delta\dot{E}_k = 0,\ \Delta\dot{E}_p = 0 \quad \text{(by hypothesis)} \end{array}$$

$$\dot{Q} = \Delta\dot{H}$$

Since the process materials are all gases and we are assuming ideal gas behavior, we may set the enthalpies of each stream equal to the sums of the individual component enthalpies and write

$$\dot{Q} = \Delta\dot{H} = \sum_{\substack{\text{outlet}\\ \text{components}}} \dot{m}_i\hat{H}_i - \sum_{\substack{\text{inlet}\\ \text{components}}} \dot{m}_i\hat{H}_i$$

$$= \frac{0.600 \text{ kg } C_2H_6}{\text{s}}\bigg|\frac{434.5 \text{ kJ}}{\text{kg}} + \frac{0.400 \text{ kg } C_4H_{10}}{\text{s}}\bigg|\frac{130.2 \text{ kJ}}{\text{kg}}$$

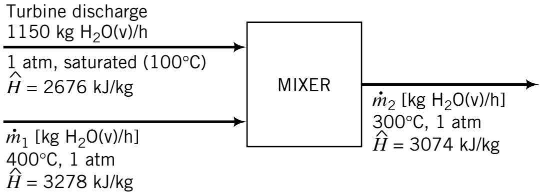
$$- [(0.600)(314.3) + (0.400)(30.0)] \text{ kJ/s} = 112 \text{ kJ/s} \Longrightarrow \frac{112 \text{ kJ/s}}{1.00 \text{ kg/s}} = \boxed{112 \frac{\text{kJ}}{\text{kg}}}$$

In the two previous examples, it was possible to complete all material balance calculations before undertaking the energy balance. In another class of problems one more stream amount or flow rate is unknown than can be determined by material balances alone. To solve problems of this type, you must write and solve material and energy balances simultaneously.

EXAMPLE 7.6-3 *Simultaneous Material and Energy Balances*

Saturated steam at 1 atm is discharged from a turbine at a rate of 1150 kg/h. Superheated steam at 300°C and 1 atm is needed as a feed to a heat exchanger; to produce it, the turbine discharge stream is mixed with superheated steam available from a second source at 400°C and 1 atm. The mixing unit operates adiabatically. Calculate the amount of superheated steam at 300°C produced and the required volumetric flow rate of the 400°C steam.

SOLUTION Specific enthalpies of the two feed streams and the product stream are obtained from the steam tables and are shown below on the flowchart.



There are two unknown quantities in this process—$\dot{m}_1$ and $\dot{m}_2$—and only one permissible material balance. (Why?) The material and energy balances must therefore be solved simultaneously to determine the two flow rates.

Mass Balance on Water $$1150\text{ kg/h} + \dot{m}_1 = \dot{m}_2 \qquad \textbf{(1)}$$

Energy Balance $$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Bigg\Downarrow \begin{array}{l} \dot{Q} = 0 \quad \text{(process is adiabatic)} \\ \dot{W}_s = 0 \quad \text{(no moving parts)} \\ \Delta\dot{E}_k \approx 0,\ \Delta\dot{E}_p \approx 0 \quad \text{(assumption)} \end{array}$$

$$\Delta\dot{H} = \sum_{\text{outlet}} \dot{m}_i\hat{H}_i - \sum_{\text{inlet}} \dot{m}_i\hat{H}_i = 0$$

$$\begin{array}{c|c} 1150\text{ kg} & 2676\text{ kJ} \\ \hline \text{h} & \text{kg} \end{array} + \dot{m}_1(3278\text{ kJ/kg}) = \dot{m}_2(3074\text{ kJ/kg}) \qquad \textbf{(2)}$$

Solving Equations 1 and 2 simultaneously yields

$$\dot{m}_1 = 2240\text{ kg/h}$$

$$\boxed{\dot{m}_2 = 3390\text{ kg/h}} \qquad \text{(product flow rate)}$$

From Table B.7, the specific volume of steam at 400°C and 1 atm (≈1 bar) is 3.11 m^3/kg. The volumetric flow rate of this stream is therefore

$$\begin{array}{c|c} 2240\text{ kg} & 3.11\text{ m}^3 \\ \hline \text{h} & \text{kg} \end{array} = \boxed{6980\text{ m}^3/\text{h}}$$

If specific-volume data were not available, the ideal gas equation of state could be used as an approximation for the last calculation.

7.7 MECHANICAL ENERGY BALANCES

In chemical process units such as reactors, distillation columns, evaporators, and heat exchangers, shaft work and kinetic and potential energy changes tend to be negligible compared with heat flows and internal energy and enthalpy changes. Energy balances on such units therefore usually omit the former terms and so take the simple form $Q = \Delta U$ (closed system) or $\dot{Q} = \Delta\dot{H}$ (open system).

Another important class of operations is one for which the opposite is true—heat flows and internal energy changes are secondary in importance to kinetic and potential energy changes and shaft work. Most of these operations involve the flow of fluids to, from, and between tanks, reservoirs, wells, and process units. Accounting for energy flows in such processes is most conveniently done with **mechanical energy balances.**

The general form of the mechanical energy balance can be derived starting with the open-system balance and a second equation expressing the law of conservation of momentum, a derivation beyond the scope of this book. This section presents a simplified form for a single incompressible liquid flowing into and out of a process system at steady state.

Consider such a system, letting $\dot{m}$ be the mass flow rate and $\hat{V}$ the specific volume of the liquid. If $\hat{V}$ is replaced by $1/\rho$, where ρ is the liquid density, then the open-system energy balance (Equation 7.4-12) may be written

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\,\Delta z + \left(\Delta\hat{U} - \frac{\dot{Q}}{\dot{m}}\right) = -\frac{\dot{W}_s}{\dot{m}} \qquad \textbf{(7.7-1)}$$

The shaft work $\dot{W}_s$ is the work done by the fluid on moving elements in the process line.

In many cases only slight amounts of heat are transferred to or from the surroundings, there is little change in temperature from inlet to outlet, and no phase changes or reactions occur. Even under these circumstances, some kinetic or potential energy is always converted to thermal energy as a result of friction due to the movement of the fluid through the system. In consequence, the quantity $(\Delta\hat{U} - \dot{Q}/\dot{m})$ always has a positive component, termed the **friction**

loss and is given the symbol $\hat{F}$. Equation 7.7-1 may therefore be written

$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\,\Delta z + \hat{F} = \frac{-\dot{W}_s}{\dot{m}}} \tag{7.7-2}$$

Equation 7.7-2 is referred to as the **mechanical energy balance.** Once again, it is valid for steady-state flow of an incompressible fluid.

Methods of estimating friction losses for flow through straight pipes, orifices, nozzles, elbows, and so on are given in Section 10 of *Perry's Chemical Engineers' Handbook* (see footnote 2) and will not be discussed in this text. In the balance of this book we consider only processes in which friction losses are either specified or neglected.

A simplified form of the mechanical energy balance is obtained for frictionless processes ($\hat{F} \approx 0$) in which no shaft work is performed ($\dot{W}_s = 0$):

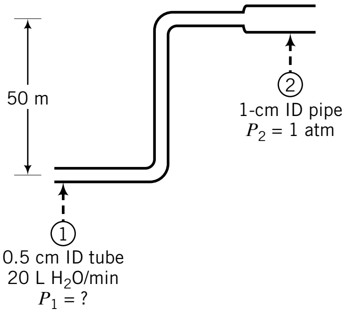
$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\,\Delta z = 0} \tag{7.7-3}$$

Equation 7.7-3 is called the **Bernoulli equation.**

EXAMPLE 7.7-1 *The Bernoulli Equation*

Water flows through the system shown here at a rate of 20 L/min. Estimate the pressure required at point ① if friction losses are negligible.

SOLUTION



All of the terms of the Bernoulli equation, Equation 7.7-3, are known except ΔP, the variable to be determined, and Δu^2, which must be calculated from the known liquid flow rate and the diameters of the inlet and outlet pipes.

Velocities $\dot{u}(\text{m/s}) = \dot{V}(\text{m}^3/\text{s})/A(\text{m}^2)$

The volumetric flow rate must be the same at points ① and ②. (Why?)

$$u_1 = \begin{array}{c|c|c|c|c} 20\text{ L} & 1\text{ m}^3 & & 10^4\text{ cm}^2 & 1\text{ min} \\ \hline \text{min} & 10^3\text{ L} & \pi(0.25)^2\text{ cm}^2 & \text{m}^2 & 60\text{ s} \end{array} = 17.0\text{ m/s}$$

$$u_2 = \begin{array}{c|c|c|c|c} 20\text{ L} & 1\text{ m}^3 & & 10^4\text{ cm}^2 & 1\text{ min} \\ \hline \text{min} & 10^3\text{ L} & \pi(0.5)^2\text{ cm}^2 & 1\text{ m}^2 & 60\text{ s} \end{array} = 4.24\text{ m/s}$$

$$\Downarrow$$

$$\begin{aligned} \Delta u^2 &= (u_2^2 - u_1^2) = (4.24^2 - 17.0^2)\text{ m}^2/\text{s}^2 \\ &= -271.0\text{ m}^2/\text{s}^2 \end{aligned}$$

Bernoulli Equation (Equation 7.7-3)

$$\frac{\Delta P(\text{N/m}^2)}{\rho(\text{kg/m}^3)} + \frac{\Delta u^2(\text{m}^2/\text{s}^2)}{2\cdot 1[(\text{kg}\cdot\text{m/s}^2)/\text{N}]} + \frac{g(\text{m/s}^2)\Delta z(\text{m})}{1[(\text{kg}\cdot\text{m/s}^2)/\text{N}]}$$

$$\Bigg\Downarrow \begin{array}{l} \Delta P = P_2 - P_1 \\ \rho = 1000\ \text{kg/m}^3 \\ \Delta u^2 = -271.0\ \text{m}^2/\text{s}^2 \\ g = 9.81\ \text{m/s}^2 \\ \Delta z = z_2 - z_1 \\ \quad = 50\ \text{m} \end{array}$$

$$\frac{P_2 - P_1}{1000\ \text{kg/m}^3} - 135.5\ \text{N}\cdot\text{m/kg} + 490\ \text{N}\cdot\text{m/kg} = 0$$

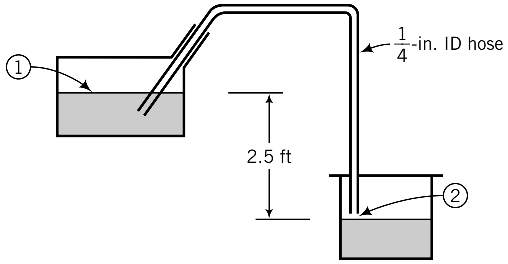
$$\Bigg\Downarrow \begin{array}{l} P_2 = 1\ \text{atm} \\ \quad = 1.01325 \times 10^5\ \text{N/m}^2 \end{array}$$

$$\begin{aligned} P_1 &= 4.56 \times 10^5\ \text{N/m}^2 \\ &= 4.56 \times 10^5\ \text{Pa} \\ &= \boxed{4.56\ \text{bar}} \end{aligned}$$

A common type of problem to which the mechanical energy balance is applicable is one that involves drainage or siphoning of a liquid from a container. A suitable choice of the locations of points ① and ② greatly simplifies such problems; it is convenient to choose as point ① a location on the liquid surface in the tank being drained and to take point ② at the discharge stream outlet. If the container is being drained relatively slowly, the kinetic energy at point ① may be neglected. Example 7.7-2 illustrates the computational procedure for such problems.

EXAMPLE 7.7-2 *Siphoning*

Gasoline ($\rho = 50.0\ \text{lb}_\text{m}/\text{ft}^3$) is to be siphoned from a tank. The friction loss in the line is $\hat{F} = 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$. Estimate how long it will take to siphon 5.00 gal, neglecting the change in liquid level in the gasoline tank during this process and assuming that both point ① (at the liquid surface in the gas tank) and point ② (in the tube just prior to the exit) are at 1 atm.



SOLUTION

Point ①: $P_1 = 1$ atm, $u_1 \approx 0$ ft/s, $z_1 = 2.5$ ft
Point ②: $P_2 = 1$ atm, $u_2 = ?$, $z_2 = 0$ ft

Mechanical Energy Balance (Equation 7.7-2)

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\,\Delta z + \hat{F} = \frac{-\dot{W}_s}{\dot{m}}$$

$$\Bigg\Downarrow\;\begin{array}{|l} \Delta P = 0 \\ \Delta u^2 \approx u_2^2 \\ g = 32.174\ \text{ft/s}^2 \\ \Delta z = -2.5\ \text{ft} \\ \hat{F} = 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m} \\ \dot{W}_s = 0 \end{array}$$

$$\begin{array}{c|c} u_2^2(\text{ft}^2/\text{s}^2) & 1\ \text{lb}_\text{f} \\ \hline 2 & 32.174\ \text{lb}_\text{m}\cdot\text{ft/s}^2 \end{array} + \begin{array}{c|c|c} 32.174\ \text{ft/s}^2 & -\,2.5\ \text{ft} & 1\ \text{lb}_\text{f} \\ \hline & & 32.174\ \text{lb}_\text{m}\cdot\text{ft/s}^2 \end{array} + 0.80\ \text{ft}\cdot\text{lb}_\text{f}/\text{lb}_\text{m}$$

$$\Downarrow$$

$$u_2 = 10.5\ \text{ft/s}$$

(Verify that each additive term in the preceding equation has the units ft·$\text{lb}_\text{f}/\text{lb}_\text{m}$.)
The volumetric flow rate of the fluid in the tube is

$$\dot{V}(\text{ft}^3/\text{s}) = u_2(\text{ft/s})\cdot A(\text{ft}^2)$$

$$= \begin{array}{c|c|c} 10.5\ \text{ft} & \pi(0.125)^2\ \text{in.}^2 & 1\ \text{ft}^2 \\ \hline \text{s} & & 144\ \text{in.}^2 \end{array} = 3.58 \times 10^{-3}\ \text{ft}^3/\text{s}$$

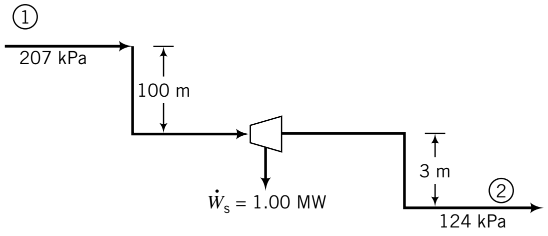
$$t(\text{s}) = \frac{\text{volume to be drained (ft}^3)}{\text{volumetric flow rate (ft}^3/\text{s)}}$$

$$= \frac{(5.00\ \text{gal})(0.1337\ \text{ft}^3/\text{gal})}{3.58 \times 10^{-3}\ \text{ft}^3/\text{s}} = \frac{187\ \text{s}}{60\ \text{s/min}} = \boxed{3.1\ \text{min}}$$

The last illustration we will consider is one in which the potential energy lost by falling water is converted to electrical energy by means of a turbine and generator. The work done by the water in rotating the turbine must be included as shaft work in the energy balance.

EXAMPLE 7.7-3 *Hydraulic Power Generation*

Water flows from an elevated reservoir through a conduit to a turbine at a lower level and out of the turbine through a similar conduit. At a point 100 m above the turbine the pressure is 207 kPa, and at a point 3 m below the turbine the pressure is 124 kPa. What must the water flow rate be if the turbine output is 1.00 MW?



SOLUTION

No data are given for the friction loss so we will set $\hat{F} = 0$, recognizing that doing so introduces an error into the calculation. Since the diameters of the conduits at points ① and ② are the same and water may be considered incompressible, $\Delta u^2 = 0$. Equation 7.7-2 then becomes

$$\frac{\Delta P}{\rho} + g\,\Delta z = \frac{-\dot{W}_s}{\dot{m}}$$

$$\Downarrow$$

$$\dot{m} = \frac{-\dot{W}_s}{\dfrac{\Delta P}{\rho} + g\,\Delta z}$$

$$\dot{W}_s = 1.00\text{ MW} = 1.00 \times 10^5\text{ N}\cdot\text{m/s} \quad \text{(convince yourself)}$$

$$\Delta P = (124 - 207)\text{ kPa} = -83\text{ kPa} = -83 \times 10^3\text{ N/m}^2$$

$$\frac{\Delta P}{\rho} = \frac{-83 \times 10^3\text{ N/m}^2}{1.00 \times 10^3\text{ kg/m}^3} = -83\text{ N}\cdot\text{m/kg}$$

$$g = 9.81\text{ m/s}^2$$

$$\Delta z = -103\text{ m}$$

$$g\,\Delta z = \frac{9.81\text{ m}}{\text{s}^2}\left|\frac{-103\text{ m}}{}\right|\frac{1\text{ N}}{1\text{ kg}\cdot\text{m/s}^2} = -1010\text{ N}\cdot\text{m/kg}$$

$$\Downarrow$$

$$\dot{m} = \frac{-1.00 \times 10^6\text{ N}\cdot\text{m/s}}{(-83 - 1010)\text{ N}\cdot\text{m/kg}} = \boxed{915\text{ kg/s}}$$

TEST YOURSELF (Answers, p. 659)

1. Under what conditions is the mechanical energy balance, Equation 7.7-2, applicable? What is the physical significance of the friction loss term, $\hat{F}$, in this equation?
2. Under what conditions is the Bernoulli equation, Equation 7.7-3, applicable?

7.8 SUMMARY

Considerable amounts of energy are required to run most chemical processes. Engineers use **energy balances** to account for the energy that flows into or out of each unit of a process, to determine the net energy requirement for the process, and to design ways to reduce the energy requirement so as to improve process profitability.

- The total energy of a process system has three components: **kinetic energy**—energy due to motion of the system as a whole; **potential energy**—energy due to the position of the system in a potential field (such as the earth's gravitational field); and **internal energy**—energy due to the translation, rotation, vibration, and electromagnetic interactions of the molecules, atoms, and subatomic particles within the system.
- In a **closed system** (no mass is transferred across the system boundaries while the process is taking place), energy may be transferred between the system and its surroundings in two ways: as **heat**—energy that flows due to a temperature difference between the system and its surroundings, and as **work**—energy that flows in response to any other stimulus such as an applied force, a torque, or a voltage. Heat always flows from a higher temperature to a lower temperature. Heat is always defined to be positive if it flows to a system from the surroundings, and in many engineering references (including this one) work is defined as positive if it flows from the system to the surroundings.
- The **kinetic energy** of a body of mass m moving with velocity u is $E_k = mu^2/2$. The **gravitational potential energy** of the body is $E_p = mgz$, where g is the acceleration of gravity and

z is the height of the object above a reference plane at which E_p is arbitrarily defined to be zero. If a stream at height z flows with mass flow rate $\dot{m}$ and velocity u, $\dot{E}_k = \dot{m}u^2/2$ and $\dot{E}_p = \dot{m}gz$ may be thought of as the rates at which the stream is transporting kinetic energy and gravitational potential energy, respectively.[3]

- The **first law of thermodynamics for a closed system** (which we will generally refer to as the *energy balance*) between two instants of time is

$$\boxed{\Delta U + \Delta E_k + \Delta E_p = Q - W} \qquad \textbf{(7.3-4)}$$

where in the context of closed systems, Δ denotes final value minus initial value. This equation states that the total energy transferred to the system in the specified time interval $(Q - W)$ equals the gain in the total energy of the system in the same time interval $(\Delta U + \Delta E_k + \Delta E_p)$. If energy is transferred *away* from the system, both sides of the equation are negative.

- When writing an energy balance for a closed system, first simplify Equation 7.3-4 by dropping negligible terms, then solve the simplified equation for whichever variable cannot be determined independently from other information in the process description.

  (a) If the system is **isothermal** (constant temperature), no phase changes or chemical reactions take place, and pressure changes are no more than a few atmospheres in magnitude, then $\Delta U \approx 0$.

  (b) If the system is not accelerating, then $\Delta E_k = 0$. If the system is not rising or falling, then $\Delta E_p = 0$. (You will almost always be able to drop these terms when writing balances on closed chemical process systems.)

  (c) If the system and its surroundings are at the same temperature or if the system is perfectly insulated, then $Q = 0$. The system is then termed **adiabatic.**

  (d) If energy is not transmitted across the system boundary by a moving part (such as a piston, an impeller, or a rotor), an electric current, or radiation, then $W = 0$.

- In an open system, work must be done to push input streams into the system $[= \sum_{\text{out}} P_j \dot{V}_j]$ and work is done by the output streams as they leave the system $[= \sum_{\text{in}} P_j \dot{V}_j]$, where P_j is the pressure of input or output stream j and $\dot{V}_j$ is the volumetric flow rate of the stream. The total rate of work done by a system on its surroundings $(\dot{W})$ is customarily divided into **flow work** $(\dot{W}_{\text{fl}})$, or work done by the output streams minus work done on the input streams at the system boundary, and **shaft work** $(\dot{W}_s)$, all other work transferred across the system boundary by moving parts or as electricity or radiation. Thus

$$\dot{W} = \dot{W}_s + \dot{W}_{\text{fl}} = \dot{W}_s + \sum_{\substack{\text{output}\\\text{streams}}} P_j \dot{V}_j - \sum_{\substack{\text{input}\\\text{streams}}} P_j \dot{V}_j$$

- The first law of thermodynamics for an open system at steady state resembles the closed-system balance:

$$\Delta \dot{U} + \Delta \dot{E}_k + \Delta \dot{E}_p = \dot{Q} - \dot{W}$$

except that each term now has units of (kJ/s) instead of (kJ) and Δ now signifies (output $-$ input) and not (final $-$ initial). The more commonly used form of the first law is derived by (a) substituting for $\dot{W}$ the previously derived expression in terms of flow work and shaft work; (b) expressing the volumetric flow rate of each input and output stream $(\dot{V}_j)$ as $\dot{m}_j \hat{V}_j$, where $\hat{V}_j$ is the **specific volume** (inverse density) of the stream fluid; (c) expressing the rate of transport of internal energy by a stream $(\dot{U}_j)$ as $\dot{m}_j \hat{U}_j$, where $\hat{U}_j$ is the **specific internal**

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[3] The unit conversion factors $[(1\ \text{N})/(1\ \text{kg·m/s}^2)]$ and $[(1\ \text{kJ})/(10^3\ \text{N·m})]$ must be applied to the right-hand side of each of these equations to express these quantities in kJ/s (kW).

energy of the stream fluid; and (d) defining the **specific enthalpy** ($\hat{H}$) of a substance as $\hat{U} + P\hat{V}$. After some algebraic manipulation (Section 7.4c) the balance equation becomes

$$\boxed{\Delta\dot{H} + \Delta\dot{E}_\text{k} + \Delta\dot{E}_\text{p} = \dot{Q} - \dot{W}_\text{s}} \qquad \textbf{(7.4-15)}$$

where

$$\Delta\dot{H} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j\hat{H}_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j\hat{H}_j$$

$$\Delta\dot{E}_\text{k} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j u_j^2/2 - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j u_j^2/2$$

$$\Delta\dot{E}_\text{p} = \sum_{\substack{\text{output}\\ \text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{input}\\ \text{streams}}} \dot{m}_j g z_j$$

- When writing an energy balance for an open system at steady state, first simplify Equation 7.4-15 by dropping negligible terms, then solve the simplified equation for whichever variable cannot be determined independently from other information in the process description.

  (a) If no temperature changes, phase changes, or chemical reactions occur in a process and pressure changes from inlet to outlet are no more than a few atmospheres in magnitude, then $\Delta\dot{H} \approx 0$. (Under these circumstances, mechanical energy balances—Section 7.7—tend to be more useful than Equation 7.4-15.)
  (b) If conditions are such that $\Delta\dot{H}$ may not be neglected (i.e., if temperature changes, phase changes, or chemical reactions occur), then $\Delta\dot{E}_\text{k}$ and $\Delta\dot{E}_\text{p}$ usually may be neglected. In any case, if there are no great vertical distances between the inlets and the outlets of a system, $\Delta\dot{E}_\text{p} \approx 0$.
  (c) If the system and its surroundings are at the same temperature or if the system is perfectly insulated, then $\dot{Q} = 0$ and the process is adiabatic.
  (d) If energy is not transmitted across the system boundary by a moving part, an electric current, or radiation, then $\dot{W}_\text{s} = 0$.

- The value of $\hat{U}$ for a pure substance in a given state (temperature, pressure, and phase) is the sum of the kinetic and potential energies of the individual molecular, atomic, and subatomic particles in a unit amount of the substance. *It is impossible to determine the true value of $\hat{U}$ for a substance, and hence also impossible to determine the true value of $\hat{H} = \hat{U} + P\hat{V}$.* However, we can measure the *change* in $\hat{U}$ or $\hat{H}$ corresponding to a specified change of state, which is all we ever need to know for energy balance calculations.
- A common practice is to arbitrarily designate a **reference state** for a substance at which $\hat{U}$ or $\hat{H}$ is declared to equal zero, and then tabulate $\hat{U}$ and/or $\hat{H}$ for the substance relative to the reference state. The statement "The specific enthalpy of CO(g) at 100°C and 1 atm relative to CO(g) at 0°C and 1 atm is 2919 J/mol" therefore has the following meaning:

  $$\text{CO(g, 0°C, 1 atm)} \rightarrow \text{CO(g, 100°C, 1 atm)}: \ \Delta\hat{H} = 2919 \text{ J/mol}$$

  The statement says nothing about the absolute specific enthalpy of CO at 100°C and 1 atm, which can never be determined.
- Both $\hat{U}$ and $\hat{H}$ are **state properties,** meaning that $\Delta\hat{U}$ and $\Delta\hat{H}$ for a given change in state for a substance are the same regardless of the path the substance follows from the initial state to the final state.
- The **steam tables** (Tables B.5, B.6, and B.7) can be used to estimate $\hat{U}$ and $\hat{H}$ for liquid water and steam (water vapor) at any specified temperature and pressure. The reference state for the tabulated internal energies and enthalpies in the steam tables is liquid water at the triple point—0.01°C and 0.00611 bar.

- At this point, you can perform energy balance calculations only for systems in which ΔU (closed system) or $\Delta \dot{H}$ (open system) can be neglected and for nonreactive systems involving species for which tables of $\hat{U}$ or $\hat{H}$ are available. Energy balance procedures for other types of systems are presented in Chapters 8 and 9.
- **Mechanical energy balances** are useful for open systems in which heat flows and internal energy (and enthalpy) changes are secondary in importance to kinetic and potential energy changes and shaft work. For a liquid of constant density ρ flowing through such a system, the steady-state mechanical energy balance is

$$\boxed{\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\,\Delta z + \hat{F} = \frac{-\dot{W}_s}{\dot{m}}} \qquad \textbf{(7.7-2)}$$

where $\hat{F}$(N·m/kg) is the **friction loss**—thermal energy generated by friction between adjacent liquid elements moving at different velocities and between liquid elements and the system walls. The friction loss shows up as a heat loss from the system ($\dot{Q} < 0$) and/or a gain in temperature and hence in internal energy from inlet to outlet ($\Delta \dot{U} > 0$). If $\hat{F}$ and $\dot{W}_s$ can be neglected, the resulting form of Equation 7.7-2 is the **Bernoulli equation.**
- At this point you can solve mechanical energy balances only for systems in which the friction loss ($\hat{F}$) is given or negligible or if it is the only unknown quantity in Equation 7.7-2. Texts on fluid mechanics present methods for estimating $\hat{F}$ from information about fluid flow rates and physical properties and various characteristics of the system through which the fluid is flowing.

PROBLEMS

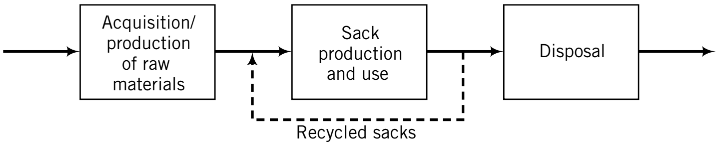
7.1. A certain gasoline engine has an efficiency of 30%; that is, it converts into useful work 30% of the heat generated by burning a fuel. If the engine consumes 0.80 L/h of a gasoline with a heating value of 3.5×10^4 kJ/L, how much power does it provide? Express the answer both in kW and horsepower.

7.2. Consider an automobile with a mass of 5500 lb_m braking to a stop from a speed of 55 miles/h.

(a) How much energy (Btu) is dissipated as heat by the friction of the braking process?

(b) Suppose that throughout the United States, 300,000,000 such braking processes occur in the course of a given day. Calculate the average rate (megawatts) at which energy is being dissipated by the resulting friction.

7.3. A simplified version of the life cycle of grocery sacks is shown below.[4]



In the late 1970s, supermarkets began to replace paper sacks with polyethylene (plastic) sacks. In the 1980s, a movement to go back to paper arose, primarily inspired by environmental considerations. In the 1990s, a countermovement arose, claiming that paper sacks have a greater negative environmental impact than plastic ones. As this book goes to press, the debate continues.

Following are estimates of the atmospheric emissions and energy consumption associated with the raw materials acquisition and processing (logging, pulping, and papermaking for paper, petroleum production and refining and polymerization for polyethylene) and disposal of sacks, and for the manufacture and use of sacks.

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[4] Problem adapted from D. T. Allen, N. Bakshani, and K. S. Rosselot, *Pollution Prevention: Homework and Design Problems for Engineering Curricula,* American Institute for Pollution Prevention, New York, 1992. The emissions and energy consumption data are from Franklin Associates, Ltd., *Resource and Environmental Profile Analysis of Polyethylene and Unbleached Paper Grocery Sacks.* Report prepared for the Council for Solid Waste Solutions, Prairie Village, KS, June 1990.

	Emissions (oz/sack)		Energy Consumed (Btu/sack)	
Stages	Paper	Plastic	Paper	Plastic
Raw materials production plus product disposal	0.0510	0.0045	724	185
Sack production and use	0.0516	0.0146	905	464

Assume that atmospheric emissions and energy consumption do not depend on whether the new sacks are made from fresh raw materials or recycled sacks, and that it takes roughly twice as many plastic sacks as paper sacks to hold a given quantity of groceries.

(a) Calculate the air emissions (lb_m) and energy consumption (Btu) per 1000 paper sacks used and per 2000 plastic sacks used, assuming that no sacks are recycled.

(b) Repeat the calculations of part (a) assuming that 60% of the used sacks are recycled. By what percentages are air emissions and energy consumption reduced for each sack material as a consequence of recycling?

(c) Estimate the number of grocery sacks used in a day in the United States (population = 300 million), and calculate the average rate of energy consumption (megawatts, MW) associated with the production, use, and disposal of these sacks, assuming that they are plastic and none are recycled. How many MW would be saved by 60% recycling?

(d) You should have found that both atmospheric emissions and energy consumption are higher when paper is used rather than plastic, although recycling reduces the differences. Nevertheless, deciding to use plastic based entirely on this result could be a serious mistake. List several important factors that were not taken into account in making the decision, including considerations of the potential environmental impact of each type of bag.

Equipment Encyclopedia
pump

7.4. Liquid methanol is pumped from a large storage tank through a 1-in. ID pipe at a rate of 3.00 gal/min.

(a) At what rate in (i) ft·lb_f/s and (ii) hp is kinetic energy being transported by the methanol in the pipe?

(b) The electrical power input to the pump transporting the methanol must be greater than the amount you calculated in part (a). What would you guess becomes of the additional energy? (There are several possible answers.)

7.5. Air at 300°C and 130 kPa flows through a horizontal 7-cm ID pipe at a velocity of 42.0 m/s.

(a) Calculate $\dot{E}_k$(W), assuming ideal gas behavior.

(b) If the air is heated to 400°C at constant pressure, what is $\Delta\dot{E}_k = \dot{E}_k(400°\text{C}) - \dot{E}_k(300°\text{C})$?

(c) Why would it be incorrect to say that the rate of transfer of heat to the gas in part (b) must equal the rate of change of kinetic energy?

7.6. Suppose you pour a gallon of water on a yowling cat 10 ft below your bedroom window.

(a) How much potential energy (ft·lb_f) does the water lose?

(b) How fast is the water traveling (ft/s) just before impact?

(c) True or false: Energy must be conserved, therefore the kinetic energy of the water before impact must equal the kinetic energy of the cat after impact.

7.7. Methane enters a 3-cm ID pipe at 30°C and 10 bar with an average velocity of 5.00 m/s and emerges at a point 200 m lower than the inlet at 30°C and 9 bar.

(a) Without doing any calculations, predict the signs (+ or −) of $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$, where Δ signifies (outlet − inlet). Briefly explain your reasoning.

(b) Calculate $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$ (W), assuming that the methane behaves as an ideal gas.

7.8. You recently purchased a large plot of land in the Amazon jungle at an extremely low cost. You are quite pleased with yourself until you arrive there and find that the nearest source of electricity is 1500 miles away, a fact that your brother-in-law, the real estate agent, somehow forgot to mention. Since the local hardware store does not carry 1500-mile-long extension cords, you decide to build a small hydroelectric generator under a 75-m high waterfall located nearby. The flow rate of the waterfall is 10^5 m^3/h, and you anticipate needing 750 kW·h/wk to run your lights, air conditioner, and television. Calculate the maximum power theoretically available from the waterfall and see if it is sufficient to meet your needs.

Equipment Encyclopedia
reactor

7.9. Write and simplify the closed-system energy balance (Equation 7.3-4) for each of the following processes, and state whether nonzero heat and work terms are positive or negative. Begin by defining the system. The solution of part (a) is given as an illustration.

(a) The contents of a closed flask are heated from 25°C to 80°C.

Solution. The system is the flask contents.

$$Q - W = \Delta U + \Delta E_{\text{k}} + \Delta E_{\text{p}}$$

$$\Bigg\Downarrow \begin{aligned} W &= 0 \quad \text{(no moving parts or generated currents)} \\ \Delta E_{\text{k}} &= 0 \quad \text{(system is stationary)} \\ \Delta E_{\text{p}} &= 0 \quad \text{(no height change)} \end{aligned}$$

$$\boxed{Q = \Delta U}$$

$$\boxed{Q > 0 \quad \text{(heat is transferred to the system)}}$$

(b) A tray filled with water at 20°C is put into a freezer. The water turns into ice at −5°C. (*Note:* When a substance expands it does work on its surroundings and when it contracts the surroundings do work on it.)

(c) A chemical reaction takes place in a closed adiabatic (perfectly insulated) rigid container.

(d) Repeat part (c), only suppose that the reactor is isothermal rather than adiabatic and that when the reaction was carried out adiabatically the temperature in the reactor increased.

Student Workbook

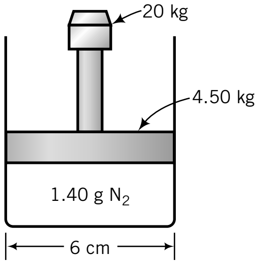
7.10. A cylinder with a movable piston contains 4.00 liters of a gas at 30°C and 5.00 bar. The piston is slowly moved to compress the gas to 8.00 bar.

(a) Considering the system to be the gas in the cylinder and neglecting ΔE_{p}, write and simplify the closed-system energy balance. Do not assume that the process is isothermal in this part.

(b) Suppose now that the process is carried out isothermally, and the compression work done on the gas equals 7.65 L·bar. If the gas is ideal so that $\hat{U}$ is a function only of T, how much heat (in joules) is transferred to or from (state which) the surroundings? (Use the gas-constant table in the back of the book to determine the factor needed to convert L·bar to joules.)

(c) Suppose instead that the process is adiabatic and that $\hat{U}$ increases as T increases. Is the final system temperature greater than, equal to, or less than 30°C? (Briefly state your reasoning.)

7.11. A piston-fitted cylinder with a 6-cm inner diameter contains 1.40 g of nitrogen. The mass of the piston is 4.50 kg, and a 20.00-kg weight rests on the piston. The gas temperature is 30°C, and the pressure outside the cylinder is 1.00 atm.



(a) Prove that the absolute pressure of the gas in the cylinder is 1.86×10^5 Pa. Then calculate the volume occupied by the gas, assuming ideal gas behavior.

(b) Suppose the weight is abruptly lifted and the piston rises to a new equilibrium position. Further suppose that the process takes place in two steps: a rapid step in which a negligible amount of heat is exchanged with the surroundings, followed by a slow step in which the gas returns to 30°C. Considering the gas as the system, write the energy balances for step 1, step 2, and the overall process. In all cases, neglect ΔE_{k} and ΔE_{p}. If $\hat{U}$ varies proportionally with T, does the gas temperature increase or decrease in step 1? Briefly explain your answer.

(c) The work done by the gas equals the restraining force (the weight of the piston plus the force due to atmospheric pressure) times the distance traveled by the piston. Calculate this quantity and use it to determine the heat transferred to or from (state which) the surroundings during the process.

7.12. Oxygen at 150 K and 41.64 atm has a tabulated specific volume of 4.684 cm^3/g and a specific internal energy of 1706 J/mol. Calculate the specific enthalpy of O_2 in this state.

7.13. Values of the specific internal energy of bromine at three conditions are listed here.

State	T(K)	P(bar)	$\hat{V}$(L/mol)	$\hat{U}$(kJ/mol)
Liquid	300	0.310	0.0516	0.000
Vapor	300	0.310	79.94	28.24
Vapor	340	1.33	20.92	29.62

(a) What reference state was used to generate the listed specific internal energies?

(b) Calculate $\Delta\hat{U}$(kJ/mol) for a process in which bromine vapor at 300 K is condensed at constant pressure. Then calculate $\Delta\hat{H}$(kJ/mol) for the same process. (See Example 7.4-1.) Finally, calculate ΔH(kJ) for 5.00 mol of bromine undergoing the process.

(c) Bromine vapor in a 5.00-liter container at 300 K and 0.205 bar is to be heated to 340 K. Calculate the heat (kJ) that must be transferred to the gas to achieve the desired temperature increase, assuming that $\hat{U}$ is independent of pressure.

(d) In reality, more heat than the amount calculated in part (c) would have to be transferred to the container to raise the gas temperature by 40 K, for several reasons. State two of them.

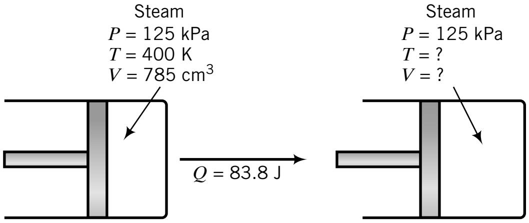
7.14. Prove that for an ideal gas, $\hat{U}$ and $\hat{H}$ are related as $\hat{H} = \hat{U} + RT$, where R is the gas constant. Then:

(a) Taking as given that the specific internal energy of an ideal gas is independent of the gas pressure, justify the claim that $\Delta\hat{H}$ for a process in which an ideal gas goes from (T_1, P_1) to (T_2, P_2) equals $\Delta\hat{H}$ for the same gas going from T_1 to T_2 at a constant pressure of P_1.

(b) Calculate ΔH(cal) for a process in which the temperature of 2.5 mol of an ideal gas is raised by 50°C, resulting in a specific internal energy change $\Delta\hat{U} = 3500$ cal/mol.

7.15. If a system expands in volume by an amount $\Delta V(m^3)$ against a constant restraining pressure $P(N/m^2)$, a quantity $P\Delta V$(J) of energy is transferred as *expansion work* from the system to its surroundings. Suppose that the following four conditions are satisfied for a closed system: (a) the system expands against a constant pressure (so that $\Delta P = 0$); (b) $\Delta E_k = 0$; (c) $\Delta E_p = 0$; and (d) the only work done by or on the system is expansion work. Prove that under these conditions, the energy balance simplifies to $Q = \Delta H$.

7.16. A horizontal cylinder equipped with a frictionless piston contains 785 cm^3 of steam at 400 K and 125 kPa. A total of 83.8 joules of heat is transferred to the steam, causing the steam temperature to rise and the cylinder volume to increase. A constant restraining force is maintained on the piston throughout the expansion, so that the pressure exerted by the piston on the steam remains constant at 125 kPa.



The specific enthalpy of steam at 125 kPa varies with temperature approximately as

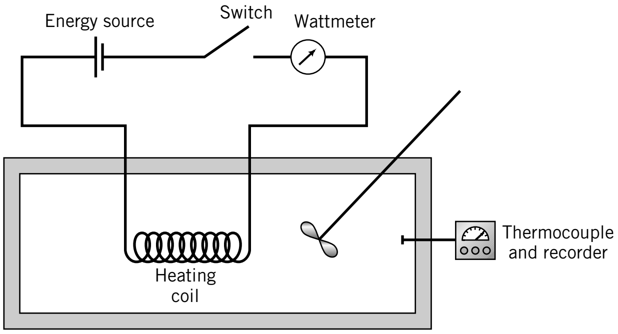
$$\hat{H}(\text{J/mol}) = 34{,}980 + 35.5T(\text{K})$$

(a) Taking the steam as the system, convince yourself that $Q = \Delta H$ for this process—that is, the four conditions specified in part (a) of Problem 7.15 are applicable. Then prove that the final steam temperature is 480 K. Finally, calculate (i) the final cylinder volume, (ii) the expansion work done by the steam, and (iii) ΔU(J).

(b) Which of the specified conditions of Problem 7.15 would have been only an approximation if the cylinder were not horizontal?

Equipment Encyclopedia
thermocouple

7.17. You are performing an experiment to measure the specific internal energy of a gas relative to a reference state of 25°C and 1 atm (at which conditions $\hat{U}$ is arbitrarily set equal to 0). The gas is placed in a closed insulated 2.10-liter container at 25°C and 1 atm. A switch is alternately closed and opened, causing a current to flow intermittently through an electrical heating coil in the chamber. The gas temperature, which is monitored with a calibrated thermocouple, increases while the circuit is closed and remains constant while it is open. A wattmeter reads 1.4 W when the circuit is closed; 90% of this power is transferred to the gas as heat. The thermocouple calibration curve is a straight line through the points ($T = 0°\text{C}, E = -0.249$ mV) and ($T = 100°\text{C}, E = 5.27$ mV), where E is the thermocouple potentiometer reading.



The following data are taken, where t represents the cumulative time during which the circuit was closed:

t(s)	0	30	60	90
E(mV)	1.13	2.23	3.34	4.44

(a) Which given item of information suggests that the chamber may be considered adiabatic? (*Note:* Simply saying the container is insulated does not guarantee that it is adiabatic.)

(b) Write the energy balance for the gas in the chamber and use it to calculate $\hat{U}$(J/mol) at each of the observed temperatures, neglecting the work done on the gas by the stirrer. Express your solution as a table of $\hat{U}$ versus T.

(c) What might the purpose of the stirrer be?

(d) What happens to the 0.14 W of power that does not go to raise the temperature of the gas?

(e) A colleague points out to you that the calculated values of $\hat{U}$ fail to take something into account and so do not precisely correspond to the values at the calculated temperatures and 1 atm. You reply that she is quite correct, but it does not matter. Justify her statement and state the basis of your reply. Suggest several ways to provide quantitative validation of your claim.

Equipment Encyclopedia
turbine, heat exchanger, pump, reactor

7.18. Define a system and simplify the open-system energy balance (Equation 7.4-15) for each of the following cases. State when possible whether nonzero heat and shaft work terms are positive or negative. The solution of part (a) is given as an illustration.

(a) Steam enters a rotary turbine and turns a shaft connected to a generator. The inlet and outlet steam ports are at the same height. Some energy is transferred to the surroundings as heat.

Solution. The system is the steam flowing from the inlet port to the outlet port:

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

$$\Big\Downarrow \Delta\dot{E}_p = 0 \quad \text{(no height change)}$$

$$\boxed{\Delta\dot{H} + \Delta\dot{E}_k = \dot{Q} - \dot{W}_s}$$

$$\boxed{\begin{array}{c}\dot{Q}\text{ is negative}\\ \dot{W}_s\text{ is positive}\end{array}}$$

(b) A liquid stream flows through a heat exchanger in which it is heated from 25°C to 80°C. The inlet and outlet pipes have the same diameter, and there is no change in elevation between these points.

(c) Water passes through the sluice gate of a dam and falls on a turbine rotor, which turns a shaft connected to a generator. The fluid velocity on both sides of the dam is negligible, and the water undergoes insignificant pressure and temperature changes between the inlet and outlet. (See Example 7.4-2.)

(d) Crude oil is pumped through a cross-country pipeline. The pipe inlet is 200 m higher than the outlet, the pipe diameter is constant, and the pump is located near the midpoint of the pipeline. Energy dissipated by friction in the line is transferred as heat through the wall.

(e) A chemical reaction takes place in a continuous reactor that contains no moving parts. Kinetic and potential energy changes from inlet to outlet are negligible.

7.19. Air is heated from 25°C to 150°C prior to entering a combustion furnace. The change in specific enthalpy associated with this transition is 3640 J/mol. The flow rate of air at the heater outlet is 1.25 m^3/min and the air pressure at this point is 122 kPa absolute.

(a) Calculate the heat requirement in kW, assuming ideal gas behavior and that kinetic and potential energy changes from the heater inlet to the outlet are negligible.

(b) Would the value of $\Delta\dot{E}_k$ [which was neglected in part (a)] be positive or negative, or would you need more information to be able to tell? If the latter, what additional information would be needed?

7.20. A **Thomas flowmeter** is a device in which heat is transferred at a measured rate from an electric coil to a flowing fluid, and the flow rate of the stream is calculated from the measured temperature increase of the fluid. Suppose a device of this sort is inserted in a stream of nitrogen, the current through the heating coil is adjusted until the wattmeter reads 1.25 kW, and the stream temperature goes from 30°C and 110 kPa before the heater to 34°C and 110 kPa after the heater.

(a) If the specific enthalpy of nitrogen is given by the formula

$$\hat{H}(\text{kJ/kg}) = 1.04[T(°\text{C}) - 25]$$

what is the volumetric flow rate of the gas (L/s) upstream of the heater (i.e., at 30°C and 110 kPa)?

(b) List several assumptions made in the calculation of part (a) that could lead to errors in the calculated flow rate.

Student Workbook

7.21. The specific enthalpy of liquid *n*-hexane at 1 atm varies linearly with temperature and equals 25.8 kJ/kg at 30°C and 129.8 kJ/kg at 50°C.

(a) Determine the equation that relates $\hat{H}$(kJ/kg) to T(°C) and calculate the reference temperature on which the given enthalpies are based. Then derive an equation for $\hat{U}(T)$(kJ/kg) at 1 atm.

(b) Calculate the average heat transfer rate required to cool 20 kg of liquid *n*-hexane from 80°C to 20°C in 5 min.

Equipment Encyclopedia
nozzle

7.22. Steam at 260°C and 7.00 bar absolute is expanded through a nozzle to 200°C and 4.00 bar. Negligible heat is transferred from the nozzle to its surroundings. The approach velocity of the steam is negligible. The specific enthalpy of steam is 2974 J/kg at 260°C and 7 bar and 2860 kJ/kg at 200°C and 4 bar. Use the open-system energy balance to calculate the exit steam velocity.

7.23. The heart pumps blood at an average rate of 5 L/min. The gauge pressure on the venous (intake) side is 0 mm Hg and that on the arterial (discharge) side is 100 mm Hg. Energy is supplied to the heart as heat released by the absorption of oxygen in the cardiac muscles: 5 mL (STP) O_2/min is absorbed, and 20.2 J is released per mL of O_2 absorbed. Part of this absorbed energy is converted to flow work (the work done to pump blood through the circulatory system), and the balance is lost as heat transferred to the tissues surrounding the heart.

(a) Simplify Equation 7.4-12 for this system, assuming (among other things) that there is no change in internal energy from inlet to outlet.

(b) What percentage of the heat input to the heart ($\dot{Q}_{\text{in}}$) is converted to flow work? (The answer may be thought of as the efficiency of the heart as a pump.)

7.24. Saturated steam at 100°C is heated to 400°C. Use the steam tables to determine (a) the required heat input (J/s) if a continuous stream flowing at 100 kg/s undergoes the process at constant pressure and (b) the required heat input (J) if 100 kg undergoes the process in a constant-volume container. What is the physical significance of the difference between the numerical values of these two quantities?

Equipment Encyclopedia
boiler

7.25. A fuel oil is burned with air in a boiler furnace. The combustion produces 813 kW of thermal energy, of which 65% is transferred as heat to boiler tubes that pass through the furnace. The combustion products pass from the furnace to a stack at 650°C. Water enters the boiler tubes as a liquid at 20°C and leaves the tubes as saturated steam at 20 bar absolute.

(a) Calculate the rate (kg/h) at which steam is produced.
(b) Use the steam tables to estimate the volumetric flow rate of the steam produced.
(c) Repeat the calculation of part (b), only assume ideal gas behavior instead of using the steam tables. Would you have more confidence in the estimate of part (b) or part (c)? Explain.
(d) What happened to the 35% of the thermal energy released by the combustion that did not go to produce the steam.

Equipment Encyclopedia
boiler

7.26. Liquid water is fed to a boiler at 24°C and 10 bar and is converted at constant pressure to saturated steam. Use the steam tables to calculate $\Delta\hat{H}$(kJ/kg) for this process, and then calculate the heat input required to produce 15,000 m^3/h of steam at the exiting conditions. Assume that the kinetic energy of the entering liquid is negligible and that the steam is discharged through a 15-cm ID pipe.

7.27. You have been assigned to collect thermodynamic data for a new liquid product your company is about to begin manufacturing and you decide to use a continuous-flow technique to generate a correlation of $\hat{H}$ versus T. You wrap an electrical heating tape around a pipe, cover the tape with a thick layer of insulation, pump the liquid through the pipe at the rate of 228 g/min, and adjust the power input to the heating tape with a variable resistor. For each resistance setting, you record the power input and the temperature of the liquid at the pipe outlet. You multiply the power input by a correction factor of 0.94 to determine the rate of heat input to the liquid. The entering fluid temperature remains at 25°C throughout the experiment.

The following data are taken:

T_{out}(°C)	Heat Input to the Liquid (W)
25.0	0.0
26.4	17.0
27.8	35.3
29.0	50.9
32.4	94.4

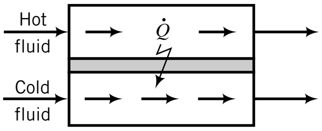
(a) Generate a table of $\hat{H}$(J/g) versus T(°C), taking 25°C and 1 atm as the reference state.
(b) Fit a line to the data (either graphically or by the method of least squares) to determine the coefficient b of an expression of the form $\hat{H} = b(T - 25)$.
(c) Estimate the heat input required to raise 350 kg/min of the liquid from 20°C to 40°C.
(d) The correction factor of 0.94 accounts for the fact that the rate of energy input to the heating tape is somewhat greater than the rate of energy input to the liquid. Where does the additional energy go? (There are several answers.)

Student Workbook

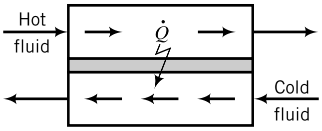
Equipment Encyclopedia
heat exchanger

7.28. Saturated steam at a gauge pressure of 2.0 bar is to be used to heat a stream of ethane. The ethane enters a heat exchanger at 16°C and 1.5 bar gauge at a rate of 795 m^3/min and is heated at constant pressure to 93°C. The steam condenses and leaves the exchanger as a liquid at 27°C. The specific enthalpy of ethane at the given pressure is 941 kJ/kg at 16°C and 1073 kJ/kg at 93°C.

(a) How much energy (kW) must be transferred to the ethane to heat it from 16°C to 93°C?
(b) Assuming that all the energy transferred from the steam goes to heat the ethane, at what rate in m^3/s must steam be supplied to the exchanger? If the assumption is incorrect, would the calculated value be too high or too low?
(c) Should the heat exchanger be set up for cocurrent or countercurrent flow (see the following schematic diagram)? Explain. (*Hint:* Remember that heat always flows from a higher temperature to a lower temperature.)



Cocurrent flow



Countercurrent flow

7.29. Superheated steam at 40 bar absolute and 500°C flows at a rate of 250 kg/min to an adiabatic turbine, where it expands to 5 bar. The turbine develops 1500 kW. From the turbine the steam flows to a heater, where it is reheated isobarically to its initial temperature. Neglect kinetic energy changes.

(a) Write an energy balance on the turbine and use it to determine the outlet stream temperature.

(b) Write an energy balance on the heater and use it to determine the required input (kW) to the steam.

(c) Verify that an overall energy balance on the two-unit process is satisfied.

(d) Suppose the turbine inlet and outlet pipes both have diameters of 0.5 meter. Show that it is reasonable to neglect the change in kinetic energy for this unit.

7.30. During a period of relative inactivity, the average rate of transport of enthalpy by the metabolic and digestive waste products leaving the body minus the rate of enthalpy transport by the raw materials ingested and breathed into the body is approximately $\Delta H = -300$ kJ/h. Heat is transferred from the body to its surroundings at a rate given by

$$Q = hA(T_s - T_0)$$

where A is the body surface area (roughly 1.8 m^2 for an adult), T_s is the skin temperature (normally 34.2°C), T_0 is the temperature of the body surroundings, and h is a **heat transfer coefficient.** Typical values of h for the human body are

$$h = 8 \text{ kJ/(m}^2\cdot\text{h}\cdot{}^\circ\text{C)} \quad \text{(fully clothed, slight breeze blowing)}$$

$$h = 64 \text{ kJ/(m}^2\cdot\text{h}\cdot{}^\circ\text{C)} \quad \text{(nude, immersed in water)}$$

(Data taken from R. C. Seagrave, *Biomedical Applications of Heat and Mass Transfer,* Iowa State University Press, Ames, Iowa, 1971.)

(a) Consider the human body as a continuous system at steady state. Write an energy balance on the body, making all appropriate simplifications and substitutions.

(b) Calculate the surrounding temperature for which the energy balance is satisfied (i.e., at which a person would feel neither hot nor cold) for a clothed person and for a nude person immersed in water.

(c) In terms of the preceding discussion, suggest why you feel colder on a windy day than on a day where the temperature is the same but there is no wind.

7.31. Liquid water at 30.0°C and liquid water at 90.0°C are combined in a ratio (1 kg cold water/2 kg hot water).

(a) Use a *simple* calculation to estimate the final water temperature. For this part, pretend you never heard of energy balances.

(b) Now assume a basis of calculation and write a closed system energy balance for the process, neglecting potential and kinetic energy changes and expansion work and assuming that the mixing is adiabatic. Use the balance to calculate the specific internal energy and hence (from the steam tables) the final temperature of the mixture. What is the percentage difference between your answer and that of part (a)?

Equipment Encyclopedia
boiler

7.32. Steam produced in a boiler is frequently "wet"—that is, it is a mist composed of saturated water vapor and entrained liquid droplets. The **quality** of a wet steam is defined as the fraction of the mixture by mass that is vapor.

A wet steam at a pressure of 5.0 bar with a quality of 0.85 is isothermally "dried" by evaporating the entrained liquid. The flow rate of the dried steam is 52.5 m^3/h.

(a) Use the steam tables to determine the temperature at which this operation occurs, the specific enthalpies of the wet and dry steams, and the total mass flow rate of the process stream.

(b) Calculate the heat input (kW) required for the evaporation process.

7.33. Two hundred kg/min of steam enters a steam turbine at 350°C and 40 bar through a 7.5-cm diameter line and exits at 75°C and 5 bar through a 5-cm line. The exiting stream may be vapor, liquid, or "wet steam" (see Problem 7.32).

(a) If the exiting stream were wet steam at 5.0 bar, what would its temperature be?

(b) How much energy is transferred to or from the turbine? (Neglect $\Delta\dot{E}_p$ but not $\Delta\dot{E}_k$.)

Equipment Encyclopedia
steam trap

7.34. A **steam trap** is a device to purge steam condensate from a system without venting uncondensed steam. In one of the crudest trap types, the condensate collects and raises a float attached to a drain plug. When the float reaches a certain level, it "pulls the plug," opening the drain valve and allowing the liquid to discharge. The float then drops down to its original position and the valve closes, preventing uncondensed steam from escaping.

(a) Suppose saturated steam at 25 bar is used to heat 100 kg/min of an oil from 135°C to 185°C. Heat must be transferred to the oil at a rate of 1.00×10^4 kJ/min to accomplish this task. The steam condenses on the exterior of a bundle of tubes through which the oil is flowing. Condensate collects in the bottom of the exchanger and exits through a steam trap set to discharge when 1200 g of liquid is collected. How often does the trap discharge?

(b) Especially when periodic maintenance checks are not performed, steam traps often fail to close completely and so leak steam continuously. Suppose a process plant contains 1000 leaking traps (not an unrealistic supposition for some plants) operating at the condition of part (a), and that on the average 10% additional steam must be fed to the condensers to compensate for the uncondensed steam venting through the leaks. Further suppose that the cost of generating the additional steam is $\$1/10^6$ Btu, where the denominator refers to the enthalpy of the leaking steam relative to liquid water at 20°C. Estimate the yearly cost of the leaks based on 24 h/day, 360 day/yr operation.

7.35. A turbine discharges 200 kg/h of saturated steam at 10.0 bar absolute. It is desired to generate steam at 250°C and 10.0 bar by mixing the turbine discharge with a second stream of superheated steam of 300°C and 10.0 bar.

(a) If 300 kg/h of the product steam is to be generated, how much heat must be added to the mixer?

(b) If instead the mixing is carried out adiabatically, at what rate is the product steam generated?

Equipment Encyclopedia
valve

7.36. Liquid water at 60 bar and 250°C passes through an adiabatic expansion valve, emerging at a pressure P_f and temperature T_f. If P_f is low enough, some of the liquid evaporates.

(a) If $P_f = 1.0$ bar, determine the temperature of the final mixture (T_f) and the fraction of the liquid feed that evaporates (y_v) by writing an energy balance about the valve and neglecting $\Delta\dot{E}_k$.

(b) If you took $\Delta\dot{E}_k$ into account in part (a), how would the calculated outlet temperature compare with the value you determined? What about the calculated value of y_v? Explain.

(c) What is the value of P_f above which no evaporation would occur?

(d) Sketch the shapes of plots of T_f versus P_f and y_v versus P_f for 1 bar $\leq P_f \leq$ 60 bar. Briefly explain your reasoning.

7.37. A 10.0-m^3 tank contains steam at 275°C and 15.0 bar. The tank and its contents are cooled until the pressure drops to 1.2 bar. Some of the steam condenses in the process.

(a) How much heat was transferred from the tank?

(b) What is the final temperature of the tank contents?

(c) How much steam condensed (kg)?

Equipment Encyclopedia
valve

7.38. Jets of high-speed steam are used in spray cleaning. Steam at 15.0 bar with 150°C of superheat is fed to a well-insulated valve at a rate of 1.00 kg/s. As the steam passes through the valve, its pressure drops to 1.0 bar. The outlet stream may be totally vapor or a mixture of vapor and liquid. Kinetic and potential energy changes may be neglected.

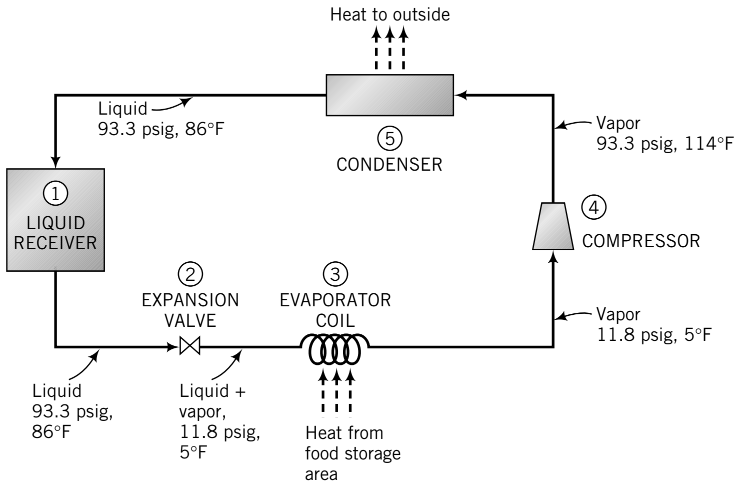
(a) Draw and label a flowchart, assuming that both liquid and vapor emerge from the valve.

(b) Write an energy balance and use it to determine the total rate of flow of enthalpy in the outlet stream ($\dot{H}_{out} = \dot{m}_l\hat{H}_l + \dot{m}_v\hat{H}_v$). Then determine whether the outlet stream is in fact a mixture of liquid and vapor or whether it is pure vapor. Explain your reasoning.

(c) What is the temperature of the outlet stream?

Equipment Encyclopedia
refrigeration,
condenser,
compressor

7.39. The following diagram shows a simplified version of how a refrigerator works:



In a **liquid receiver** ①, a liquid refrigerant (any one of a number of halogenated hydrocarbons such as CCl_2F_2) is contained at high pressure and temperature. The liquid passes through an **expansion valve** ②, where it flashes to a low pressure, cooling to its boiling point at this pressure and partially evaporating. The liquid–vapor mixture passes though an **evaporator coil** ③. Air from the food storage area circulates over the coil, and the heat absorbed by the evaporating refrigerant in the coil causes the air to cool. The cold refrigerant vapor emerging from the coil passes to a **compressor** ④, where it is brought back to a high pressure and in the process is raised to a high temperature. The hot vapor then passes through a **condenser** ⑤, where it is cooled and condensed at constant pressure. The air that absorbs the heat given up by the condensing fluid is discharged outside the refrigerator, and the liquefied refrigerant returns to the liquid receiver.

Suppose Refrigerant R-12 (the standard name for CCl_2F_2) undergoes this cycle at a circulation rate of 40 lb_m/min, with the temperatures and pressures at the different points of the cycle being those shown on the flow diagram. Thermodynamic data for Refrigerant R-12 are as follows:

Saturated Fluid: $T = 5°\text{F}, \hat{H}_{\text{liq}} = 9.6 \text{ Btu/lb}_\text{m}, \hat{H}_{\text{vap}} = 77.8 \text{ Btu/lb}_\text{m}$

$T = 86°\text{F}, \hat{H}_{\text{liq}} = 27.8 \text{ Btu/lb}_\text{m}, \hat{H}_{\text{vap}} = 85.8 \text{ Btu/lb}_\text{m}$

Superheated Vapor: $T = 114°\text{F}, P = 93.3 \text{ psig}, \hat{H}_{\text{vap}} \simeq 90 \text{ Btu/lb}_\text{m}$

(a) Suppose the expansion valve operates adiabatically and $\Delta\dot{E}_k$ is negligible. Use an energy balance about the valve to calculate the fraction of the refrigerant that evaporates in this stage of the process.

(b) Calculate the rate in Btu/min at which heat is transferred to the refrigerant that evaporates in the coil. (This is the useful cooling done in the system.)

(c) If the heat loss in the condenser is 2500 Btu/min, how much horsepower must the compressor deliver to the system? (Use an overall energy balance to solve this problem.)

7.40. Three hundred L/h of a 20 mole% C_3H_8–80% n-C_4H_{10} gas mixture at 0°C and 1.1 atm and 200 L/h of a 40 mole% C_3H_8–60% n-C_4H_{10} mixture at 25°C and 1.1 atm are mixed and heated to 227°C at constant pressure. Calculate the heat requirement in kJ/h. (See Example 7.6-2.) Enthalpies of propane and n-butane are listed below. Assume ideal gas behavior.

T(°C)	Propane $\hat{H}$(J/mol)	Butane $\hat{H}$(J/mol)
0	0	0
25	1772	2394
227	20,685	27,442

Student Workbook

Equipment Encyclopedia condenser

Equipment Encyclopedia distillation column

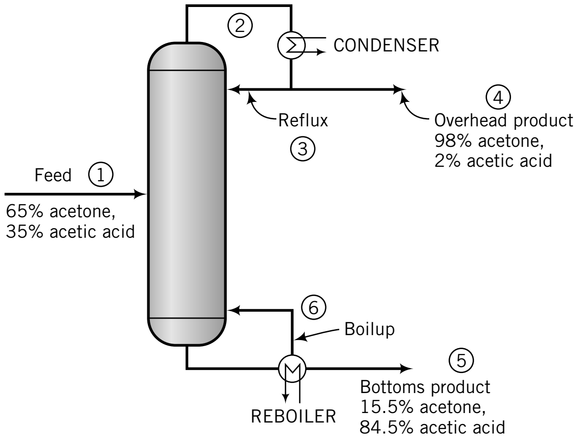
7.41. Air at 38°C and 97% relative humidity is to be cooled to 18°C and fed into a plant area at a rate of 510 m^3/min.

(a) Calculate the rate (kg/min) at which water condenses.

(b) Calculate the cooling requirement in tons (1 ton of cooling = 12,000 Btu/h), assuming that the enthalpy of water vapor is that of saturated steam at the same temperature and the enthalpy of dry air is given by the expression

$$\hat{H}(\text{kJ/mol}) = 0.0291[T(^\circ\text{C}) - 25]$$

7.42. A mixture containing 65.0 mole% acetone (Ac) and the balance acetic acid (AA) is separated in a continuous distillation column at 1 atm. A flowchart for the operation is as follows:



The overhead stream from the column is a vapor that passes though a condenser. The condensed liquid is divided into two equal streams: one is taken off as the overhead product (distillate) and the other (the *reflux*) is returned to the column. The bottom stream from the column is a liquid that is partially vaporized in a reboiler. The liquid stream emerging from the reboiler is taken off as the bottoms product, and the vapor is returned to the column as *boilup*. Negligible heat is lost from the column, so that the only places in the system where external heat transfer takes place are the condenser and the reboiler.

Stream Data

Feed ①	Liquid, 67.5°C, 65 mole% Ac, 35% AA
Overhead ②	Vapor, 63.0°C, 98 mole% Ac, 2% AA
Distillate ③ **Reflux** ④	Liquid, 56.8°C, 98 mole% Ac, 2% AA
Bottoms ⑤	Liquid, 98.7°C, 15.5 mole% Ac, 84.5% AA
Boilup ⑥	Vapor, 98.7°C, 54.4 mole% Ac, 45.6% AA

Thermodynamic Data

	$\hat{H}$(cal/mol)			
	Acetone		*Acetic Acid*	
T(°C)	$\hat{H}_l$	$\hat{H}_v$	$\hat{H}_l$	$\hat{H}_v$
56.8	0	7205	0	5723
63.0	205	7322	194	6807
67.5	354	7403	335	6884
98.7	1385	7946	1312	7420

(a) Taking 100 mol of feed as a basis, calculate the net heat requirement (cal) for the process. (You may neglect heats of mixing, although doing so for dissimilar liquids like acetone and acetic acid may introduce some error.)

(b) For the same basis, calculate the required heat input to the reboiler and the required heat removal from the condenser.

7.43. Superheated steam at T_1(°C) and 10.0 bar is combined with saturated steam at T_2(°C) and 7.0 bar in a ratio (1.96 kg of steam at 10 bar)/(1.0 kg of steam at 7 bar). The product stream is at 250°C and 7.0 bar. The process operates at steady state.

(a) Calculate T_1 and T_2, assuming that the blender operates adiabatically.

(b) If in fact heat is being lost from the blender to the surroundings, is your estimate of T_1 too high or too low? Briefly explain.

7.44. A 200.0-liter water tank can withstand pressures up to 20.0 bar absolute before rupturing. At a particular time the tank contains 165.0 kg of liquid water, the fill and exit valves are closed, and the absolute pressure in the vapor head space above the liquid (which may be assumed to contain only water vapor) is 3.0 bar. A plant technician turns on the tank heater, intending to raise the water temperature to 155°C, but is called away and forgets to return and shut off the heater. Let t_1 be the instant the heater is turned on and t_2 the moment before the tank ruptures. Use the steam tables for the following calculations.

(a) Determine the water temperature, the liquid and head-space volumes (L), and the mass of water vapor in the head space (kg) at time t_1.

(b) Determine the water temperature, the liquid and head-space volumes (L), and the mass of water vapor (g) that evaporates between t_1 and t_2. (*Hint:* Make use of the fact that the total mass of water in the tank and the total tank volume both remain constant between t_1 and t_2.)

(c) Calculate the amount of heat (kJ) transferred to the tank contents between t_1 and t_2. Give two reasons why the actual heat input to the tank must have been greater than the calculated value.

(d) List three different factors responsible for the increase in pressure resulting from the transfer of heat to the tank. (*Hint:* One has to do with the effect of temperature on the density of liquid water.)

(e) List ways in which this accident could have been avoided.

Student Workbook

Equipment Encyclopedia
steam trap

7.45. A wet steam at 20 bar with a quality of 0.97 (see Problem 7.32) leaks through a defective steam trap and expands to a pressure of 1 atm. The process can be considered to take place in two stages: a rapid adiabatic expansion to 1 atm accompanied by complete evaporation of the liquid droplets in the wet steam, followed by cooling at 1 atm to ambient temperature. $\Delta \dot{E}_k$ may be neglected in both stages.

(a) Estimate the temperature of the superheated steam immediately following the rapid adiabatic expansion.

(b) Someone looking at the steam trap would see a clear space just outside the leak and a white plume forming a short distance away. (The same phenomenon can be observed outside the spout of a kettle in which water is boiling.) Explain this observation. What would the temperature be at the point where the plume begins?

7.46. Eight fluid ounces (1 qt = 32 oz) of a beverage in a glass at 18.0°C is to be cooled by adding ice and stirring. The properties of the beverage may be taken to be those of liquid water. The enthalpy of the ice relative to liquid water at the triple point is −348 kJ/kg. Estimate the mass of ice (g) that must melt to bring the liquid temperature to 4°C, neglecting energy losses to the surroundings. (*Note:* For this isobaric batch process, the energy balance reduces to $Q = \Delta H$.)

7.47. A 25-g block of iron at 175°C is dropped into a liter of water in an insulated flask at 20°C and 1 atm. The specific enthalpy of iron is given by the expression $\hat{H}(\text{J/g}) = 17.3T(°\text{C})$.

(a) What reference temperature was used as the basis for the enthalpy formula?

(b) Calculate the final temperature of the flask contents, assuming that the process is adiabatic, negligible evaporation of water occurs, negligible heat is transferred to the flask wall, and the specific enthalpy of liquid water at 1 atm and a given temperature is that of the saturated liquid at the same temperature. (*Note:* For this isobaric batch process, the energy balance reduces to $Q = \Delta H$.)

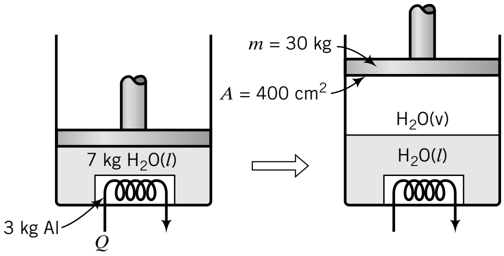
7.48. Horatio Meshuggeneh has his own ideas of how to do things. For instance, when given the task of determining an oven temperature, most people would use a thermometer. Being allergic to doing anything most people would do, however, Meshuggeneh instead performs the following experiment. He puts a copper bar with a mass of 5.0 kg in the oven and puts $\Delta\hat{H} = 2919$ an identical bar in a well-insulated 20.0-liter vessel containing 5.00 L of liquid water and the remainder saturated steam at 760 mm Hg absolute. He waits long enough for both bars to reach thermal equilibrium with their surroundings, then quickly takes the first bar out of the oven, removes the second bar from the vessel, drops the first bar in its place, covers the vessel tightly, waits for the contents to come to equilibrium, and notes the reading on a pressure gauge built into the vessel. The value he reads is 50.1 mm Hg. He then uses the facts that copper has a specific gravity of 8.92 and a specific internal energy given by the expression $\hat{U}(\text{kJ/kg}) = 0.36T(°\text{C})$ to calculate the oven temperature.

(a) The Meshuggeneh assumption is that the bar can be transferred from the oven to the vessel without any heat being lost. If he makes this assumption, what oven temperature does Meshuggeneh calculate? How many grams of water evaporate in the process? (Neglect the heat transferred to the vessel wall—i.e., assume that the heat lost by the bar is transferred entirely to the water in the vessel. Also, remember that you are dealing with a closed system once the hot bar goes into the vessel.)

(b) In fact, the bar lost 8.3 kJ of heat between the oven and the vessel. What is the true oven temperature?

(c) The experiment just described was actually Meshuggeneh's second attempt. The first time he tried it, the final gauge pressure in the vessel was negative. What had he forgotten to do?

7.49. A perfectly insulated cylinder fitted with a leakproof frictionless piston with a mass of 30.0 kg and a face area of 400.0 cm^2 contains 7.0 kg of liquid water and a 3.0-kg bar of aluminum. The aluminum bar has an electrical coil imbedded in it, so that known amounts of heat can be transferred to it. Aluminum has a specific gravity of 2.70 and a specific internal energy given by the formula $\hat{U}(\text{kJ/kg}) = 0.94T(°\text{C})$. The internal energy of liquid water at any temperature may be taken to be that of the saturated liquid at that temperature. Negligible heat is transferred to the cylinder wall. Atmospheric pressure is 1.00 atm. The cylinder and its contents are initially at 20°C.



Suppose that 3310 kJ is transferred to the bar from the heating coil and the contents of the cylinder are then allowed to equilibrate.

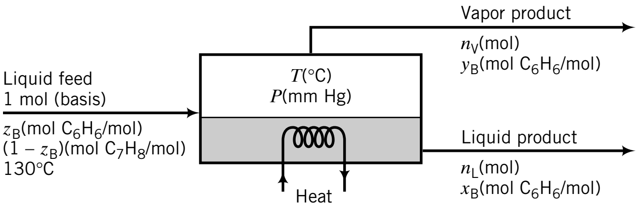
(a) Calculate the pressure of the cylinder contents throughout the process. Then determine whether the amount of heat transferred to the system is sufficient to vaporize any of the water.

(b) Determine the following quantities: (i) the final system temperature; (ii) the volumes (cm^3) of the liquid and vapor phases present at equilibrium; and (iii) the vertical distance traveled by the piston from the beginning to the end of the process. [*Suggestion:* Write an energy balance on the complete process, taking the cylinder contents to be the system. Note that the system is closed and that work is done by the system when it moves the piston through a vertical displacement. The magnitude of this work is $W = P\Delta V$, where P is the constant system pressure and ΔV is the change in system volume from the initial to the final state.]

(c) Calculate an upper limit on the temperature attainable by the aluminum bar during the process, and state the condition that would have to apply for the bar to come close to this temperature.

7.50. A rigid 5.00-liter vessel contains 4.00 L of liquid water in equilibrium with 1.00 L of water vapor at 25°C. Heat is transferred to the water by means of an immersed electrical coil. The volume of the coil is negligible. Use the steam tables to calculate the final temperature and pressure (bar) of the system and the mass of water vaporized (g) if 2915 kJ is added to the water and no heat is transferred from the water to its surroundings. (*Note:* A trial-and-error calculation is required.)

7.51. A liquid mixture of benzene and toluene is to be separated in a continuous single-stage equilibrium flash tank.



The pressure in the unit may be adjusted to any desired value, and the heat input may similarly be adjusted to vary the temperature at which the separation is conducted. The vapor and liquid product streams both emerge at the temperature T(°C) and pressure P(mm Hg) maintained in the vessel.

Assume that the vapor pressures of benzene and toluene are given by the Antoine equation, Table 6.1-1; that Raoult's law—Equation 6.4-1—applies; and that the enthalpies of benzene and toluene liquid and vapor are linear functions of temperature. Specific enthalpies at two temperatures are given here for each substance in each phase.

$C_6H_6(l)$	(T = 0°C, $\hat{H}$ = 0 kJ/mol)	(T = 80°C, $\hat{H}$ = 10.85 kJ/mol)
$C_6H_6(v)$	(T = 80°C, $\hat{H}$ = 41.61 kJ/mol)	(T = 120°C, $\hat{H}$ = 45.79 kJ/mol)
$C_7H_8(l)$	(T = 0°C, $\hat{H}$ = 0 kJ/mol)	(T = 111°C, $\hat{H}$ = 18.58 kJ/mol)
$C_7H_8(v)$	(T = 89°C, $\hat{H}$ = 49.18 kJ/mol)	(T = 111°C, $\hat{H}$ = 52.05 kJ/mol)

(a) Suppose the feed is equimolar in benzene and toluene ($z_B = 0.500$). Take a basis of 1 mol of feed and do the degree-of-freedom analysis on the unit to show that if T and P are specified, you can calculate the molar compositions of each phase (x_B and y_B), the moles of the liquid and vapor products (n_L and n_V), and the required heat input (Q). *Don't do any numerical calculations in this part.*

(b) Do the calculations of part (a) for $T = 90$°C and $P = 652$ mm Hg. (*Suggestion:* First derive an equation for x_B that can be solved by trial and error from known values of T and P.)

(c) For $z_B = 0.5$ and $T = 90$°C, there is a range of feasible operating pressures for the evaporator, $P_{min} < P < P_{max}$. If the evaporator pressure P fell outside this range, no separation of benzene and toluene would be achieved. Why not? What would emerge from the unit if $P < P_{min}$? What would emerge if $P > P_{max}$? [*Hint:* Look at your solution to part (b) and think about how it would change if you lowered P.]

***(d)** Set up a spreadsheet to perform the calculation of part (b) and then use it to determine P_{max} and P_{min}. The spreadsheet should appear as follows (some solutions are shown):

Problem 7.51—Flash vaporization of benzene and toluene									
zB	T	P	pB*	pT*	xB	yB	nL	nV	Q
0.500	90.0	652	1021				0.5543		8.144
0.500	90.0	714							−6.093
0.500	90.0								

---

*Computer problem.

Additional columns may be used to store other calculated variables (e.g., specific enthalpies). Briefly explain why Q is positive when $P = 652$ mm Hg and negative when $P = 714$ mm Hg.

(e) In successive rows, repeat the calculation for the same z_B and T at several pressures between $p_{\min}$ and $p_{\max}$. Generate a plot (using the spreadsheet program itself, if possible) of n_V versus P. At approximately what pressure is half of the feed stream vaporized?

7.52. An aqueous solution with a specific gravity of 1.12 flows through a channel with a variable cross section. Data taken at two axial positions in the channel are shown here.

	Point 1	Point 2
P_{gauge}	1.5×10^5 Pa	9.77×10^4 Pa
u	5.00 m/s	?

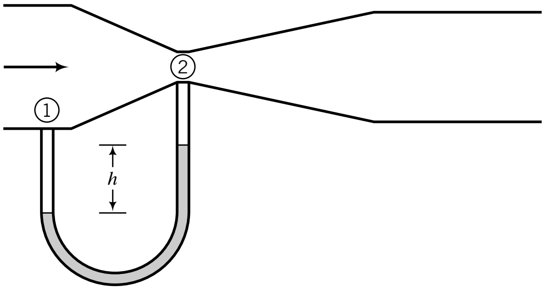
Point 2 is 6.00 meters higher than point 1.

(a) Neglecting friction, calculate the velocity at point 2. (See Example 7.7-1.)

(b) If the pipe diameter at point 2 is 6.00 cm, what is the diameter at point 1?

Equipment Encyclopedia
process parameters/differential pressure flowmeters/venturi tube

7.53. A **venturi meter** is a device to measure fluid flow rates, which in its operation resembles the orifice meter (Section 3.2b). It consists of a tapered constriction in a line, with pressure taps leading to a differential manometer at points upstream of the constriction and at the point of maximum constriction (the **throat**). The manometer reading is directly related to the flow rate in the line.



Suppose the flow rate of an incompressible fluid is to be measured in a venturi meter in which the cross-sectional area at point 1 is four times that at point 2.

(a) Derive the relationship between the velocities u_1 and u_2 at points 1 and 2.

(b) Write the Bernoulli equation for the system between points 1 and 2, and use it to prove that to the extent friction is negligible

$$P_1 - P_2 = \frac{15\rho\dot{V}^2}{2A_1^2}$$

where P_1 and P_2 are the pressures at point 1 and 2, ρ and $\dot{V}$ are the density and volumetric flow rate of the flowing fluid, and A_1 is the cross-sectional area of the pipe at point 1.

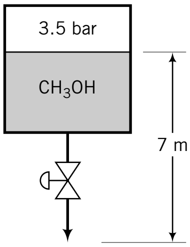
(c) Suppose this meter is used to measure the flow rate of a stream of water, using mercury as the manometer fluid, and a manometer reading $h = 38$ cm is recorded. What is the volumetric flow rate of the water if the pipe diameter at point 1 is 15 cm? (Recall the differential manometer equation, Equation 3.4-6.)

Equipment Encyclopedia
valve

7.54. Methanol is contained in a large tank under a pressure of 3.1 bar absolute. When a valve on the bottom of the tank is opened, the methanol drains freely though a 1-cm ID tube whose outlet is 7.00 m below the surface of the methanol. The pressure at the outlet of the discharge pipe is 1 atm.

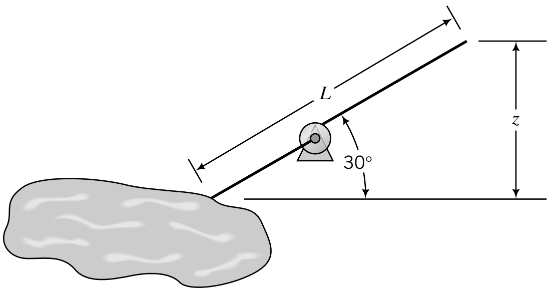
(a) Use the Bernoulli equation to estimate the methanol discharge velocity and flow rate in L/min when the discharge valve is fully opened. Neglect the rate of fall of the methanol level in the tank. (See Example 7.7-2.)

(b) When the discharge valve is partially closed, the flow rate decreases, which means that $\Delta u^2/2$ changes. However, the other two terms in the Bernoulli equation ($\Delta P/\rho$ and $g\,\Delta z$) remain the same. How do you account for this apparently contradictory result? (*Hint:* Examine the assumptions made in the derivation of the Bernoulli equation.)



Equipment Encyclopedia pump

7.55. Water is to be pumped from a lake to a ranger station on the side of a mountain (see figure). The flow rate is to be 95 gal/min, and the flow channel is a standard 1-in. Schedule 40 steel pipe (ID = 1.049 in.). A pump capable of delivering 8 hp ($= -\dot{W}_s$) is available. The friction loss $\hat{F}$ ($\text{ft}\cdot\text{lb}_f/\text{lb}_m$) equals $0.041L$, where L(ft) is the length of the pipe. Calculate the maximum elevation, z, of the ranger station above the lake if the pipe rises at an angle of 30°.



7.56. Water from a reservoir passes over a dam through a turbine and discharges from a 70-cm ID pipe at a point 65 m below the reservoir surface. The turbine delivers 0.80 MW. Calculate the required flow rate of water in m^3/min if friction is neglected. (See Example 7.7-3.) If friction were included, would a higher or lower flow rate be required? (*Note:* The equation you will solve in this problem has multiple roots. Find a solution less than 2 m^3/s.)

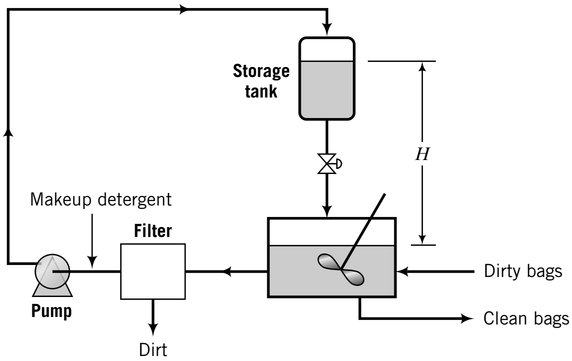
Equipment Encyclopedia filter, pump

7.57. Cloth bag filters are used to remove particulate matter from the gases passing out through several process and boiler stacks in a large industrial plant. The bags become clogged and must be replaced frequently. Since they are quite expensive, rather than being discarded they are emptied, washed, and reused. In the washing process, a detergent solution with a specific gravity of 0.96 flows from a storage tank to a washing machine. The liquid effluent from the machine is pumped through a filter to remove dirt, and the cleaned detergent is recycled back to the storage tank.

Detergent flows from the storage tank to the washing machine by gravity feed at a rate of 600 L/min. All pipes in the line have 4.0-cm inner diameters. Friction losses are negligible in the line from the tank to the washing machine when the valve is fully opened, and $\hat{F} = 72$ J/kg in the return line, which includes the pump and filter.

(a) Calculate the value of the height H (see figure) required to provide the desired flow rate of detergent into the washing machine when the valve is fully opened.

(b) Suppose the pump has an efficiency of 75%; that is, it delivers 75% of its rated value as shaft work. What must the rated value (kW) of the pump be to return 600 L/min of detergent to the storage tank?



Equipment Encyclopedia
pump

7.58. One thousand liters of a 95 wt% glycerol–5% water solution is to be diluted to 60% glycerol by adding a 35% solution pumped from a large storage tank through a 5-cm ID pipe at a steady rate. The pipe discharges at a point 23 m higher than the liquid surface in the storage tank. The operation is carried out isothermally and takes 13 min to complete. The friction loss ($\hat{F}$ of Equation 7.7-2) is 50 J/kg. Calculate the final solution volume and the shaft work in kW that the pump must deliver, assuming that the surface of the stored solution and the pipe outlet are both at 1 atm.

Data: $\rho_{H2O} = 1.00$ kg/L, $\rho_{gly} = 1.26$ kg/L. (Use to estimate solution densities.)

Chapter 8

Balances on Nonreactive Processes

We have seen that for an open system in which shaft work and kinetic and potential energy changes can be neglected, the energy balance reduces to

$$\begin{aligned}\dot{Q} &= \Delta\dot{H} \\ &= \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i\end{aligned}$$

where the $\hat{H}_i$'s are the specific enthalpies of the inlet and outlet stream components at their respective process conditions (temperatures, pressures, and states of aggregation) relative to those components at some reference conditions. For an integral balance on a closed constant-volume system ($W = 0$), n (amount) would replace $\dot{n}$ (flow rate) in this equation, U (internal energy) would replace $\dot{H}$ (rate of enthalpy transport) and $\hat{U}$ (specific internal energy) would replace $\hat{H}$ (specific enthalpy).

In Chapter 7, we dealt only with processes involving species for which specific enthalpies and internal energies at specified conditions could be found in tables. Unfortunately, you cannot count on finding such data for every species with which you work. This chapter presents procedures for evaluating $\Delta\dot{H}$ or ΔU when tables of $\hat{H}$ and $\hat{U}$ are not available for all process species. Once these calculations have been performed, the energy balance may be written and solved as before.

8.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to do the following:

- Define both formally (in terms of internal energies and enthalpies) and in words a high school senior could understand the variables $C_v(T)$ (heat capacity at constant volume), $C_p(T)$ (heat capacity at constant pressure), $\Delta\hat{H}_\text{m}$ (heat of fusion or heat of melting), $\Delta\hat{H}_\text{v}$ (heat of vaporization), standard heats of fusion and vaporization, and $\Delta\hat{H}_\text{s}$ (heat of solution or heat of mixing).
- Calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for the following changes in state of a species, when possible using enthalpies and internal energies, heat capacities, latent heats, and liquid and solid specific gravities tabulated in this text: (a) isothermal changes in pressure, (b) isobaric (constant-pressure) changes in temperature, (c) isothermal isobaric phase changes, and (d) isothermal isobaric mixing of two or more species. State when the formulas you use for these calculations are exact, good approximations, and poor approximations.
- Given a reference state (phase, temperature, and pressure) and a process state for a species, (a) choose a path from the reference state to the process state consisting of a series of

isothermal pressure changes, isobaric temperature changes, and isothermal isobaric phase changes; (b) calculate $\hat{U}$ and $\hat{H}$ for the species at the process state relative to the species at the reference state.

- High school physics and chemistry texts commonly state that the heat (Q) required to raise the temperature of a mass m of a substance by an amount ΔT is $Q = mC_p \Delta T$, where C_p is defined as the heat capacity of the substance. Explain why this formula is only an approximation. List the assumptions required to obtain it from the closed system energy balance ($Q + W = \Delta U + \Delta E_\text{k} + \Delta E_\text{p}$).
- If your class covers Section 8.3e, evaluate

$$\int_{T_1}^{T_2} C_p(T)\,dT$$

  using the trapezoidal rule or Simpson's rule (Appendix A.3) from data for C_p at several temperatures between T_1 and T_2.
- Estimate the heat capacity of a liquid or solid species using Kopp's rule. Estimate the heat of fusion and heat of vaporization of a species using correlations in Section 8.4b.
- Given any nonreactive process for which the required heat transfer Q or heat transfer rate $\dot{Q}$ is to be calculated, (a) draw and label the flowchart, including Q or $\dot{Q}$ in the labeling; (b) carry out a degree-of-freedom analysis; (c) write the material and energy balances and other equations you would use to solve for all requested quantities; (d) perform the calculations; and (e) list the assumptions and approximations built into your calculations.
- Given an adiabatic process or any other nonreactive process for which the value of Q (closed system) or $\dot{Q}$ (open system) is specified, write material and energy balance equations and solve them simultaneously for requested quantities.
- Define the *dry-bulb temperature, wet-bulb temperature,* and *humid volume* of humid air. Given values of any two of the variables plotted on the psychrometric chart (dry-bulb and wet-bulb temperatures, absolute and relative humidity, dew point, humid volume), determine the remaining variable values and the specific enthalpy of the humid air. Use the psychrometric chart to carry out material and energy balance calculations on a heating, cooling, humidification, or dehumidification process involving air and water at 1 atm.
- Explain the meaning of the apparently contradictory term *adiabatic cooling.* Explain how spray cooling and humidification, spray dehumidification, and spray drying work. Explain how it is possible to *de*humidify air by spraying water into it. Use the psychrometric chart to carry out material and energy balance calculations on an adiabatic cooling operation involving air and water at 1 atm.
- Explain to a first-year engineering student why a beaker containing acid gets hot if you add water to it.
- Use the heat of solution data in Table B.10 and solution heat capacity data to (a) calculate the enthalpy of a hydrochloric acid, sulfuric acid, or sodium hydroxide solution of a known composition (solute mole fraction) relative to the pure solute and water at 25°C; (b) calculate the required rate of heat transfer to or from a process in which an aqueous solution of HCl, H_2SO_4, or NaOH is formed, diluted, or combined with another solution of the same species; and (c) calculate the final temperature if an aqueous solution of HCl, H_2SO_4, or NaOH is formed, diluted, or combined with another solution of the same species adiabatically.
- Perform material and energy balance calculations for a process that involves solutions for which enthalpy–concentration charts are available.

8.1 ELEMENTS OF ENERGY BALANCE CALCULATIONS

In this section, we outline a procedure for solving energy balance problems that will be applied to both nonreactive processes (this chapter) and reactive processes (Chapter 9). Section

8.1a reviews the concept of a *reference state* for specific internal energy and enthalpy calculations, and Section 8.1b reviews the fact that $\hat{U}$ and $\hat{H}$ are state properties, so that the values of ΔU or ΔH (closed system) and $\Delta \dot{H}$ (open system) calculated for a process are independent of the reference states chosen for calculations of $\hat{U}_i$ and $\hat{H}_i$. Section 8.1c outlines a procedure for organizing energy balance calculations and presents an extended illustrative example. The remainder of the chapter presents formulas and methods for calculating ΔU, ΔH, and $\Delta \dot{H}$ for processes that involve heating and cooling, compression and decompression, phase changes, mixing of liquids, and dissolving of gases and solids in liquids.

8.1a Reference States—A Review

Recall that we can never know the absolute values of $\hat{U}$ and $\hat{H}$ for a species at a given state. $\hat{U}$(kJ/mol) is the sum of the energies of motion of all 6.02×10^{23} molecules in one gram-mole of the species plus the intramolecular kinetic and potential energies of all the atoms and subatomic particles, which are quantities we cannot determine. Since $\hat{H} = \hat{U} + P\hat{V}$ and we cannot know the value of $\hat{U}$, we also cannot know the value of $\hat{H}$ at a specified state.

Fortunately, we never need to know the absolute values of $\hat{U}$ or $\hat{H}$ at specified states: we only need to know $\Delta\hat{U}$ and $\Delta\hat{H}$ for specified *changes* of state, and we can determine these quantities experimentally.[1] We may therefore arbitrarily choose a **reference state** for a species and determine $\Delta\hat{U} = \hat{U} - \hat{U}_{\text{ref}}$ for the transition from the reference state to a series of other states. If we set $\hat{U}_{\text{ref}}$ equal to zero, then $\hat{U}(= \Delta\hat{U})$ for a specified state is the *specific internal energy at that state relative to the reference state*. The specific enthalpies at each state can then be calculated from the definition, $\hat{H} = \hat{U} + P\hat{V}$, provided that the specific volume ($\hat{V}$) of the species at the given temperature and pressure is known.

The values of $\hat{U}$ and $\hat{H}$ in the steam tables were generated using this procedure. The reference state was chosen to be liquid water at the triple point [H_2O(l, 0.01°C, 0.00611 bar)], at which point $\hat{U}$ was defined to be zero. According to Table B.7, for water vapor at 400°C and 10.0 bar, $\hat{U} = 2958$ kJ/kg. This does *not* mean that the absolute value of $\hat{U}$ for water in the specified state is 2958 kJ/kg; remember, we cannot know the absolute value of $\hat{U}$. It means that $\hat{U}$ of water vapor at 400°C and 10.0 bar is 2958 kJ/kg *relative to water at the reference state,* or

$$\mathrm{H_2O(l, 0.01^\circ C, 0.00611\ bar)} \longrightarrow \mathrm{H_2O(v, 400^\circ C, 10.0\ bar)}, \quad \Delta\hat{U} = 2958\ \mathrm{kJ/kg}$$

Relative to water at the same reference state, the specific enthalpy of water vapor at 400°C and 10.0 bar is

$$\begin{aligned} \hat{H} &= \hat{U} + P\hat{V} \\ &= 2958\ \mathrm{kJ/kg} + \frac{10\ \mathrm{bar}}{} \left| \frac{0.307\ \mathrm{m^3}}{\mathrm{kg}} \right| \frac{10^3\ \mathrm{L}}{1\ \mathrm{m^3}} \left| \frac{8.314 \times 10^{-3}\ \mathrm{kJ/(mol\cdot K)}}{0.08314\ \mathrm{L\cdot bar/(mol\cdot K)}} \right. \\ &= 3264\ \mathrm{kJ/kg} \end{aligned}$$

The quantities 8.314×10^{-3} and 0.08314 are values of the gas constant expressed in different units (see inside back cover).

TEST YOURSELF (Answers, p. 660)

Suppose water vapor at 300°C and 5 bar is chosen as a reference state at which $\hat{H}$ is defined to be zero. Relative to this state, what is the specific enthalpy of liquid water at 75°C and 1 bar? What is the specific internal energy of liquid water at 75°C and 1 bar? (Use Table B.7.)

---

[1] The method is to transfer a measured amount of energy, Q, to a known mass of a species, m, in a closed system under conditions such that $W = 0$, $\Delta E_{\mathrm{k}} = 0$, and $\Delta E_{\mathrm{p}} = 0$; measure any changes in temperature, pressure, and phase; and calculate $\Delta\hat{U}$ corresponding to these changes from the energy balance, $Q = m\Delta\hat{U}$.

8.1b Hypothetical Process Paths

In Chapter 7, we observed that $\hat{U}$ and $\hat{H}$ are **state properties** of a species: that is, their values depend only on the state of the species—primarily on its temperature and state of aggregation (solid, liquid, or gas) and, to a lesser extent, on its pressure (and for mixtures of some species, on its mole fraction in the mixture). A state property does not depend on how the species reached its state. Consequently, *when a species passes from one state to another, both* $\Delta\hat{U}$ *and* $\Delta\hat{H}$ *for the process are independent of the path taken from the first state to the second one.*

In most of this chapter and in Chapter 9, you will learn how to calculate internal energy and enthalpy changes associated with certain processes: specifically,

1. ***Changes in P at constant T and state of aggregation*** (Section 8.2).
2. ***Changes in T at constant P and state of aggregation*** (Section 8.3).
3. ***Phase changes at constant T and P***—melting, solidifying, vaporizing, condensing, sublimating (Section 8.4).
4. ***Mixing of two liquids or dissolving of a gas or a solid in a liquid at constant T and P*** (Section 8.5).
5. ***Chemical reaction at constant T and P*** (Chapter 9).

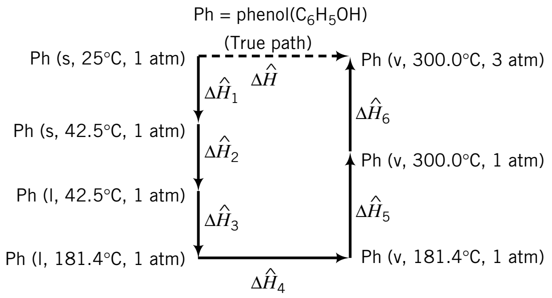
For example, compressing hydrogen gas from 1 atm to 300 atm at 25°C is a Type 1 process; melting ice at 0°C and then heating the liquid water to 30°C, all at 1 atm, is a Type 3 process followed by a Type 2 process; mixing sulfuric acid and water at a constant temperature of 20°C and a constant pressure of 1 atm is a Type 4 process.

Once we know how to calculate $\Delta\hat{U}$ and $\Delta\hat{H}$ for these five types of processes, we can calculate these quantities for *any* process by taking advantage of the fact that $\hat{U}$ and $\hat{H}$ are state properties. The procedure is to construct a hypothetical **process path** from the initial state to the final state consisting of a series of steps of the given five types. Having done this, we calculate $\Delta\hat{H}$ for each of the steps, and then add the $\Delta\hat{H}$'s for the steps to calculate $\Delta\hat{H}$ for the total process. *Since* $\hat{H}$ *is a state property,* $\Delta\hat{H}$ *calculated for the hypothetical process path—which we constructed for convenience—is the same as* $\Delta\hat{H}$ *for the path actually followed by the process.* The same procedure can be followed to calculate $\Delta\hat{U}$ for any process.

Suppose, for example, that we wish to calculate $\Delta\hat{H}$ for a process in which solid phenol at 25°C and 1 atm is converted to phenol vapor at 300°C and 3 atm. If we had a table of enthalpies for phenol, we could simply subtract $\hat{H}$ at the initial state from $\hat{H}$ at the final state, or

$$\Delta\hat{H} = \hat{H}(\text{vapor, 300°C, 3 atm}) - \hat{H}(\text{solid, 25°C, 1 atm})$$

However, we do not have such a table. Our task is then to construct a hypothetical process path from the solid at 25°C and 1 atm to the vapor at 300°C and 3 atm. To do so, we will look ahead a bit and note that Table B.1 gives enthalpy changes for the melting of phenol at 1 atm and 42.5°C (the normal melting point of phenol) and for the vaporization of phenol at 1 atm and 181.4°C (the normal boiling point of phenol). We therefore choose the following hypothetical process path:



Notice that in this path, the first, third, and fifth steps are Type 2 (change in T at constant P), the second and fourth steps are Type 3 (change in phase at constant T and P), and the sixth step is Type 1 (change in P at constant T). Also notice that the phase changes were made to occur at the conditions for which tabulated enthalpy changes are available.

The next step in the calculation would be to determine the values of $\Delta\hat{H}$ for Steps 1, 3, 5, and 6 using methods to be given in Section 8.2; read the values of $\Delta\hat{H}_2$ and $\Delta\hat{H}_4$ from Table B.1; and then use the fact that enthalpy is a state property to calculate the desired $\Delta\hat{H}$ ($\Delta\hat{H}$ for the upper dashed line in the figure) as

$$\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2 + \Delta\hat{H}_3 + \Delta\hat{H}_4 + \Delta\hat{H}_5 + \Delta\hat{H}_6$$

TEST YOURSELF (Answers, p. 660)

Construct a process path for each of the following processes consisting of sequential steps of the five types listed in the preceding section. (An illustrative solution is given for the first process.)

1. Nitrogen at 20°C and 200 mm Hg is heated and compressed to 140°C and 40 atm. (One of an infinite number of possible solutions: Heat at 200 mm Hg from 20°C to 140°C, then compress isothermally from 200 mm Hg to 40 atm.)
2. Cyclohexane vapor at 180°C and 5 atm is cooled and condensed to liquid cyclohexane at 25°C and 5 atm. The enthalpy change for the condensation of cyclohexane at 80.7°C and 1 atm is known.
3. Water at 30°C and 1 atm and NaOH at 25°C and 1 atm are mixed to form an aqueous NaOH solution at 50°C and 1 atm. The enthalpy change for the dissolution of NaOH in water at 25°C and 1 atm is known.
4. O_2 at 170°C and 1 atm and CH_4 at 25°C and 1 atm are mixed and react completely to form CO_2 and H_2O at 300°C and 1 atm. The enthalpy change for the reaction occurring at 25°C and 1 atm is known.

8.1c Procedure for Energy Balance Calculations

Most of the problems at the end of this chapter and Chapter 9 look very much like the problems in Chapters 4 to 6: given values of some process variables (feed and product stream temperatures, pressures, phases, amounts or flow rates, and component mole fractions), calculate values of other process variables. Starting in this chapter, you will also be asked to calculate the heat transferred to or from the process system (one additional variable), which will require writing and solving an energy balance (one additional equation).

Here is the procedure to follow for the energy balance calculation.

1. ***Perform all required material balance calculations.***
2. ***Write the appropriate form of the energy balance (closed or open system) and delete any of the terms that are either zero or negligible for the given process system.*** For a stationary closed system, drop ΔE_k and ΔE_p, and neglect W if the system volume is constant, there are no moving parts (such as a mixing impeller in a stirred tank), and no energy is transferred to or from the system by electricity or radiation. For an open system at steady state, drop $\Delta\dot{E}_p$ if there is no appreciable vertical separation between the inlet and outlet ports and drop $\dot{W}_s$ if there are no moving parts (such as a pump or turbine impeller) and no energy is transferred by electricity or radiation. In addition, if temperature changes of more than a few degrees, phase changes, or chemical reactions occur in the process, $\Delta\dot{E}_k$ may usually be neglected.
3. ***Choose a reference state—phase, temperature, and pressure—for each species involved in the process.*** If $\hat{H}$ or $\hat{U}$ for a species will be looked up in a table (such as the steam tables for water), choose the reference state used to generate the table; otherwise, choose one of the inlet or outlet states as the reference state for the species (so that at least one $\hat{H}$ or $\hat{U}$ may be set equal to zero).

4. ***For a closed constant-volume system, construct a table with columns for initial and final amounts of each species (m_i or n_i) and specific internal energies relative to the chosen reference states ($\hat{U}_i$).*** [2] ***For an open system, construct a table with columns for inlet and outlet stream component flow rates ($\dot{m}_i$ or $\dot{n}_i$) and specific enthalpies relative to the chosen reference states ($\hat{H}_i$).*** Insert known values of the amounts or flow rates and the specific internal energies and enthalpies, and insert labels for the entries that must be calculated (e.g., $\hat{H}_1, \hat{H}_2, \ldots$). The next example illustrates the construction of such a table.
5. ***Calculate all required values of $\hat{U}_i$ (or $\hat{H}_i$) and insert the values in the appropriate places in the table.*** To perform the calculation for a species in a particular state (inlet or outlet), choose any convenient path from the reference state to the process state and determine $\hat{U}_i$ ($\hat{H}_i$) as $\Delta\hat{U}$ ($\Delta\hat{H}$) for that path. Sections 8.2–8.5 outline these calculations for different types of processes.
6. ***Calculate***

   Closed System: $$\Delta U = \sum_{\text{final}} n_i\hat{U}_i - \sum_{\text{initial}} n_i\hat{U}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i\hat{U}_i - \sum_{\text{in}} \dot{m}_i\hat{U}_i$$

   Open System: $$\Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i \quad \text{or} \quad \sum_{\text{out}} \dot{m}_i\hat{H}_i - \sum_{\text{in}} \dot{m}_i\hat{H}_i$$
7. ***Calculate any work, kinetic energy, or potential energy terms that you have not dropped from the energy balance.***
8. ***Solve the energy balance for whichever variable is unknown (often Q or $\dot{Q}$).***

   Closed System: $$Q - W = \Delta U + \Delta E_k + \Delta E_p$$

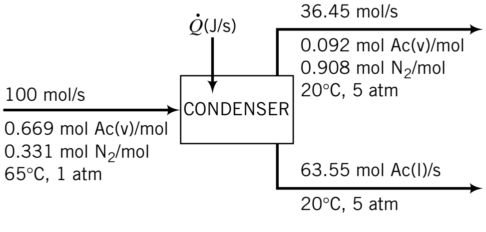
   Open System: $$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$$

The complete procedure for an open system is illustrated in the next example. We encourage you to take the time to follow each step, even though some parts may not be completely clear until you get to material that comes later in the chapter. The better you understand this example, the easier it will be for you to understand the rest of the chapter and to solve the chapter-end problems.

EXAMPLE 8.1-1 Energy Balance on a Condenser

Equipment Encyclopedia
condenser

Acetone (denoted as Ac) is partially condensed out of a gas stream containing 66.9 mole% acetone vapor and the balance nitrogen. Process specifications and material balance calculations lead to the flowchart shown below.



The process operates at steady state. Calculate the required cooling rate.

SOLUTION We will follow the procedure given preceding this example.

1. ***Perform required material balance calculations.*** None are required in this example.
2. ***Write and simplify the energy balance.***

---

[2] Use $\hat{H}_i$ instead of $\hat{U}_i$ for a closed constant-pressure system, since $Q = \Delta H$ for such systems.

For this open steady-state system, $\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$. There are no moving parts in the system and no energy is transferred by electricity or radiation, so $\dot{W}_s = 0$. No significant vertical distance separates the inlet and outlet ports, so $\Delta\dot{E}_p \approx 0$. Phase changes and nonnegligible temperature changes occur, so $\Delta\dot{E}_k \approx 0$ (relative to $\Delta\dot{H}$). The energy balance reduces to

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

3. ***Choose reference states for acetone and nitrogen.***

The reference states may be chosen for computational convenience, since the choice has no effect on the calculated value of $\Delta\dot{H}$. You will later learn that Table B.8 lists specific enthalpies of nitrogen relative to N_2(g, 25°C, 1 atm), which makes this state a convenient choice for nitrogen. There are no tabulated enthalpy data for acetone in the text, so we will choose one of the process stream conditions, Ac(l, 20°C, 5 atm), as the reference state for this species, which will enable us to set the corresponding $\hat{H}$ value equal to zero rather than having to calculate it.

4. ***Construct an inlet–outlet enthalpy table.***

We first write the chosen reference states, then construct the table shown below:

References: Ac(l, 20°C, 5 atm), N_2(g, 25°C, 1 atm)

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
Ac(v)	66.9	$\hat{H}_1$	3.35	$\hat{H}_3$
Ac(l)	—	—	63.55	0
N_2	33.1	$\hat{H}_2$	33.1	$\hat{H}_4$

Note the following points about the table:

- Nitrogen has only one inlet state (gas, 65°C, 1 atm) and one outlet state (gas, 20°C, 5 atm), so we need only one row in the table for N_2. Acetone has one inlet state (vapor, 65°C, 1 atm) but two outlet states (vapor and liquid, each at 20°C and 5 atm), so we need two rows for this species.
- We mark out (using dashes) the two cells corresponding to $\dot{n}_{in}$ and $\hat{H}_{in}$ for liquid acetone, since no liquid acetone enters the system.
- The $\dot{n}$ values are obtained from the flowchart. The flow rate of acetone vapor at the inlet, for example, is determined as (100 mol/s)[0.669 mol Ac(v)/mol] = 66.9 mol Ac(v)/s.
- Since the liquid acetone leaving the system is at the reference state, we set its specific enthalpy equal to zero.
- Four unknown specific enthalpies have been labeled and must be determined in Step 5.

5. ***Calculate all unknown specific enthalpies.***

To calculate the four unknown specific enthalpies in the table, we construct hypothetical process paths from the reference states to the states of the species in the process and evaluate $\Delta\hat{H}$ for each path. This is the part of the calculation you have not yet learned to do. We will show you the calculation of $\hat{H}_1$ to illustrate the method, give the results of the other calculations, and go into detail about the required procedures in Sections 8.2–8.5.

$$\begin{aligned}\hat{H}_1 &= \text{specific enthalpy of Ac(v, 65°C, 1 atm) relative to Ac(l, 20°C, 5 atm)}\\ &= \Delta\hat{H} \text{ for Ac(l, 20°C, 5 atm)} \longrightarrow \text{Ac(v, 65°C, 1 atm)}\end{aligned}$$

When choosing a process path for the determination of $\Delta\hat{H}$, it helps to know that formulas and data are given in this chapter for enthalpy changes corresponding to certain types of processes:

- Section 8.2 gives the formula $\Delta\hat{H} = \hat{V}\,\Delta P$ for a change in pressure (ΔP) undergone by a liquid or solid with constant specific volume $\hat{V}$. The value of $\hat{V}$ for liquid acetone may be determined as 0.0734 L/mol from the specific gravity (0.791) given in Table B.1.

- Section 8.3 shows that $\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT$ for a change from T_1 to T_2 at constant P. Formulas for $C_p(T)$, the *heat capacity at constant pressure,* are given in Table B.2. The formulas for acetone liquid and vapor are as follows:

$$\text{Ac(l)}:\quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot{}^\circ\text{C}}\right) = 0.123 + 18.6 \times 10^{-5}T$$

$$\text{Ac(v)}:\quad C_p\left(\frac{\text{kJ}}{\text{mol}\cdot{}^\circ\text{C}}\right) = 0.07196 + 20.10 \times 10^{-5}T - 12.78 \times 10^{-8}T^2 + 34.76 \times 10^{-12}T^3$$

  where T is in °C.
- Section 8.4 defines the *heat of vaporization,* $\Delta\hat{H}_v(T_{bp})$, as $\Delta\hat{H}$ for a change from liquid to vapor at the normal boiling point, T_{bp}. Table B.1 lists T_{bp} for acetone as 56.0°C and $\Delta\hat{H}_v(T_{bp})$ as 30.2 kJ/mol.

The following process path from the reference state [Ac(l), 20°C, 5 atm] to the process state [Ac(v, 56°C, 1 atm)] enables us to use all this information in the determination of $\hat{H}_1$:[3]

$$\text{Ac(l, 20°C, 5 atm)} \xrightarrow{\Delta\hat{H}_{1a}} \text{Ac(l, 20°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1b}} \text{Ac(l, 56°C, 1 atm)}$$

$$\xrightarrow{\Delta\hat{H}_{1c}} \text{Ac(v, 56°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1d}} \text{Ac(v, 65°C, 1 atm)}$$

$$\Downarrow$$

$$\begin{aligned} \hat{H}_1 &= \Delta\hat{H}_{\text{path}} \\ &= \Delta\hat{H}_{1a} + \Delta\hat{H}_{1b} + \Delta\hat{H}_{1c} + \Delta\hat{H}_{1d} \\ &= \hat{V}_{\text{Ac(l)}}(1\text{ atm} - 5\text{ atm}) + \int_{20^\circ\text{C}}^{56^\circ\text{C}} (C_p)_{\text{Ac(l)}}\,dT + (\Delta\hat{H}_v)_{\text{Ac}} + \int_{56^\circ\text{C}}^{65^\circ\text{C}} (C_p)_{\text{Ac(v)}}\,dT \end{aligned}$$

When we substitute the values of $\hat{V}_{\text{Ac(l)}}$ and $\Delta\hat{H}_v$ and the formulas for $C_p(T)$ into the expression for $\hat{H}_1$ and carry out the necessary unit conversions and integrations, we obtain $\hat{H}_1 = (0.0297 + 4.68 + 30.2 + 0.753)$ kJ/mol = 35.7 kJ/mol.

Proceeding in a similar manner, we obtain the values for $\hat{H}_2$, $\hat{H}_3$, and $\hat{H}_4$ shown in the following revised enthalpy table:

References: Ac(l, 20°C, 5 atm), N_2(g, 25°C, 1 atm)

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\hat{H}_{\text{out}}$ (kJ/mol)
Ac(v)	66.9	35.7	3.35	32.0
Ac(l)	—	—	63.55	0
N_2	33.1	1.16	33.1	−0.10

6. *Calculate $\Delta\dot{H}$.*

$$\begin{aligned} \Delta\dot{H} &= \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i \\ &= (3.35\text{ mol/s})(32.0\text{ kJ/mol}) + [(63.55)(0) + (33.1)(-0.10) - (66.9)(35.7) - (33.1)(1.16)]\text{ kJ/s} \\ &= -2320\text{ kJ/s} \end{aligned}$$

The factors in the last equation come directly from the inlet–outlet enthalpy table.

7. *Calculate nonzero work, kinetic energy, and potential energy terms.*

Since there is no shaft work and we are neglecting kinetic and potential energy changes, there is nothing to do in this step.

---

[3] To be completely accurate, we would include a step in which the acetone and nitrogen are mixed since the references are the pure species; however, enthalpy changes when gases are mixed are generally negligible (Section 8.5).

8. *Solve the energy balance for $\dot{Q}$.*

$$\dot{Q} = \Delta\dot{H} = -2320\ \text{kJ/s} = \boxed{-2320\ \text{kW}}$$

Heat must be transferred from the condenser at a rate of 2320 kW to achieve the required cooling and condensation.

Before we leave this section, let us consider what we just did from a different perspective. The process for which we need to calculate $\Delta\dot{H}$ $(= \dot{Q})$ may be depicted as shown below:

$$\begin{array}{l} 66.9\ \text{mol Ac(v)} \\ 33.1\ \text{mol}\ N_2 \\ 65^\circ\text{C}, 1\ \text{atm} \\ \end{array} \xrightarrow{\Delta\dot{H}} \begin{array}{l} 63.55\ \text{mol Ac(l)} \\ \ \ 3.35\ \text{mol Ac(v)} \\ 33.1\ \text{mol}\ N_2 \\ 20^\circ\text{C}, 5\ \text{atm} \end{array}$$

To calculate $\Delta\dot{H}$, in effect we constructed the following process path:

$$\begin{tikzcd}
\begin{array}{l} 66.9\ \text{mol Ac(v)} \\ 33.1\ \text{mol}\ N_2 \\ 65^\circ\text{C}, 1\ \text{atm} \end{array} \arrow[rr, dashed, "\Delta\dot{H}"] \arrow[dr, "\Delta\dot{H}_a"'] & & \begin{array}{l} 63.55\ \text{mol Ac(l)} \\ \ \ 3.35\ \text{mol Ac(v)} \\ 33.1\ \text{mol}\ N_2 \\ 20^\circ\text{C}, 5\ \text{atm} \end{array} \\
& \begin{array}{l} \text{Reference conditions} \\ 66.9\ \text{mol Ac(l)}, 20^\circ\text{C}, 1\ \text{atm} \\ 33.1\ \text{mol}\ N_2, 25^\circ\text{C}, 1\ \text{atm} \end{array} \arrow[ur, "\Delta\dot{H}_b"'] &
\end{tikzcd}$$

The total enthalpy change for the first step, $\Delta\dot{H}_a$, is the negative of $\Delta\dot{H}$ for the process in which acetone and nitrogen go from the reference conditions to the inlet conditions, or

$$\Delta\dot{H}_a = -\sum_{\text{in}} \dot{n}_i\hat{H}_i$$

Similarly, $\Delta\dot{H}_b$ is the enthalpy change for the process in which acetone and nitrogen go from the reference conditions to the outlet conditions, or

$$\Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i$$

Since enthalpy is a state function, the overall enthalpy change for the process must be

$$\Delta\dot{H} = \Delta\dot{H}_a + \Delta\dot{H}_b = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

It remains for us to outline methods for calculating $\Delta\hat{U}$ and $\Delta\hat{H}$ for the different types of processes we have discussed. The methods for the first four (change in P at constant T, change in T at constant P, change in phase at constant T and P, and mixing or dissolving at constant T and P) are outlined in Sections 8.2–8.5 of this chapter, and methods for chemical reactions at constant T and P are given in Chapter 9.

8.2 CHANGES IN PRESSURE AT CONSTANT TEMPERATURE

It has been observed experimentally that internal energy is nearly independent of pressure for solids and liquids at a fixed temperature, as is specific volume. Therefore, *if the pressure of a solid or liquid changes at constant temperature, you may write $\Delta\hat{U} \approx 0$ and $\Delta\hat{H}$ $[= \Delta\hat{U} + \Delta(P\hat{V})] \approx \hat{V}\,\Delta P$.*

Both $\hat{U}$ and $\hat{H}$ are independent of pressure for ideal gases. Consequently, *you may generally assume* $\Delta\hat{U} \approx 0$ *and* $\Delta\hat{H} \approx 0$ *for a gas undergoing an isothermal pressure change unless gases at temperatures well below* 0°C *or well above 1 atm are involved.* [If tables of $\hat{U}(T, P)$ or $\hat{H}(T, P)$ are available for the gas, there is of course no need to make this assumption.] If gases are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations beyond the scope of this text to determine $\Delta\hat{U}$ or $\Delta\hat{H}$. A good source for such correlations is Chapter 5 of Reid, Prausnitz, and Poling.[4]

TEST YOURSELF (Answers, p. 660)

1. Which of the following assumptions appears reasonable for each of the isothermal processes to be described below? (i) $\Delta\hat{U} \approx 0$, $\Delta\hat{H} \approx 0$; (ii) $\Delta\hat{U} \approx 0$, $\Delta\hat{H} \neq 0$; (iii) neither (i) or (ii).
   (a) H_2O (l, 1 atm) → H_2O (l, 1200 atm), $T = 25°C$
   (b) N_2 (g, 1 atm) → N_2 (g, 1.2 atm), $T = 25°C$
   (c) N_2 (g, 1 atm) → N_2 (g, 200 atm), $T = 25°C$
2. Consider the process

$$C_2H_6\ (g, 25°C, 1\ atm) \rightarrow C_2H_6\ (g, 25°C, 30\ atm)$$

How would you use the compressibility charts to determine whether it is reasonable to neglect $\Delta\hat{H}$ for this process?

8.3 CHANGES IN TEMPERATURE

8.3a Sensible Heat and Heat Capacities

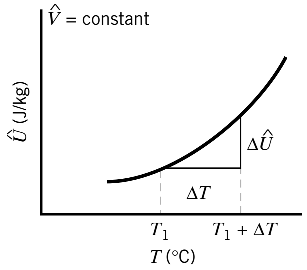
The term **sensible heat** signifies heat that must be transferred to raise or lower the temperature of a substance or mixture of substances. The quantity of heat required to produce a temperature change in a system can be determined from the appropriate form of the first law of thermodynamics:

$$Q = \Delta U \quad \text{(closed system)} \qquad \textbf{(8.3-1)}$$

$$\dot{Q} = \Delta\dot{H} \quad \text{(open system)} \qquad \textbf{(8.3-2)}$$

(We have neglected kinetic and potential energy changes and work.) To determine the sensible heat requirement for a heating or cooling process, you must therefore be able to determine ΔU or $\Delta\dot{H}$ for the specified temperature change.

The specific internal energy of a substance depends strongly on temperature. If the temperature is raised or lowered in such a way that the system volume remains constant, the specific internal energy might vary as shown in the following plot:



A temperature change ΔT from T_1 leads to a change $\Delta\hat{U}$ in specific internal energy. As $\Delta T \rightarrow 0$, the ratio $\Delta\hat{U}/\Delta T$ approaches a limiting value (i.e., the slope of the curve at T_1), which is by definition the **heat capacity at constant volume** of the substance, denoted by C_v.

---

[4] R. C. Reid, J. H. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th Edition, McGraw-Hill, New York, 1987.

$$C_v(T) = \left\{ \lim_{\Delta T \to 0} \frac{\Delta \hat{U}}{\Delta T} \right\} = \left(\frac{\partial \hat{U}}{\partial T} \right)_V \tag{8.3-3}$$

Since the plot of $\hat{U}$ versus T is not generally a straight line, C_v (the slope of the curve) is a function of temperature.

The change in $\hat{U}$ for a temperature rise from T to $T + dT$ at constant volume is from Equation 8.3-3

$$d\hat{U} = C_v(T)\, dT \tag{8.3-4}$$

and the change $\Delta \hat{U} = \hat{U}_2 - \hat{U}_1$ associated with a temperature change from T_1 to T_2 at constant volume is, accordingly,

$$\Delta \hat{U} = \int_{T_1}^{T_2} C_v(T)\, dT \tag{8.3-5}$$

Now, suppose both the temperature and the volume of a substance change. To calculate $\Delta \hat{U}$, you may break the process into two steps—a change in $\hat{V}$ at constant T followed by a change in T at constant $\hat{V}$.

$$\begin{tikzcd}
A(T_1, \hat{V}_1) \arrow[r, "\Delta \hat{U}_1"] \arrow[rr, bend right, "\Delta \hat{U}"'] & A(T_1, \hat{V}_2) \arrow[r, "\Delta \hat{U}_2"] & A(T_2, \hat{V}_2)
\end{tikzcd}$$

Since $\hat{U}$ is a state property, $\Delta \hat{U}$ (the desired quantity) equals $\Delta \hat{U}_1 + \Delta \hat{U}_2$. But for ideal gases and (to a good approximation) liquids and solids, $\hat{U}$ depends only on T, so that since T is constant in step 1, $\Delta U_1 \approx 0$ for any substance but a nonideal gas. Moreover, since the second step is a change in temperature at constant volume, $\Delta \hat{U}_2$ is given by Equation 8.3-5. In summary, then, for a temperature change from T_1 to T_2

$$\boxed{\Delta \hat{U} \approx \int_{T_1}^{T_2} C_v(T)\, dT} \tag{8.3-6}$$

Ideal gas: exact
Solid or liquid: good approximation
Nonideal gas: valid only if V is constant

EXAMPLE 8.3-1 *Evaluation of an Internal Energy Change from Tabulated Heat Capacity*

Calculate the heat required to raise 200 kg of nitrous oxide from 20°C to 150°C in a constant-volume vessel. The constant-volume heat capacity of N_2O in this temperature range is given by the equation

$$C_v\ (\text{kJ/kg}\cdot°\text{C}) = 0.855 + 9.42 \times 10^{-4} T$$

where T is in °C.

SOLUTION From Equation 8.3-6,

$$\begin{aligned}
\Delta \hat{U}(\text{kJ/kg}) &= \int_{20°\text{C}}^{150°\text{C}} (0.855 + 9.42 \times 10^{-4} T) \left(\frac{\text{kJ}}{\text{kg}\cdot°\text{C}} \right) dT \\
&= 0.855T \Big]_{20°\text{C}}^{150°\text{C}} + \frac{9.42 \times 10^{-4} T^2}{2} \Bigg]_{20°\text{C}}^{150°\text{C}} \\
&= (111 + 10.4)\ \text{kJ/kg} = 121\ \text{kJ/kg}
\end{aligned}$$

The energy balance for this closed system is

$$Q = \Delta U = m(\text{kg})\, \Delta \hat{U}(\text{kJ/kg}) = (200\ \text{kg})(121\ \text{kJ/kg}) = \boxed{24{,}200\ \text{kJ}}$$

Next, let us suppose that we heat a substance at constant pressure and consider the resulting change in enthalpy. Like internal energy, enthalpy depends strongly on temperature. If $\Delta \hat{H}$

is the change in specific enthalpy resulting from a temperature increase at constant pressure from T to $T + \Delta T$, then as ΔT approaches zero the ratio $\Delta\hat{H}/\Delta T$ approaches a limiting value, defined as the **heat capacity at constant pressure** and denoted by C_p.

$$C_p(T) = \left\{ \lim_{\Delta T \to 0} \frac{\Delta\hat{H}}{\Delta T} \right\} = \left(\frac{\partial\hat{H}}{\partial T} \right)_P \tag{8.3-7}$$

Proceeding as before, we observe that the change in $\hat{H}$ for a temperature change at constant pressure from T to $T + dT$ is

$$d\hat{H} = C_p(T)\, dT$$

and so for a change from T_1 to T_2 at constant pressure

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\, dT \tag{8.3-8}$$

For a process $A(T_1, P_1) \to A(T_2, P_2)$, we may construct a two-step process path

$$\begin{tikzcd} A(T_1,P_1) \arrow[r, "\Delta\hat{H}_1"] \arrow[rr, bend right, "\Delta\hat{H}"'] & A(T_1,P_2) \arrow[r, "\Delta\hat{H}_2"] & A(T_2,P_2) \end{tikzcd}$$

The first step is a change in pressure at constant temperature, the type of process described in Section 8.2. We saw in that section that

$$\begin{aligned} \Delta\hat{H}_1 &= 0 \quad \text{(ideal gas)} \\ &\approx \hat{V}\,\Delta P \quad \text{(solid or liquid)} \end{aligned} \tag{8.3-9}$$

The second step is a change in temperature at constant pressure, so that $\Delta\hat{H}_2$ is given by Equation 8.3-8. Finally, since $\Delta\hat{H} = \Delta\hat{H}_1 + \Delta\hat{H}_2$ (why?), we obtain

$$\boxed{\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\, dT} \quad \begin{array}{l} \text{Ideal gas: exact} \\ \text{Nonideal gas: exact only if } P \text{ is constant} \end{array} \tag{8.3-10a}$$

$$\boxed{\Delta\hat{H} = \hat{V}\,\Delta P + \int_{T_1}^{T_2} C_p(T)\, dT} \quad \text{Solid or liquid} \tag{8.3-10b}$$

For all but large pressure changes and small temperature changes, the first term of Eq. 8.3-10b is usually negligible relative to the second term.

Evaluating $\Delta\hat{H}$ for a nonideal gas undergoing a temperature and pressure change is best done using tabulated enthalpies. If none are available, a thermodynamic relation for variations of $\hat{H}$ with P must be combined with Equation 8.3-8 to determine the enthalpy change; such relations are given by Reid, Prausnitz, and Poling (see footnote 4).

TEST YOURSELF (Answers, p. 660)

1. By definition, what are C_v and C_p?
2. Suppose the formula

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\, dT$$

is used to calculate the specific enthalpy change for a change in temperature *and pressure* undergone by (a) an ideal gas, (b) a highly nonideal gas, and (c) a liquid. For which of these is the formula exact, and for which is it most likely to lead to significant error?

3. If C_p for an ideal gas is 0.5 cal/(g·°C) (i.e., a constant), what is the enthalpy change in calories corresponding to a change from 10°C to 30°C undergone by five grams of the gas?

CREATIVITY EXERCISE

Your task this time is to estimate the heat capacity of an unknown liquid. You have available a laboratory balance, a very well-insulated container, a sensitive thermometer that can measure liquid temperatures, and a thermocouple that can measure temperatures of solids. The container is a very poor conductor of heat, so that virtually all heat transferred to or from its contents goes entirely into changing the temperature of those contents. If you need anything else (within reason), you can get it. Devise as many ways as you can to estimate C_v, which you may assume is independent of temperature. [*Example:* Mix in the insulated flask a known mass, m_1, of your liquid at temperature T_1, and a known mass, m_2, of hot water at temperature T_2, and measure the final temperature T_f. Since you can calculate the heat lost by water, $Q = m_2 C_{v\text{w}}(T_2 - T_\text{f})$, and you know Q must also equal the heat gained by the other liquid, $m_1 C_v(T_\text{f} - T_1)$, you can solve for C_v.]

8.3b Heat Capacity Formulas

The heat capacities C_v and C_p are physical properties of materials and are tabulated in standard references such as *Perry's Chemical Engineers' Handbook.*[5] They may be expressed in any units of energy per unit amount per unit temperature interval—for example, J/(mol·K), or Btu/(lb_m·°F). The term **specific heat** is also used for this physical property.

Heat capacities are functions of temperature and are frequently expressed in polynomial form ($C_p = a + bT + cT^2 + dT^3$). Values of the coefficients *a, b, c,* and *d* are given in Table B.2 of Appendix B for a number of species at 1 atm, and listings for additional substances are given on pp. 2-161 to 2-186 of *Perry's Chemical Engineers' Handbook.*

When reading the coefficients of a heat capacity formula from Table B.2, do not mistake their orders of magnitude: if a value of 72.4 is read from the column labeled $b \cdot 10^5$, then the value of b must be five orders of magnitude *less* than 72.4, or $b = 72.4 \times 10^{-5}$.

Simple relationships exist between C_p and C_v in two cases:

$$\boxed{\textbf{\textit{Liquids and Solids}}: C_p \approx C_v} \tag{8.3-11}$$

$$\boxed{\textbf{\textit{Ideal Gases}}: C_p = C_v + R} \tag{8.3-12}$$

where R is the gas constant. (Try to prove the second relation.) The relationship between C_p and C_v for nonideal gases is complex and will not be discussed in this text.

EXAMPLE 8.3-2 *Cooling of an Ideal Gas*

Assuming ideal gas behavior, calculate the heat that must be transferred in each of the following cases.

1. A stream of nitrogen flowing at a rate of 100 mol/min is heated from 20°C to 100°C.
2. Nitrogen contained in a 5-liter flask at an initial pressure of 3 bar is cooled from 90°C to 30°C.

SOLUTION Neglecting kinetic energy changes, the energy balance equation for the open system of part 1 is $Q = \Delta H$, and that for the closed system of part 2 is $Q = \Delta U$. (Prove it.) The problem is therefore to evaluate ΔH and ΔU for the two specified processes.

1. From Table B.2, Appendix B, the heat capacity of N_2 at a constant pressure of 1 atm is

$$C_p[\text{kJ/(mol}\cdot{}^\circ\text{C)}] = 0.02900 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3$$

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[5] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook,* 7th Edition, McGraw-Hill, New York, 1997.

where T is in °C. Since we are assuming ideal gas behavior, the enthalpy change for the gas is independent of any pressure change that may occur, and hence, from Equation 8.3-10a,

$$\Delta\hat{H} = \int_{20^\circ\mathrm{C}}^{100^\circ\mathrm{C}} C_p(T)\,dT$$

$$\Downarrow$$

$$\Delta\hat{H}(\mathrm{kJ/mol}) = 0.02900T\Big]_{20^\circ\mathrm{C}}^{100^\circ\mathrm{C}} + 0.2199\times10^{-5}\frac{T^2}{2}\Big]_{20^\circ\mathrm{C}}^{100^\circ\mathrm{C}} + 0.5723\times10^{-8}\,\frac{T^3}{3}\Big]_{20^\circ\mathrm{C}}^{100^\circ\mathrm{C}}$$

$$-\,2.871\times10^{-12}\frac{T^4}{4}\Big]_{20^\circ\mathrm{C}}^{100^\circ\mathrm{C}}$$

$$= (2.320 + 0.0106 + 1.9\times10^{-3} - 7\times10^{-5})\ \mathrm{kJ/mol} = 2.332\ \mathrm{kJ/mol}$$

Finally,

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H}$$

$$= 100\ \frac{\mathrm{mol}}{\mathrm{min}}\left|\frac{2.332\ \mathrm{kJ}}{\mathrm{mol}}\right. = \boxed{233\ \mathrm{kJ/min}}$$

2. To evaluate ΔU, we need the number of moles n, which may be calculated using the ideal gas equation of state, and $\Delta\hat{U}$. To determine the latter quantity we need the constant-volume heat capacity, which from Equation 8.3-12 is

$$C_v = C_p - R$$

$$\Big\Downarrow \begin{array}{l} C_p \text{ given above} \\ R = [8.314\ \mathrm{J\ (/mol\cdot K)}](1\ \mathrm{K}/1^\circ\mathrm{C})(1\ \mathrm{kJ}/10^3\ \mathrm{J}) \end{array}$$

$$C_v[\mathrm{kJ/(mol\cdot{}^\circ C)}] = 0.02069 + 0.2199\times10^{-5}T + 0.5723\times10^{-8}T^2 - 2.871\times10^{-12}T^3$$

Calculate $\Delta\hat{U}$

$$\Delta\hat{U} = \int_{90^\circ\mathrm{C}}^{30^\circ\mathrm{C}} C_v(T)\,dT$$

$$\Downarrow$$

$$\Delta\hat{U} = 0.02069T\Big]_{90^\circ\mathrm{C}}^{30^\circ\mathrm{C}} + 0.2199\times10^{-5}\,\frac{T^2}{2}\Big]_{90^\circ\mathrm{C}}^{30^\circ\mathrm{C}} + 0.5723\times10^{-8}\,\frac{T^3}{3}\Big]_{90^\circ\mathrm{C}}^{30^\circ\mathrm{C}} - 2.871\times10^{-12}\,\frac{T^4}{4}\Big]_{90^\circ\mathrm{C}}^{30^\circ\mathrm{C}}$$

$$= (-1.241 - 7.92\times10^{-3} - 1.34\times10^{-3} + 5\times10^{-5})\ \mathrm{kJ/mol} = -1.250\ \mathrm{kJ/mol}$$

Calculate n

At the initial condition (the only point at which we know P, V, and T)

$$n = PV/RT$$

$$= \frac{(3.00\ \mathrm{bar})(5.00\ \mathrm{L})}{[0.08314\ \mathrm{L\cdot bar/(mol\cdot K)}](363\ \mathrm{K})} = 0.497\ \mathrm{mol}$$

Calculate Q

$$Q = \Delta U = n\,\Delta\hat{U}$$

$$= (0.497\ \mathrm{mol})(-1.250\ \mathrm{kJ/mol}) = \boxed{-0.621\ \mathrm{kJ}}$$

When enthalpies must be calculated frequently for a species, it is convenient to prepare a table of $\hat{H}(T)$ for the species (as was done for water in the steam tables) to avoid having to integrate the formula for $C_p(T)$ again and again. Tables B.8 and B.9 in Appendix B list specific enthalpies of species involved in combustion reactions—air, O_2, N_2, H_2 (a fuel), CO, CO_2, and $H_2O(v)$. The values in these tables were generated by integrating $C_p(T)$ from the specified reference state (25°C for Table B.8, 77°F for Table B.9) to the listed temperatures. The next example illustrates the use of these tables.

EXAMPLE 8.3-3 *Evaluation of $\Delta\dot{H}$ Using Heat Capacities and Tabulated Enthalpies*

Fifteen kmol/min of air is cooled from 430°C to 100°C. Calculate the required heat removal rate using (1) heat capacity formulas from Table B.2 and (2) specific enthalpies from Table B.8.

SOLUTION

$$\text{air(g, 430°C)} \longrightarrow \text{air(g, 100°C)}$$

With $\Delta\dot{E}_k$, $\Delta\dot{E}_p$, and $\dot{W}_s$ deleted, the energy balance is

$$\dot{Q} = \Delta\dot{H} = \dot{n}_{\text{air}}\hat{H}_{\text{air,out}} - \dot{n}_{\text{air}}\hat{H}_{\text{air,in}} = \dot{n}_{\text{air}}\,\Delta\hat{H}$$

Assume ideal gas behavior, so that pressure changes (if there are any) do not affect $\Delta\hat{H}$.

1. ***The hard way.*** Integrate the heat capacity formula in Table B.2.

$$\Delta\hat{H}\left(\frac{\text{kJ}}{\text{mol}}\right) = \int_{430^\circ\text{C}}^{100^\circ\text{C}} C_p(T)\,dT$$

$$= \int_{430^\circ\text{C}}^{100^\circ\text{C}} \left[0.02894 + 0.4147 \times 10^{-5}T + 0.3191 \times 10^{-8}T^2 - 1.965 \times 10^{-12}T^3\right] dT$$

$$= \left[0.02894(100 - 430) + \frac{0.4147 \times 10^{-5}}{2}(100^2 - 430^2) + \frac{0.3191 \times 10^{-8}}{3}(100^3 - 430^3) - \frac{1.965 \times 10^{-12}}{4}(100^4 - 430^4)\right] \text{kJ/mol}$$

$$= (-9.5502 - 0.3627 - 0.0835 + 0.0167)\ \text{kJ/mol} = -9.98\ \text{kJ/mol}$$

2. ***The easy way.*** Use tabulated enthalpies from Table B.8.

$\hat{H}$ for air at 100°C can be read directly from Table B.9 and $\hat{H}$ at 430°C can be estimated by linear interpolation from the values at 400°C (11.24 kJ/mol) and 500°C (14.37 kJ/mol).

$$\hat{H}(100^\circ\text{C}) = 2.19\ \text{kJ/mol}$$

$$\hat{H}(430^\circ\text{C}) = [11.24 + 0.30(14.37 - 11.24)]\ \text{kJ/mol} = 12.17\ \text{kJ/mol}$$

$$\Downarrow$$

$$\Delta\hat{H} = (2.19 - 12.17)\ \text{kJ/mol} = -9.98\ \text{kJ/mol}$$

Either way $\Delta\hat{H}$ is determined,

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H} = \begin{array}{r|r|r|l|l} 15.0\ \text{kmol} & 10^3\ \text{mol} & -9.98\ \text{kJ} & 1\ \text{min} & 1\ \text{kW} \\ \hline \text{min} & 1\ \text{kmol} & \text{mol} & 60\ \text{s} & 1\ \text{kJ/s} \end{array} = \boxed{-2500\ \text{kW}}$$

Reminder: The enthalpies listed in Tables B.8 and B.9 (and for that matter, the heat capacity formulas of Table B.2) apply strictly to heating and cooling at a constant pressure of 1 atm. The tabulated enthalpies and heat capacities may also be used for nonisobaric heating and cooling of ideal or nearly ideal gases; however, at pressures high enough (or temperatures low enough) for the gases to be far from ideal, enthalpy tables or more accurate heat capacity formulas should be used.

TEST YOURSELF (Answers, p. 660)

1. The heat capacity of a species is 28.5 J/(mol·K). Remembering that the temperature unit in the denominator refers to a temperature *interval,* what is the heat capacity of this species in J/(mol·°C)?

2. The gas constant R is approximately equal to 2 cal/(mol·K). If C_p for a vapor is 7 cal/(mol·°C), estimate C_v for the vapor. If C_p for a liquid is 7 cal/(mol·°C), estimate C_v for the liquid.
3. Use Table B.8 or B.9 to calculate the following quantities:
   (a) The specific enthalpy (kJ/mol) of N_2 at 1000°C relative to N_2 at 300°C.
   (b) $\Delta\hat{H}$(kJ/mol) for the process CO_2(g, 800°C, 1 atm) $\longrightarrow$ CO_2(g, 300°C, 1 atm).
   (c) $\Delta\dot{H}$(Btu/h) for 100 lb-mole O_2/h being cooled from 500°F and 1.5 atm to 200°F and 0.75 atm.

8.3c Estimation of Heat Capacities

The polynomial expressions for C_p in Table B.2 are based on experimental data for the listed compounds and provide a basis for accurate calculations of enthalpy changes. Several approximate methods follow for estimating heat capacities in the absence of tabulated formulas.

Kopp's rule is a simple empirical method for estimating the heat capacity of a solid or liquid at or near 20°C. According to this rule, C_p for a molecular compound is the sum of contributions (given in Table B.10) for each element in the compound. For example, the heat capacity of solid calcium hydroxide, $Ca(OH)_2$, would be estimated from Kopp's rule as

$$\begin{aligned}(C_p)_{Ca(OH)_2} &= (C_{pa})_{Ca} + 2(C_{pa})_{O} + 2(C_{pa})_{H} \\ &= [26 + (2 \times 17) + (2 \times 9.6)]\ \text{J/(mol}\cdot{}^\circ\text{C)} = 79\ \text{J/(mol}\cdot{}^\circ\text{C)}\end{aligned}$$

[The true value is 89.5 J/(mol·°C).]

More accurate heat capacity estimation formulas for various types of gases and liquids are given in Chapter 5 of Reid, Prausnitz, and Poling (see footnote 4), and several correlations are presented by Gold and Ogle.[6]

Suppose you wish to calculate the enthalpy change associated with a change in temperature undergone by a mixture of substances. Enthalpies and heat capacities of certain mixtures are tabulated in standard references. Lacking such data, you may use the following approximation:

Rule 1. *For a mixture of gases or liquids, calculate the total enthalpy change as the sum of the enthalpy changes for the pure mixture components.* You are in effect neglecting enthalpy changes associated with the mixing of the components, which is an excellent approximation for mixtures of gases and for mixtures of similar liquids such as pentane and hexane but a poor one for dissimilar liquids such as nitric acid and water. Enthalpies of mixing for systems of the latter type are discussed in detail in Section 8.5.

Rule 2. *For highly dilute solutions of solids or gases in liquids, neglect the enthalpy change of the solute.* The more dilute the solution, the better this approximation.

The calculation of enthalpy changes for the heating or cooling of a mixture of known composition may often be simplified by calculating a heat capacity for the mixture in the following manner:

$$(C_p)_{\text{mix}}(T) = \sum_{\substack{\text{all}\\\text{mixture}\\\text{components}}} y_i C_{pi}(T) \qquad \textbf{(8.3-13)}$$

where

$(C_p)_{\text{mix}}$ = heat capacity of the mixture
y_i = mass or mole fraction of the ith component
C_{pi} = heat capacity of the ith component

---

[6] P. I. Gold and G. J. Ogle, "Estimating Thermochemical Properties of Liquids, Part 7—Heat Capacity," *Chem. Eng.*, Apr. 7, 1969, p. 130.

If C_{pi} and $(C_p)_{\text{mix}}$ are expressed in molar units, then y_i must be the mole fraction of the ith component, and if the heat capacities are expressed in mass units, then y_i must be the mass fraction of the ith component. Once $(C_p)_{\text{mix}}$ is known, $\Delta\hat{H}$ for a change in temperature from T_1 to T_2 may be calculated as

$$\Delta\hat{H} = \int_{T_1}^{T_2} (C_p)_{\text{mix}}(T)\,dT \qquad \textbf{(8.3-14)}$$

Equation 8.3-14 is valid to the extent that enthalpies of mixing may be neglected.

EXAMPLE 8.3-4 *Heat Capacity of a Mixture*

Calculate the heat required to bring 150 mol/h of a stream containing 60% C_2H_6 and 40% C_3H_8 by volume from 0°C to 400°C. Determine a heat capacity for the mixture as part of the problem solution.

SOLUTION The polynomial heat capacity formulas for ethane and propane given in Table B.2 are substituted into Equation 8.3-13 to yield

$$\begin{aligned}(C_p)_{\text{mix}}[\text{kJ/(mol}\cdot{}^\circ\text{C)}] &= 0.600(0.04937 + 13.92\times10^{-5}T - 5.816\times10^{-8}T^2 + 7.280\times10^{-12}T^3)\\ &\quad + 0.400(0.06803 + 22.59\times10^{-5}T - 13.11\times10^{-8}T^2 + 31.71\times10^{-12}T^3)\\ &= 0.05683 + 17.39\times10^{-5}T - 8.734\times10^{-8}T^2 + 17.05\times10^{-12}T^3\end{aligned}$$

$$\Delta\hat{H} = \int_{0^\circ\text{C}}^{400^\circ\text{C}} (C_p)_{\text{mix}}\,dT = 34.89\text{ kJ/mol}$$

where T is in °C. If potential and kinetic energy changes and shaft work are neglected, the energy balance becomes

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H} = \frac{150\text{ mol}}{\text{h}}\left|\frac{34.89\text{ kJ}}{\text{mol}}\right. = \boxed{5230\ \frac{\text{kJ}}{\text{h}}}$$

As usual, we have assumed that the gases are sufficiently close to ideal for the formulas for C_p at 1 atm to be valid.

TEST YOURSELF (Answers, p. 660)

1. Estimate the heat capacity of solid calcium carbonate ($CaCO_3$) using Kopp's rule and Table B.10.
2. Two kilograms of liquid *n*-hexane [$C_p = 2.5$ kJ/(kg·°C)] and 1 kg of liquid cyclohexane [$C_p = 1.8$ kJ/(kg·°C)] are mixed and heated from 20°C to 30°C. Use the rule for liquid mixtures (Rule 1) given in this section to show that $\Delta H \approx 68$ kJ for this process. What is $\Delta\hat{H}$(kJ/kg mixture)?
3. A 0.100 wt% aqueous solution of sodium chloride is heated from 25°C to 50°C. Use the rule for solutions (Rule 2) given in this section to estimate $\Delta\hat{H}$(cal/g) for this process. C_p for water is 1 cal/(g·°C).
4. The heat capacity of liquid water is 1 cal/(g·°C), and that of ethanol is 0.54 cal/(g·°C). Estimate the heat capacity of a mixture containing 50% ethanol and 50% water by mass.

8.3d Energy Balances on Single-Phase Systems

We are now in a position to perform energy balances on any processes that do not involve phase changes, mixing steps for which enthalpy changes cannot be neglected, or chemical reactions.

If a process only involves heating or cooling a single species from T_1 to T_2, the procedure is straightforward:

1. Evaluate $\Delta\hat{U} = \int_{T_1}^{T_2} C_v\,dT$ or $\Delta\hat{H} = \int_{T_1}^{T_2} C_p\,dT$, correcting for pressure changes if necessary.

2. For a closed system at constant volume, calculate $\Delta U = n\,\Delta\hat{U}$ (where n is the amount of the species being heated or cooled). For a closed system at constant pressure, calculate $\Delta H = n\,\Delta\hat{H}$. For an open system, calculate $\Delta\dot{H} = \dot{n}\,\Delta\hat{H}$, where $\dot{n}$ is the species flow rate.
3. Substitute for ΔU, ΔH, or $\Delta\dot{H}$ in the appropriate energy balance equation to determine the required heat transfer, Q, or heat transfer rate, $\dot{Q}$. (See Example 8.3-2.)

If more than one species is involved or if there are several input or output streams instead of just one of each, the procedure given in Section 8.1 should be followed: choose reference states for each species, prepare and fill in a table of amounts and specific internal energies (closed system) or species flow rates and specific enthalpies (open system), and substitute the calculated values into the energy balance equation. The next example illustrates the procedure for a continuous heating process.

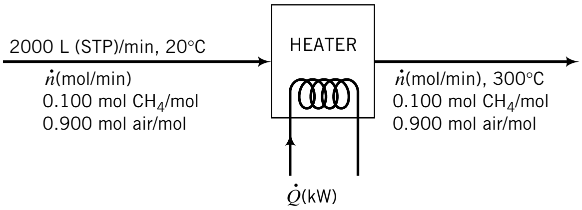
EXAMPLE 8.3-5 *Energy Balance on a Gas Preheater*

Equipment Encyclopedia
heat exchanger

A stream containing 10% CH_4 and 90% air by volume is to be heated from 20°C to 300°C. Calculate the required rate of heat input in kilowatts if the flow rate of the gas is 2.00×10^3 liters (STP)/min.

SOLUTION ***Basis: Given Flow Rate***

Assume ideal gas behavior.



Recall that specifying the flow rate in liters (STP)/min does not imply that the feed gas is at standard temperature and pressure; it is simply an alternative way of giving the molar flow rate.

$$\dot{n} = \frac{2000\ \text{L (STP)}}{\text{min}}\left|\frac{1\ \text{mol}}{22.4\ \text{L (STP)}}\right. = 89.3\ \text{mol/min}$$

The energy balance with kinetic and potential energy changes and shaft work omitted is $\dot{Q} = \Delta\dot{H}$. The task is to evaluate $\Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$. Since each species has only one inlet condition and one outlet condition in the process, two rows are sufficient for the enthalpy table.

References: CH_4(g, 20°C, 1 atm), air(g, 25°C, 1 atm)

Substance	$\dot{n}_{\text{in}}$ (mol/min)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/min)	$\hat{H}_{\text{out}}$ (kJ/mol)
CH_4	8.93	0	8.93	$\hat{H}_1$
Air	80.4	$\hat{H}_2$	80.4	$\hat{H}_3$

The reference condition for methane was chosen so that $\hat{H}_{\text{in}}$ could be set equal to zero, and that for air was chosen so that $\hat{H}_{\text{in}}$ and $\hat{H}_{\text{out}}$ could be determined directly from Table B.8.

The next step is to evaluate all of the unknown specific enthalpies in the table. $\hat{H}_1$, for example, is the specific enthalpy of methane in the outlet gas mixture at 300°C relative to pure methane at its reference temperature of 20°C. In other words, it is the specific enthalpy change for the process

$$CH_4(\text{g, 20°C, 1 atm}) \longrightarrow CH_4(\text{g, 300°C, } P \text{ in outlet mixture})$$

We neglect the effect of pressure on enthalpy (i.e., we assume ideal gas behavior) and we always neglect heats of mixing of gases, so that the enthalpy change is calculated for the heating of pure methane at 1 atm:

$$\hat{H}_1 = \int_{20°\text{C}}^{300°\text{C}} (C_p)_{\text{CH}_4}\, dT$$

$$\Big\Downarrow \text{Substitute for } C_p \text{ from Table B.2}$$

$$= \int_{20°\text{C}}^{300°\text{C}} (0.03431 + 5.469 \times 10^{-5}T + 0.3661 \times 10^{-8}T^2 - 11.0 \times 10^{-12}T^3)\, dT$$

$$= 12.09 \text{ kJ/mol}$$

The enthalpies of air at the inlet and outlet conditions relative to air at the reference state ($\hat{H}_2$ and $\hat{H}_3$, respectively) are determined from Table B.8 as

$$\hat{H}_2 = -0.15 \text{ kJ/mol}, \qquad \hat{H}_3 = 8.17 \text{ kJ/mol}$$

The energy balance now yields

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

$$= (8.93 \text{ mol/min})(12.09 \text{ kJ/mol}) + [(80.4)(8.17) - (8.93)(0) - (80.4)(-0.15)] \text{ kJ/min}$$

$$\Big\Downarrow$$

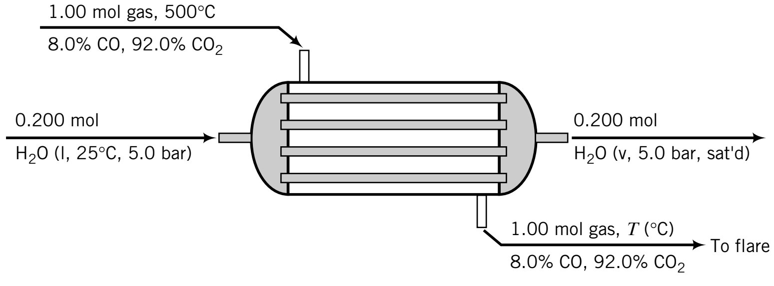
$$\dot{Q} = \frac{776 \text{ kJ}}{\text{min}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| \frac{1 \text{ kW}}{1 \text{ kJ/s}} = \boxed{12.9 \text{ kW}}$$

In the last example the temperatures of all input and output streams were specified, and the only unknown in the energy balance equation was the heat transfer rate required to achieve the specified conditions. You will also encounter problems in which the heat input is known but the temperature of an output stream is not. For these problems, you must evaluate the outlet stream component enthalpies in terms of the unknown T, substitute the resulting expressions in the energy balance equation, and solve for T. Example 8.3-6 illustrates this procedure.

EXAMPLE 8.3-6 *Energy Balance on a Waste Heat Boiler*

Equipment Encyclopedia
boiler

A gas stream containing 8.0 mole% CO and 92.0 mole% CO_2 at 500°C is fed to a **waste heat boiler,** a large metal shell containing a bundle of small-diameter tubes. The hot gas flows over the outside of the tubes. Liquid water at 25°C is fed to the boiler in a ratio 0.200 mol feedwater/mol hot gas and flows inside the tubes. Heat is transferred from the hot gas through the tube walls to the water, causing the gas to cool and the water to heat to its boiling point and evaporate to form saturated steam at 5.0 bar. The steam may be used for heating or power generation in the plant or as the feed to another process unit. The gas leaving the boiler is flared (burned) and discharged to the atmosphere. The boiler operates adiabatically—all the heat transferred from the gas goes into the water, as opposed to some of it leaking through the outside boiler wall. The flowchart for an assumed basis of 1.00 mol feed gas is shown below.



What is the temperature of the exiting gas?

SOLUTION Since no material balances are required in this problem, we may proceed directly to the energy balance, which for this adiabatic unit reduces to

$$\Delta H = \sum_{\text{out}} n_i \hat{H}_i - \sum_{\text{in}} n_i \hat{H}_i = 0$$

We do not write $\Delta \dot{H}$ and $\dot{n}_i$ since a quantity (1 mol feed gas) and not a flow rate has been assumed as a basis of calculation.

(*Exercise*: What assumptions have been made in writing the energy balance?)

References: CO(g, 500°C, 1 atm), CO_2(g, 500°C, 1 atm), H_2O(l, triple point)

Substance	n_{in}	$\hat{H}_{\text{in}}$	n_{out}	$\hat{H}_{\text{out}}$
CO	0.080 mol	0 kJ/mol	0.080 mol	$\hat{H}_1$ (kJ/mol)
CO_2	0.920 mol	0 kJ/mol	0.920 mol	$\hat{H}_2$ (kJ/mol)
H_2O	0.00360 kg	$\hat{H}_3$ (kJ/kg)	0.00360 kg	$\hat{H}_4$ (kJ/kg)

The solution strategy will be to calculate $\hat{H}_1(T)$ and $\hat{H}_2(T)$ by integrating the heat capacity formulas of Table B.2 from the reference temperature (500°C) to the unknown T at the gas outlet, look up $\hat{H}_3$ and $\hat{H}_4$ in the steam tables, substitute for $\hat{H}_1$ through $\hat{H}_4$ in the energy balance, and solve the resulting equation for T using a spreadsheet.

Note the following points about the enthalpy table.

- We chose the reference states for CO and CO_2 as the gas inlet temperature and 1 atm. We assume ideal gas behavior so that deviations of the pressure from 1 atm have no effect on enthalpies, and accordingly set the inlet enthalpies of the gas species equal to zero.
- We will find the enthalpies of the feedwater and product steam in the steam tables. Knowing this, we chose the reference state for the steam tables (liquid water at the triple point) as our reference for water, and knowing that the enthalpies in the steam tables are in kJ/kg, we list the quantity of water in kg ($m = 0.200$ mol $H_2O \times 0.0180$ kg/mol $= 0.00360$ kg).
- We will integrate the heat capacity formulas of Table B.2 for CO and CO_2 even though enthalpies for those species are listed in Table B.8, since we do not know the temperature at which to look them up.

The specific enthalpies are

$$\hat{H}_1 = \int_{500^\circ\text{C}}^{T} (C_p)_{\text{CO}}\, dT$$

$$= \int_{500^\circ\text{C}}^{T} (0.02895 + 0.4110 \times 10^{-5}T + 0.3548 \times 10^{-8}T^2 - 2.220 \times 10^{-12}T^3)\, dT$$

$$\hat{H}_2 = \int_{500^\circ\text{C}}^{T} (C_p)_{\text{CO}_2}\, dT$$

$$= \int_{500^\circ\text{C}}^{T} (0.03611 + 4.223 \times 10^{-5}T - 2.887 \times 10^{-8}T^2 + 7.464 \times 10^{-12}T^3)\, dT$$

$$\hat{H}_3 = \hat{H}[\text{H}_2\text{O(l, 25°C, 5 bar)}] \approx 105 \text{ kJ/kg} \quad (\text{Table B.5: neglect effect of pressure on } \hat{H})$$

$$\hat{H}_4 = \hat{H}[\text{H}_2\text{O(v, 5 bar, sat'd)}] = 2747.5 \text{ kJ/kg} \quad (\text{Table B.6})$$

Integrating the expressions for $\hat{H}_1$ and $\hat{H}_2$ and substituting the resulting expressions and the values of $\hat{H}_3$ and $\hat{H}_4$ into the energy balance ($\Delta H = 0$) yields the following equation:

$$1.672 \times 10^{-12}T^4 - 0.8759 \times 10^{-8}T^3 + 1.959 \times 10^{-5}T^2 + 0.03554T - 12.16 = 0$$

The problem is to find the value of T (°C) that satisfies this equation. The calculations can be done conveniently using a spreadsheet. Let us first estimate the solution by neglecting all terms of second-order and higher in T:

$$0.03554T - 12.16 = 0 \Longrightarrow T \approx 342^\circ\text{C}$$

We will use this estimate as the first guess in the spreadsheet solution. In one cell (Cell A1 in this illustration) we insert the initial guess for T (342°C), and in the next cell (B1) we insert the formula for the fourth-order polynomial on the left-hand side of the equation to be solved:

Cell A1: 342

Cell B1: = 1.672e−12 * A1^4 − 0.8759e−8 * A1^3 + 1.959e−5 * A1^2 + 0.3554 * A1 − 12.16

(In some spreadsheet programs, the exponentiation function would be ** instead of ^.) The two cells of the spreadsheet would then display the following values:

	A	**B**
1	342	1.9585

Our goal is to find the value in Cell A1 that drives the value in Cell B1 to zero. We could perform the trial-and-error search manually, but if the spreadsheet program has a goalseek tool (most programs do), we would select it and use it to perform the search automatically (Set Cell B1 to 0 by varying Cell A1). Either way, at the end of the search the two cells would display values close to those shown below:

	A	**B**
1	299.0654	3.791E − 06

The solution is therefore $\boxed{T = 299^\circ\text{C}}$. The heat transferred from the specified quantity of gas as it cools from 500°C to 299°C goes to convert the specified amount of feedwater into steam.

8.3e Numerical Integration of Tabulated Heat Capacities

You have now seen two ways to evaluate an expression of the type

$$\int_{T_1}^{T_2} C_p(T)\, dT$$

If a functional relation for $C_p(T)$ is available, such as one of the polynomials of Table B.2, the integration can be carried out analytically; and if tabulated specific enthalpies are available for the substance being heated or cooled, a simple subtraction replaces the integration.

Suppose, however, that the only information you have about C_p is its value at a series of temperatures that span the range from T_1 to T_2. The question is how to estimate the value of the integral from these data.

One way would of course be to plot C_p versus T, draw a curve by visual inspection through the points at which C_p is known, and estimate the integral graphically as the area under the curve from T_1 to T_2. This is a cumbersome procedure, however, even if you have access to a *planimeter,* a device that can calculate the area under a traced-out curve.

A better solution is to use one of the many existing **quadrature formulas**—algebraic expressions that provide estimates of the integrals of tabulated data. Several such formulas are presented and illustrated in Appendix A.3; the use of one of them, **Simpson's rule,** is required for the integration of heat capacity data in several problems at the end of this chapter.

8.4 PHASE CHANGE OPERATIONS

Consider liquid water and water vapor, each at 100°C and 1 atm. Which would you expect to be greater, $\hat{U}_{\text{liquid}}$ or $\hat{U}_{\text{vapor}}$? (Recall that $\hat{U}$ is related among other things to the energy of motion of the individual molecules at the specified condition.)

If you said $\hat{U}_{\text{vapor}}$, you would be correct. One way to think of it is that the molecules of a vapor, which can move around relatively freely, are much more energetic than the densely packed molecules of a liquid at the same T and P. Also think about the fact that liquid molecules are held in close proximity to each other by attractive forces between the molecules. The energy required to overcome these forces when a liquid is vaporized is reflected in the higher internal energy of the vapor molecules.

Inspection of Table B.5 reveals how dramatic the difference between $\hat{U}_{\text{liquid}}$ and $\hat{U}_{\text{vapor}}$ can be. For water at 100°C and 1 atm, $\hat{U}_\ell = 419$ kJ/kg and $\hat{U}_\text{v} = 2507$ kJ/kg. The difference in specific enthalpy ($= \hat{U} + P\hat{V}$) is even greater, owing to the much greater specific volume of the vapor: at the same temperature and pressure, $\hat{H}_\ell = 419.1$ kJ/kg and $\hat{H}_\text{v} = 2676$ kJ/kg.

Phase changes such as melting and evaporation are usually accompanied by large changes in internal energy and enthalpy, as in the example just given. Heat transfer requirements in phase-change operations consequently tend to be substantial, since $Q \approx \Delta U$ (closed constant-volume system) or $\dot{Q} \approx \Delta \dot{H}$ (open system). The paragraphs that follow outline procedures for setting up and solving energy balances on such operations. The discussion will be limited to phase changes between liquid and vapor (evaporation, condensation) and solid and liquid (melting, freezing); however, the methods may be extended directly to other phase changes, such as sublimation (conversion from solid to vapor) and conversion from one solid phase to another.

8.4a Latent Heats

The specific enthalpy change associated with the transition of a substance from one phase to another at constant temperature and pressure is known as the **latent heat** of the phase change (as distinguished from *sensible heat*, which is associated with temperature changes for a single-phase system). For example, the specific enthalpy change $\Delta\hat{H}$ for the transition of liquid water to steam at 100°C and 1 atm, which equals 40.6 kJ/mol, is by definition the **latent heat of vaporization** (or simply the **heat of vaporization**) of water at this temperature and pressure.

Since condensation is the reverse of vaporization and enthalpy is a state property, the heat of condensation must be the negative of the heat of vaporization. Thus, the heat of condensation of water at 100°C and 1 atm must be −40.6 kJ/mol. Similarly, the heat of solidification is the negative of the heat of fusion at the same temperature and pressure.

Latent heats for the two most commonly encountered phase changes are defined as follows:

1. ***Heat of fusion*** (or heat of melting). $\Delta\hat{H}_\text{m}(T, P)$ is the specific enthalpy difference between the solid and liquid forms of a species at T and P.[7]
2. ***Heat of vaporization.*** $\Delta\hat{H}_\text{v}(T, P)$ is the specific enthalpy difference between the liquid and vapor forms of a species at T and P.

Tabulated values of these two latent heats, such as those in Table B.1 and on pp. 2-151 through 2-160 of *Perry's Chemical Engineers' Handbook,* (see footnote 5) usually apply to a substance at its normal melting or boiling point—that is, at a pressure of 1 atm. These quantities are referred to as *standard* heats of fusion and vaporization.

The latent heat of a phase change may vary considerably with the temperature at which the change occurs but hardly varies at all with the pressure at the transition point. For example, the heat of vaporization of water at 25°C is 2442.5 J/g at $P = 23.78$ mm Hg and 2442.3 J/g at $P = 760$ mm Hg.[8] *When using a tabulated latent heat, you must therefore be sure that the phase*

---

[7] We call it $\Delta\hat{H}_\text{m}$ rather than $\Delta\hat{H}_\text{f}$ because the latter symbol is used for the *heat of formation,* a quantity defined in Chapter 9.

[8] In a system containing only pure water at 25°C, evaporation can only occur at $P = p_w^*(25°\text{C}) = 23.78$ mm Hg, but if the system contains several species evaporation can occur over a range of pressures.

change in question takes place at the temperature for which the tabulated value is reported, but you may ignore moderate variations in pressure.

EXAMPLE 8.4-1 Heat of Vaporization

At what rate in kilowatts must heat be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 g/min of saturated methanol vapor?

SOLUTION From Table B.1, $\Delta\hat{H}_v = 35.3$ kJ/mol at $T_{bp} = 64.7°C$. The energy balance with potential and kinetic energy changes neglected is

$$\dot{Q} = \Delta\dot{H} = \dot{n}\,\Delta\hat{H}_v$$

$$\Downarrow$$

$$\dot{Q} = \frac{1500 \text{ g CH}_3\text{OH}}{\text{min}} \left| \frac{1 \text{ mol}}{32.0 \text{ g CH}_3\text{OH}} \right| \frac{35.3 \text{ kJ}}{\text{mol}} \left| \frac{1 \text{ min}}{60 \text{ s}} \right| \frac{1 \text{ kW}}{1 \text{ kJ/s}} = \boxed{27.6 \text{ kW}}$$

Phase changes often occur at temperatures other than the temperature for which the latent heat is tabulated. When faced with this situation, you must select a hypothetical process path that permits the available data to be used.

Suppose, for example, that a substance is to be vaporized isothermally at 130°C, but the only available value of the heat of vaporization is at 80°C. A process path from the liquid at 130°C to the vapor at the same temperature must then be chosen that includes an isothermal vaporization step at 80°C: specifically, cool the liquid from 130°C to 80°C, vaporize the liquid at 80°C, and then heat the vapor back to 130°C. Summing the changes in enthalpy for each of these steps yields the change in enthalpy for the given process. (By definition, the calculated value is the latent heat of vaporization at 130°C.)

EXAMPLE 8.4-2 Vaporization and Heating

One hundred g-moles per hour of liquid *n*-hexane at 25°C and 7 bar is vaporized and heated to 300°C at constant pressure. Neglecting the effect of pressure on enthalpy, estimate the rate at which heat must be supplied.

SOLUTION An energy balance yields

$$\dot{Q} = \Delta\dot{H} \qquad (\dot{W}_s = \Delta\dot{E}_p = 0, \Delta\dot{E}_k \approx 0)$$

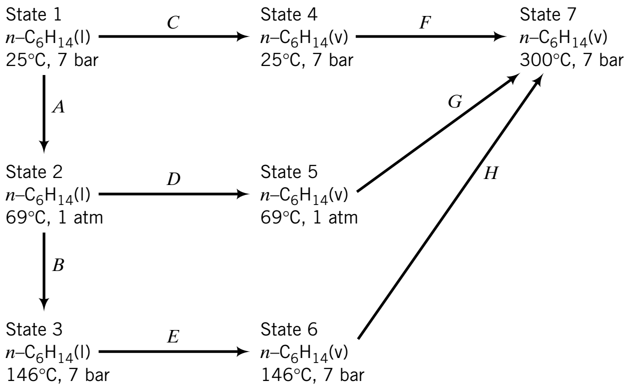
Therefore an evaluation of $\Delta\dot{H}$ will yield the desired value of $\dot{Q}$.

From Figure 6.1-4, the temperature at which the vapor pressure of *n*-hexane is 7 bar (104 psia) is approximately 295°F (146°C), and this is therefore the temperature at which the vaporization actually occurs. However, Table B.1 lists a value of $\Delta\hat{H}_v$ at the normal boiling point of *n*-hexane,

$$\Delta\hat{H}_v = 28.85 \text{ kJ/mol at } 69°\text{C}$$

We must therefore find a path that takes hexane from a liquid to a vapor at 69°C, rather than at the true vaporization temperature of 146°C.

As noted previously, the change in enthalpy associated with a process may be determined from any convenient path as long as the initial and final points of the chosen path correspond to those of the process. The diagram shown on the following page illustrates several possible paths from liquid hexane at 25°C to hexane vapor at 300°C.



If we knew $\Delta\hat{H}_v$ at 146°C, we would follow path *ABEH* (the true process path) to evaluate the overall $\Delta\hat{H}$ for the process, or if we knew $\Delta\hat{H}_v$ at 25°C, we would follow path *CF*, which would require only two calculations. Since we have $\Delta\hat{H}_v$ at 69°C, we must follow path *ADG*, which includes vaporization at that temperature.

$$\begin{tikzcd}
n\text{-C}_6\text{H}_{14}(\text{l, }25^\circ\text{C, 7 bar}) \arrow[r, "\Delta\hat{H}_A"] & n\text{-C}_6\text{H}_{14}(\text{l, }69^\circ\text{C, 1 atm}) \arrow[d, "\Delta\hat{H}_D"] & \\
& n\text{-C}_6\text{H}_{14}(\text{v, }69^\circ\text{C, 1 atm}) \arrow[r, "\Delta\hat{H}_G"] & n\text{-C}_6\text{H}_{14}(\text{v, }300^\circ\text{C, 7 bar})
\end{tikzcd}$$

$$\Delta\hat{H}_A = \hat{V}\,\Delta P + \int_{25^\circ\text{C}}^{69^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_{14}(\text{l})}\,dT \quad \text{(from Equation 8.3-10b)}$$

$$\Bigg\Downarrow \begin{array}{l} \text{Table B.1} \Longrightarrow \text{SG} = 0.659 \Longrightarrow \rho = 0.659\ \text{kg/L} \\ \text{Table B.2} \Longrightarrow C_p = 0.2163\ \text{kJ/(mol·°C)} \\ 1\ \text{atm} = 1.013\ \text{bar} \end{array}$$

$$\Delta\hat{H}_A = \begin{array}{c|c|c|c} 1\ \text{L} & (1.013-7.0)\ \text{bar} & 86.17\ \text{kg} & 0.008314\ \text{kJ/(mol·K)} \\ \hline 0.659\ \text{kg} & & 1000\ \text{mol} & 0.08314\ \text{L·bar/(mol·K)} \end{array}$$

$$+ \begin{array}{c|c} 0.2163\ \text{kJ} & (69-25)^\circ\text{C} \\ \hline \text{mol·°C} & \end{array} = (-0.0782 + 9.517)\ \text{kJ/mol} = 9.44\ \text{kJ/mol}$$

$$\Delta\hat{H}_D = (\Delta\hat{H}_v)_{\text{C}_6\text{H}_{14}}(69^\circ\text{C, 1 atm}) = 28.85\ \text{kJ/kg}$$

$$\Delta\hat{H}_G = \int_{69^\circ\text{C}}^{300^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_{14}(\text{v})}\,dT \qquad \text{(from Equation 8.3-10a)}$$

$$\Big\Downarrow C_p[\text{kJ/(mol·°C)}] = 0.13744 + 40.85 \times 10^{-5}T - 23.92 \times 10^{-8}T^2 + 57.66 \times 10^{-12}T^3$$

$$\Delta\hat{H}_G = 47.1\ \text{kJ/mol}$$

For the overall process

$$\dot{Q} = \Delta\dot{H} = \dot{n}(\text{mol/h})\Delta\hat{H}(\text{kJ/mol})$$

$$\Big\Downarrow \Delta\hat{H} = \Delta\hat{H}_A + \Delta\hat{H}_D + \Delta\hat{H}_G = 85.5\ \text{kJ/mol}$$

$$\dot{Q} = \begin{array}{c|c|c|c} 100\ \text{mol} & 85.5\ \text{kJ} & 1\ \text{h} & 1\ \text{kW} \\ \hline \text{h} & \text{mol} & 3600\ \text{s} & 1\ \text{kJ/s} \end{array} = \boxed{2.38\ \text{kW}}$$

Notice that the pressure change term in the first step ($\hat{V}\,\Delta P = -0.0782$ kJ/mol) accounts for less than 0.1% of the overall process enthalpy change. We will generally neglect the effects of pressure changes on $\Delta\hat{H}$ unless ΔP is on the order of 50 atm or more.

If a phase change takes place in a closed system, you must evaluate $\Delta\hat{U} = \Delta\hat{H} - \Delta(P\hat{V})$ for the phase change to substitute into the energy balance equation. For phase changes such as fusion, which involve only liquids and solids, changes in $P\hat{V}$ are generally negligible compared to changes in $\hat{H}$, so that

$$\Delta \hat{U}_{\text{m}} \approx \Delta \hat{H}_{\text{m}} \tag{8.4-1}$$

For vaporization, $P\hat{V}$ for the vapor (which equals RT if ideal gas behavior may be assumed) is normally orders of magnitude greater than $P\hat{V}$ for the liquid, so that $\Delta(PV) \approx RT$, and

$$\Delta \hat{U}_{\text{v}} \approx \Delta \hat{H}_{\text{v}} - RT \tag{8.4-2}$$

TEST YOURSELF (Answers, p. 660)

1. If you are given a value of a heat of vaporization at 100°C and 1 atm, would you be confident about using it to estimate the enthalpy change for a vaporization at 100°C and 2 atm? What about 200°C and 1 atm?
2. The enthalpies of a pure liquid and its vapor at 75°C and 1 atm are 100 J/mol and 1000 J/mol, respectively, both measured relative to the liquid at 0°C.
   (a) What is the enthalpy of the liquid at 0°C?
   (b) What is the heat of vaporization at 75°C?
   (c) Suppose you have heat capacity data for both the liquid and its vapor. What path would you follow to calculate the enthalpy change associated with 100 mol of the vapor at 400°C being cooled and condensed to form a liquid at 25°C?
3. The heat of fusion of zinc chloride at 556 K is $\Delta \hat{H}_{\text{m}} = 5500$ cal/mol, and the heat of vaporization of this substance at 1000 K is $\Delta \hat{H}_{\text{v}} = 28{,}710$ cal/mol. Estimate $\Delta \hat{U}_{\text{m}}(556\text{ K})$ and $\Delta \hat{U}_{\text{v}}(1000\text{ K})$ for ZnCl_2. [Say $R = 2$ cal/(mol·K).]

8.4b Estimation and Correlation of Latent Heats

Reid, Prausnitz, and Poling (see footnote 4) review procedures for estimating latent heats of vaporization, fusion, and sublimation. Several of the methods given in this reference are summarized below.

A simple formula for estimating a standard heat of vaporization ($\Delta \hat{H}_{\text{v}}$ at the normal boiling point) is **Trouton's rule**:

$$\Delta \hat{H}_{\text{v}}(\text{kJ/mol}) \begin{array}{ll} \approx 0.088 T_{\text{b}}(\text{K}) & \text{(nonpolar liquids)} \\ \approx 0.109 T_{\text{b}}(\text{K}) & \text{(water, low molecular weight alcohols)} \end{array} \tag{8.4-3}$$

where T_{b} is the normal boiling point of the liquid. Trouton's rule provides an estimate of $\Delta \hat{H}_{\text{v}}$ accurate to within 30%. Another formula that provides roughly 2% accuracy is **Chen's equation**:

$$\Delta \hat{H}_{\text{v}}(\text{kJ/mol}) = \frac{T_{\text{b}}[0.0331(T_{\text{b}}/T_{\text{c}}) - 0.0327 + 0.0297 \log_{10} P_{\text{c}}]}{1.07 - (T_{\text{b}}/T_{\text{c}})} \tag{8.4-4}$$

where T_{b} and T_{c} are the normal boiling point and critical temperature in kelvin and P_{c} is the critical pressure in atmospheres.

A formula for approximating a standard heat of fusion is

$$\Delta \hat{H}_{\text{m}}(\text{kJ/mol}) \begin{array}{ll} \approx 0.0092 T_{\text{m}}(\text{K}) & \text{(metallic elements)} \\ \approx 0.0025 T_{\text{m}}(\text{K}) & \text{(inorganic compounds)} \\ \approx 0.050 T_{\text{m}}(\text{K}) & \text{(organic compounds)} \end{array} \tag{8.4-5}$$

Latent heats of vaporization may be estimated from vapor pressure data by using the Clausius–Clapeyron equation, which was discussed in Section 6.1b.

$$\ln p^* = -\frac{\Delta \hat{H}_{\text{v}}}{RT} + B \tag{8.4-6}$$

Provided that $\Delta \hat{H}_{\text{v}}$ is constant over the range of temperatures encompassed by the vapor pressure data, the latent heat of vaporization may be determined from a plot of $\ln p^*$ versus $1/T$. (See Example 6.1-1.)

In many cases the latent heat of vaporization varies considerably with temperature, invalidating Equation 8.4-6. It is then necessary to use the **Clapeyron equation,** from which Equation

8.4-6 was derived. From Equation 6.1-2,

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \tag{8.4-7}$$

The heat of vaporization at a temperature T may be estimated from vapor pressure data by plotting $\ln p^*$ versus $1/T$, determining $[d(\ln p^*)/d(1/T)]$ at the temperature of interest as the slope of the tangent to the curve, and solving Equation 8.4-7 for $\Delta\hat{H}_v$. The slope may be determined graphically or by any of several numerical differentiation techniques outlined in texts on numerical analysis.

A procedure for calculating the latent heat of vaporization at one temperature from a known value at any other temperature was presented in Section 8.4a. The technique outlined is rigorous but time-consuming, and it requires heat capacity data that might not be available for the substance of interest. A useful approximation for estimating $\Delta\hat{H}_v$ at T_2 from a known value at T_1 is **Watson's correlation**:

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38} \tag{8.4-8}$$

where T_c is the critical temperature of the substance.

EXAMPLE 8.4-3 *Estimation of a Heat of Vaporization*

The normal boiling point of methanol is 337.9 K, and the critical temperature of this substance is 513.2 K. Estimate the heat of vaporization of methanol at 200°C.

SOLUTION We first use Trouton's rule to estimate $\Delta\hat{H}_v$ at the normal boiling point, and then Watson's correlation to estimate $\Delta\hat{H}_v$(473 K) from $\Delta\hat{H}_v$(337.9 K).

Trouton's Rule $\Delta\hat{H}_v(337.9\text{ K}) = (0.109)(337.9) = 36.8\text{ kJ/mol}$

(The measured value is 35.3 kJ/mol. Chen's equation yields 37.2 kJ/mol, so in this unusual case Trouton's rule provides the better estimate.)

Watson's Correlation

Using the value of $\Delta\hat{H}_v$ estimated by Trouton's rule

$$\Delta\hat{H}_v(473\text{ K}) = 36.8\left(\frac{513.2 - 473}{513.2 - 337.9}\right)^{0.38} = \boxed{21.0\text{ kJ/mol}}$$

The measured value is 19.8 kJ/mol.

TEST YOURSELF (Answers, p. 660)

How would you estimate $\Delta\hat{H}_v$ for a pure hydrocarbon at its normal boiling point under each of the following conditions?

1. You know only the normal boiling point.
2. You know the normal boiling point and the critical constants.
3. You have vapor pressure data over a range that encompasses $p^* = 1$ atm, and a semilog plot of p^* versus $1/T$ is a straight line.
4. Repeat 3, only suppose the plot is curved.
5. You know $\Delta\hat{H}_v$ at a temperature other than T_{bp} and do not know the heat capacities of the substance in its gaseous and liquid forms.
6. Repeat 5, only suppose that you have the heat capacity data.

8.4c Energy Balances on Processes Involving Phase Changes

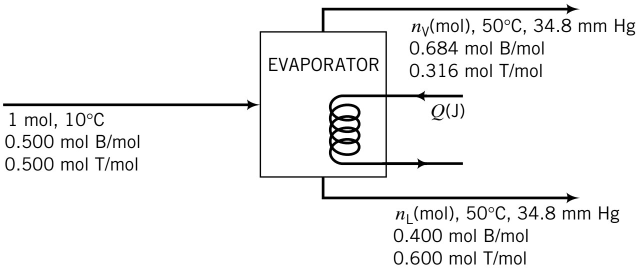
When writing an energy balance on a process in which a component exists in two phases, you must choose a reference state for that component by specifying both a phase and a temperature and calculate the specific enthalpy of the component in all process streams relative to this state. If the substance is a liquid at its reference state and a vapor in a process stream, $\hat{H}$ may be calculated as outlined in Section 8.4a: that is, bring the liquid from the reference temperature to a point at which $\Delta\hat{H}_v$ is known, vaporize the liquid, bring the vapor to the process stream temperature, and sum the individual enthalpy changes for the three steps.

EXAMPLE 8.4-4 *Partial Vaporization of a Mixture*

Equipment Encyclopedia
evaporator

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?

SOLUTION ***Basis: 1 mol Feed***



We start with a degree-of-freedom analysis:

$$\begin{array}{l} 3 \text{ unknown variables } (n_V, n_L, Q) \\ -2 \text{ material balances} \\ \underline{-1 \text{ energy balance}} \\ = 0 \text{ degrees of freedom} \end{array}$$

We could count each specific enthalpy to be determined as an unknown variable, but then we would also count the equations for each of them in terms of heat capacities and latent heats, leaving the number of degrees of freedom unchanged.

We next determine n_V and n_L from material balances, and then Q from an energy balance.

Total Mass Balance: $1.00 \text{ mol} = n_V + n_L$

Benzene Balance: $0.500 \text{ mol} = 0.684 n_V + 0.400\, n_L$

$$\Longrightarrow \quad n_V = 0.352 \text{ mol}, \quad n_L = 0.648 \text{ mol}$$

The energy balance for this process has the form $Q = \Delta H$. An enthalpy table for the process appears as follows:

References: B(l, 10°C, 1 atm), T(l, 10°C, 1 atm)

Substance	n_{in} mol	$\hat{H}_{\text{in}}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{\text{out}}$ (kJ/mol)
B(l)	0.500	0	0.259	$\hat{H}_1$
T(l)	0.500	0	0.389	$\hat{H}_2$
B(v)	—	—	0.241	$\hat{H}_3$
T(v)	—	—	0.111	$\hat{H}_4$

The values of n_{out} were determined from the known mole fractions of benzene and toluene in the outlet streams and the calculated values of n_V and n_L. We do not know the feed-stream pressure and so we assume that ΔH for the change from 1 atm to P_{feed} is negligible, and since the process is not running at an unusually low temperature or high pressure, we neglect the effects of pressure on enthalpy in the calculations of $\hat{H}_1$ through $\hat{H}_4$. The heat capacity and latent heat data needed to calculate the outlet enthalpies are obtained from Tables B.1 and B.2.

The formulas and values of the unknown specific enthalpies are given below. Convince yourself that the formulas represent $\Delta\hat{H}$ for the transitions from the reference states to the process states.

$$\hat{H}_1 = \int_{10^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{l})}\, dT = 5.332 \text{ kJ/mol}$$

$$\hat{H}_2 = \int_{10^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{l})}\, dT = 6.340 \text{ kJ/mol}$$

$$\hat{H}_3 = \int_{10^\circ\text{C}}^{80.1^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{l})}\, dT + (\Delta\hat{H}_\text{v})_{\text{C}_6\text{H}_6}(80.1^\circ\text{C}) + \int_{80.1^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_6\text{H}_6(\text{v})}\, dT$$
$$= 37.52 \text{ kJ/mol}$$

$$\hat{H}_4 = \int_{10^\circ\text{C}}^{110.62^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{l})}\, dT + (\Delta\hat{H}_\text{v})_{\text{C}_7\text{H}_8}(110.62^\circ\text{C}) + \int_{110.62^\circ\text{C}}^{50^\circ\text{C}} (C_p)_{\text{C}_7\text{H}_8(\text{v})}\, dT$$
$$= 42.93 \text{ kJ/mol}$$

The energy balance is

$$Q = \Delta H = \sum_{\text{out}} n_i\hat{H}_i - \sum_{\text{in}} n_i\hat{H}_i \Longrightarrow \boxed{Q = 17.7 \text{ kJ}}$$

CREATIVITY EXERCISE

A gas emerges from a stack at 1200°C. Rather than being released directly to the atmosphere, it can be passed through one or several heat exchangers, and the heat it loses can be put to use in a variety of ways. Think of as many uses of this heat as you can. (*Example:* During the winter, pass the gas through a series of radiators, thereby getting free heating.)

8.4d Psychrometric Charts

On a **psychrometric chart** (or **humidity chart**) several properties of a gas–vapor mixture are cross-plotted, providing a concise compilation of a large quantity of physical property data. The most common of these charts—that for the air-water system at 1 atm—is used extensively in the analysis of humidification, drying, and air-conditioning processes.

A psychrometric chart in SI units for the air–water system at 1 atm is shown in Figure 8.4-1, and a second chart in American engineering units is shown in Figure 8.4-2. Charts that cover wider temperature ranges are given on pp. 12-4 through 12-7 of *Perry's Chemical Engineers' Handbook* (see footnote 5).

The following paragraphs define and describe the different properties of humid air at 1 atm that appear on the psychrometric chart. Once you know the values of any two of these properties, you can use the chart to determine the values of the others. We will use the abbreviation DA for dry air.

- ***Dry-bulb temperature,*** T—the abscissa of the chart. This is the air temperature as measured by a thermometer, thermocouple, or other conventional temperature-measuring instrument.
- ***Absolute humidity,*** h_a [kg H_2O(v)/kg DA] (called **moisture content** on Figure 8.4-1)—the ordinate of the chart.

  This ratio can easily be calculated from or converted to the mass fraction of water. If, for example, the absolute humidity is 0.0150 kg H_2O/kg DA, then for every kilogram of dry air there is 0.015 kg of water vapor, for a total of 1.015 kg. The mass fraction of water is (0.0150 kg H_2O)/(1.015 kg humid air) = 0.0148 kg H_2O/kg.

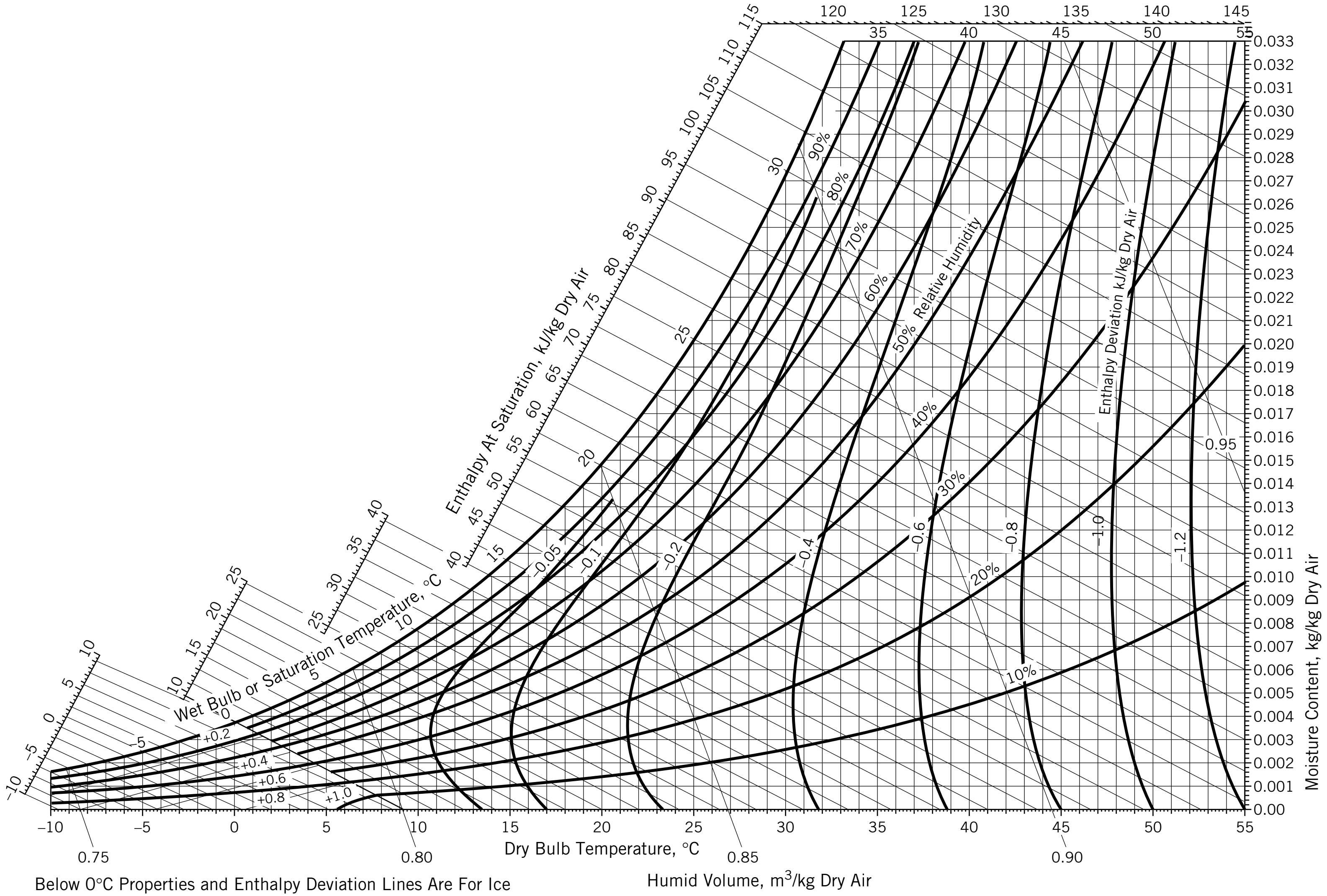


Figure 8.4-1 Psychrometric chart—SI units. Reference states: H_2O (L, 0°C, 1 atm), dry air (0°C, 1 atm). (Reprinted with permission of Carrier Corporation.)

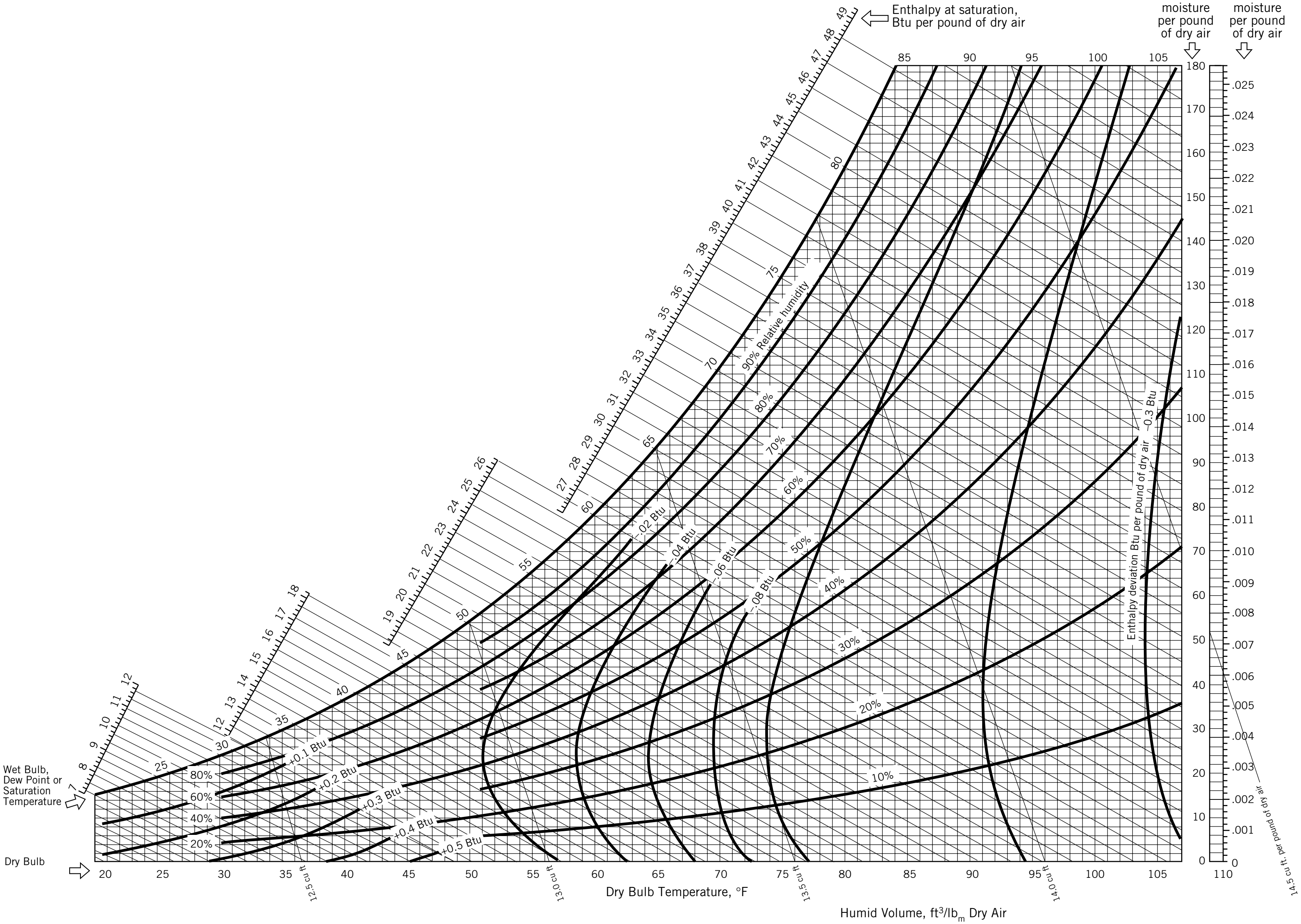


Figure 8.4-2 Psychrometric chart—American Engineering units. Reference states: H_2O (L, 32°F, 1 atm), dry air (0°F, 1 atm). (Reprinted with permission of Carrier Corporation.)

- ***Relative humidity***, $h_r = [100 \times p_{H_2O}/p^*_{H_2O}(T)]$.

  Curves on the psychrometric chart correspond to specified values of h_r (100%, 90%, 80%, etc.). The curve that forms the left boundary of the chart is the **100% relative humidity curve**, also known as the **saturation curve.**
- ***Dew point,*** T_{dp}—the temperature at which humid air becomes saturated if it is cooled at constant pressure.

  The dew point of humid air at a given point on the psychrometric chart can easily be determined. For example, locate the point on Figure 8.4-1 corresponding to air at 29°C and 20% relative humidity. Cooling this air at constant pressure ($= 1$ atm) corresponds to moving horizontally (at constant absolute humidity) to the saturation curve. T_{dp} is the temperature at the intersection, or 4°C. (Verify this statement.)
- ***Humid volume,*** $\hat{V}_H$ (m^3/kg DA).

  The humid volume is the volume occupied by 1 kg of dry air plus the water vapor that accompanies it. Lines of constant humid volume on the psychrometric chart are steep and have negative slopes. On Figure 8.4-1, humid volume lines are shown corresponding to 0.75, 0.80, 0.85, and 0.90 m^3/kg dry air.

  To determine the volume of a given mass of wet air using the psychrometric chart, you must first determine the corresponding mass of dry air from the absolute humidity, then multiply this mass by $\hat{V}_H$. Suppose, for example, you wish to know the volume occupied by 150 kg of humid air at $T = 30°\text{C}$ and $h_r = 30\%$. From Figure 8.4-1, $h_a = 0.0080$ kg $H_2O(v)$/kg DA and $\hat{V}_H \approx 0.87$ m^3/kg DA. The volume may then be calculated as

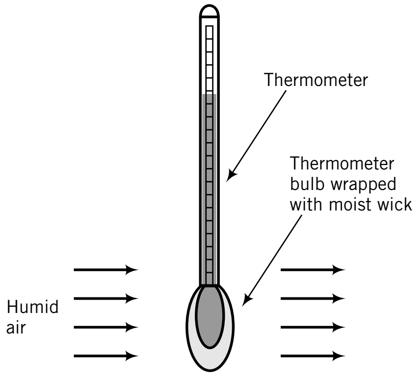
$$V = \frac{150 \text{ kg humid air}}{} \left| \frac{1.00 \text{ kg DA}}{1.008 \text{ kg humid air}} \right| \frac{0.87 \text{ m}^3}{\text{kg DA}} = 129 \text{ m}^3$$

  (In this calculation, we used the fact that if the absolute humidity is 0.008 kg H_2O/kg DA, then 1 kg DA is accompanied by 0.008 kg water for a total of 1.008 kg humid air.)

Equipment Encyclopedia
thermometer

- ***Wet-bulb temperature,*** T_{wb}.

  This quantity is best defined in terms of how it is measured. A porous material like cloth or cotton is soaked in water and wrapped around the bulb of a thermometer to form a *wick*, and the thermometer is placed in a stream of flowing air, as in the figure shown below.[9] Evaporation of water from the wick into the flowing air is accompanied by a transfer of heat from the bulb, which in turn causes a drop in the bulb temperature and hence in the thermometer reading.[10] Provided that the wick remains moist, the bulb temperature falls to a certain value and remains there. The final temperature reading is the wet-bulb temperature of the air flowing past the wick.



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[9] Alternatively, the thermometer may be mounted in a *sling psychrometer* and whirled around in stationary air.

[10] Think about what happens when you step out of a shower or swimming pool. Water evaporates, your skin temperature drops, and you feel cold, even if you felt perfectly comfortable when you were dry.

The wet-bulb temperature of humid air depends on both the dry-bulb temperature and the moisture content of the air. If the air is saturated (100% relative humidity), no water evaporates from the wick, and the wet-bulb and dry-bulb temperatures are the same. The lower the humidity, the greater the difference between the two temperatures.

The humid air conditions that correspond to a given wet-bulb temperature fall on a straight line on the psychrometric chart, called a **constant wet-bulb temperature line.** The constant wet-bulb temperature lines for air–water at 1 atm appear on Figures 8.4-1 and 8.4-2 as lines with negative slopes extending beyond the saturation curve that are less steep than the lines of constant humid volume. The value of T_{wb} corresponding to a given line can be read at the intersection of the line with the saturation curve.

For example, suppose you wish to determine the wet-bulb temperature of air at 30°C (dry bulb) with a relative humidity of 30%. Locate the point on Figure 8.4-1 at the intersection of the vertical line corresponding to $T = 30°\text{C}$ and the curve corresponding to $h_r = 30\%$. The diagonal line through the point is the constant wet-bulb temperature line for air at the given condition. Follow that line upward to the left until you reach the saturation curve. The temperature value you read on the curve (or vertically down from it on the abscissa) is the wet-bulb temperature of the air. You should get a value of 18°C. This means that if you wrap a wet wick around a thermometer bulb and blow air with $T = 30°\text{C}$ and $h_r = 30\%$ past the bulb, the thermometer reading will drop and eventually stabilize at 18°C.

- ***Specific enthalpy of saturated air***

The diagonal scale above the saturation curve on the psychrometric chart shows the enthalpy of a unit mass (1 kg or 1 lb_m) of dry air plus the water vapor it contains at saturation. The reference states are liquid water at 1 atm and 0°C (32°F) and dry air at 1 atm and 0°C (Figure 8.4-1) or 0°F (Figure 8.4-2). To determine the enthalpy from the chart, follow the constant wet-bulb temperature line from the saturation curve at the desired temperature to the enthalpy scale.

For example, saturated air at 25°C and 1 atm—which has an absolute humidity $h_a = 0.0202$ kg H_2O/kg DA—has a specific enthalpy of 76.5 kJ/kg DA. (Verify these values of both h_a and $\hat{H}$ on Figure 8.4-1.) The enthalpy is the sum of the enthalpy changes for 1.00 kg dry air and 0.0202 kg water going from their reference conditions to 25°C. The computation shown below uses heat capacity data from Table B.2 for air and data from the steam tables (Table B.5) for water.

$$1.00 \text{ kg DA}(0°\text{C}) \rightarrow 1 \text{ kg DA}(25°\text{C})$$

$$\Downarrow$$

$$\Delta H_{\text{air}} = (1.00 \text{ kg DA})\left(\frac{1 \text{ kmol}}{29.0 \text{ kg}}\right)\left[\int_0^{25} C_{\text{p,air}}(T)\, dT\right]\left(\frac{\text{kJ}}{\text{kmol}}\right) = 25.1 \text{ kJ}$$

$$0.0202 \text{ kg H}_2\text{O(l, 0°C)} \rightarrow 0.0202 \text{ kg H}_2\text{O(v, 25°C)}$$

$$\Downarrow$$

$$\Delta H_{\text{water}} = (0.0202 \text{ kg})[\hat{H}_{\text{H}_2\text{O(v,25°C)}} - \hat{H}_{\text{H}_2\text{O(l,0°C)}}]\left(\frac{\text{kJ}}{\text{kg}}\right) = 51.4 \text{ kJ}$$

$$\hat{H} = \frac{(\Delta H_{\text{air}} + \Delta H_{\text{water}})(\text{kJ})}{1.00 \text{ kg DA}} = \frac{(25.1 + 51.4) \text{ kJ}}{1.00 \text{ kg DA}} = 76.5 \text{ kJ/kg DA}$$

- ***Enthalpy deviation***

The remaining curves on the psychrometric chart are almost vertical and convex to the left, with labeled values (on Figure 8.4-1) of −0.05, −0.1, −0.2, and so on. (The units of these numbers are kJ/kg DA). These curves are used to determine the enthalpy of humid air that is not saturated. The procedure is as follows: (a) locate the point on the chart corresponding to air at its specified condition; (b) interpolate to estimate the enthalpy deviation at this point;

(c) follow the constant wet-bulb temperature line to the enthalpy scale above the saturation curve, read the value on that scale, and add the enthalpy deviation to it.

For example, air at 35°C and 10% relative humidity has an enthalpy deviation of about −0.52 kJ/kg DA. The specific enthalpy of saturated air at the same wet-bulb temperature is 45.0 kJ/kg DA. (Verify both of these numbers.) The specific enthalpy of the humid air at the given condition is therefore (45.0 − 0.52) kJ/kg DA = 44.5 kJ/kg DA.

The basis for the construction of the psychrometric chart is the Gibbs phase rule (Section 6.3a), which states that specifying a certain number of the intensive variables (temperature, pressure, specific volume, specific enthalpy, component mass or mole fractions, etc.) of a system automatically fixes the value of the remaining intensive variables. Humid air contains one phase and two components,[11] so that from Equation 6.2-1 the number of degrees of freedom is

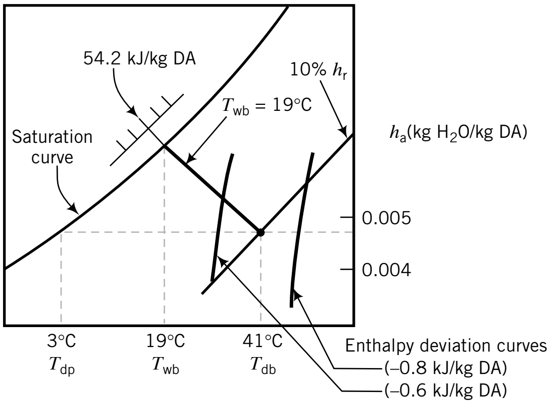
$$F = 2 + 2 - 1 = 3$$

Specifying three intensive variables therefore fixes all other system properties. If the system pressure is fixed at 1 atm, then all other properties may be plotted on a two-dimensional plot, such as those shown in Figures 8.4-1 and 8.4-2.

EXAMPLE 8.4-5 The Psychrometric Chart

Use the psychrometric chart to estimate (1) the absolute humidity, wet-bulb temperature, humid volume, dew point, and specific enthalpy of humid air at 41°C and 10% relative humidity, and (2) the amount of water in 150 m^3 of air at these conditions.

SOLUTION Following is a sketch of the psychrometric chart (Figure 8.4-1) showing the given state of the air:



1. Reading from the chart,

$$\boxed{\begin{aligned} &h_a \approx 0.0048 \text{ kg H}_2\text{O/kg DA} \\ &T_{wb} = 19°\text{C} \\ &\hat{V}(\text{m}^3/\text{kg DA}) \approx 0.897 \text{ (curve not shown)} \end{aligned}}$$

The dew point is the temperature at which the air with the given water content would be saturated at the same total pressure (1 atm) and is therefore located at the intersection of the horizontal constant absolute humidity line ($h_a \equiv 0.0048$) and the saturation curve, or

$$\boxed{T_{dp} = 3°\text{C}}$$

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[11] Since the components of dry air do not condense and are present in fixed proportion, dry air may be considered a single species (designated DA) in humidity calculations.

The specific enthalpy of saturated air at $T_{\text{wb}} = 19°\text{C}$ is 54.2 kJ/kg DA. Since the point corresponding to 41°C and 10% relative humidity falls roughly midway between the enthalpy deviation curves corresponding to −0.6 kJ/kg and −0.8 kJ/kg, we may calculate $\hat{H}$ as

$$\hat{H} = (54.2 - 0.7)\ \text{kJ/kg DA}$$

$$\Downarrow$$

$$\boxed{\hat{H} = 53.5\ \text{kJ/kg DA}}$$

2. ***Moles of humid air.*** From Figure 8.4-1, the humid volume of the air is 0.897 m^3/kg DA. We therefore calculate

$$\begin{array}{c|c|c} 150\ \text{m}^3 & 1.00\ \text{kg DA} & 0.0048\ \text{kg H}_2\text{O} \\ \hline & 0.897\ \text{m}^3 & 1.00\ \text{kg DA} \end{array} = \boxed{0.803\ \text{kg H}_2\text{O}}$$

The psychrometric chart can be used to simplify the solution of material and energy balance problems for constant-pressure air–water systems, at the expense of some precision. Note the following points:

1. Heating or cooling humid air at temperatures above the dew point corresponds to horizontal movement on the psychrometric chart. The ordinate on the chart is the ratio kg H_2O/kg dry air, which does not change as long as no condensation occurs.
2. If superheated humid air is cooled at 1 atm, the system follows a horizontal path to the left on the chart until the saturation curve (dew point) is reached; thereafter, the gas phase follows the saturation curve.
3. Since the psychrometric chart plots the mass ratio kg H_2O/kg dry air rather than the mass fraction of water, it is usually convenient to assume a quantity of dry air in a feed or product stream as a basis of calculation if the chart is to be used in the solution.

EXAMPLE 8.4-6 *Material and Energy Balances on an Air Conditioner*

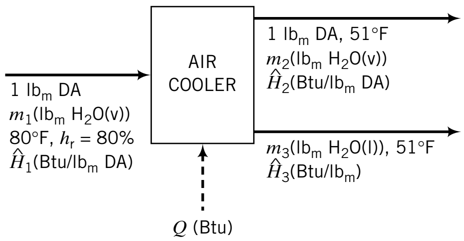
Equipment Encyclopedia
heat exchanger

Air at 80°F and 80% relative humidity is cooled to 51°F at a constant pressure of 1 atm. Use the psychrometric chart to calculate the fraction of the water that condenses and the rate at which heat must be removed to deliver 1000 ft^3/min of humid air at the final condition.

SOLUTION

Basis: 1 lb_m Dry Air[12]

A flowchart for the process is shown below. By convention we show heat transfer (Q) into the process unit, but since the air is being cooled we know that Q will be negative.



Note: In labeling the outlet gas stream, we have implicitly written a balance on dry air.

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[12] In assuming this basis, we are temporarily ignoring the specification of the volumetric flow rate at the outlet. After the process is balanced for the assumed basis, we will scale up to an outlet flow rate of 1000 ft^3/min.

Degree-of-Freedom Analysis

$$\begin{array}{l}
\ \ 7 \text{ unknowns } (m_1, m_2, m_3, \hat{H}_1, \hat{H}_2, \hat{H}_3, Q)\\
-1 \text{ material balance } (\text{H}_2\text{O—dry air is already balanced on the chart})\\
-2 \text{ absolute humidities from psychrometric chart (for inlet and outlet air)}\\
-2 \text{ enthalpies from psychrometric chart (for inlet and outlet air)}\\
-1 \text{ enthalpy of condensate (from known heat capacity of liquid water)}\\
\underline{-1 \text{ energy balance}\qquad\qquad\qquad}\\
= 0 \text{ degrees of freedom}
\end{array}$$

Point 1

$$\left.\begin{array}{r}80^\circ\text{F}\\ 80\%\ \text{RH}\end{array}\right\}\xrightarrow{\text{Figure 8.4-2}}\begin{array}{l} h_a = 0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O/lb}_\text{m}\ \text{DA}\\ \hat{H}_1 = 38.8\ \text{Btu/lb}_\text{m}\ \text{DA}\end{array}$$

$$m_1 = \begin{array}{c|c}1.0\ \text{lb}_\text{m}\ \text{DA} & 0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O}\\ \hline & \text{lb}_\text{m}\ \text{DA}\end{array} = 0.018\ \text{lb}_\text{m}\ \text{H}_2\text{O}$$

Point 2

$$\left.\begin{array}{r}51^\circ\text{F}\\ \text{Saturated}\end{array}\right\}\xrightarrow{\text{Figure 8.4-2}}\begin{array}{l} h_a = 0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O/lb}_\text{m}\ \text{DA}\\ \hat{H}_2 = 20.9\ \text{Btu/lb}_\text{m}\ \text{DA}\end{array}$$

$$m_2 = \begin{array}{c|c}1.0\ \text{lb}_\text{m}\ \text{DA} & 0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O}\\ \hline & \text{lb}_\text{m}\ \text{DA}\end{array} = 0.0079\ \text{lb}_\text{m}\ \text{H}_2\text{O}$$

Balance on H_2O

$$\begin{array}{l} m_1 = m_2 + m_3\\ \Bigg\Downarrow \begin{array}{l} m_1 = 0.018\ \text{lb}_\text{m}\\ m_2 = 0.0079\ \text{lb}_\text{m}\end{array}\\ m_3 = 0.010\ \text{lb}_\text{m}\ \text{H}_2\text{O condensed}\end{array}$$

Fraction H_2O Condensed

$$\frac{0.010\ \text{lb}_\text{m}\ \text{condensed}}{0.018\ \text{lb}_\text{m}\ \text{fed}} = \boxed{0.555}$$

Enthalpy of Condensate

Since the reference condition for water on Figure 8.4-2 is liquid water at 32°F, we must use the same condition to calculate $\hat{H}_3$.

$$\text{H}_2\text{O(l, 32°F)} \longrightarrow \text{H}_2\text{O(l, 51°F)}$$

$$\Delta\hat{H} = \hat{H}_3 = 1.0\ \frac{\text{Btu}}{\text{lb}_\text{m}\cdot{}^\circ\text{F}}(51^\circ\text{F} - 32^\circ\text{F}) = 19.0\ \text{Btu/lb}_\text{m}\ \text{H}_2\text{O}$$

Energy Balance

The open-system energy balance with W_s, ΔE_k, and ΔE_p set equal to zero is

$$Q = \Delta H = \sum_{\text{out}} m_i\hat{H}_i - \sum_{\text{in}} m_i\hat{H}_i$$

(There are no dots over the extensive variables in this equation because the basis of calculation is an amount, not a flow rate.) The enthalpy table for the process is shown below. Since (1) the enthalpies ($\hat{H}_i$) of the humid air streams are obtained from the psychrometric chart in Btu/lb_m dry air, and (2) the mass units of m_i and $\hat{H}_i$ must cancel when the two are multiplied in the energy balance, the tabulated values of m_i for these streams must be in lb_m dry air.

References: **Dry air (DA) (g, 0°F, 1 atm), H_2O (l, 32°F, 1 atm)**

Substance	m_in	$\hat{H}_\text{in}$	m_out	$\hat{H}_\text{out}$
Humid air	1.0 lb_m DA	38.8 Btu/lb_m DA	1.0 lb_m DA	20.9 Btu/lb_m DA
$H_2O(l)$	—	—	0.010 lb_m	19 Btu/lb_m

The references were of necessity chosen to be the ones used to generate the psychrometric chart. Substituting the values in the table into the energy balance yields

$$\begin{aligned} Q = \Delta H &= \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{} \left| \frac{20.9\ \text{Btu}}{\text{lb}_\text{m}\ \text{DA}} \right. + \frac{0.010\ \text{lb}_\text{m}\ \text{H}_2\text{O(l)}}{} \left| \frac{19\ \text{Btu}}{\text{lb}_\text{m}\ \text{H}_2\text{O}} \right. - \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{} \left| \frac{38.8\ \text{Btu}}{\text{lb}_\text{m}\ \text{DA}} \right. \\ &= -17.7\ \text{Btu} \end{aligned}$$

To calculate the cooling requirement for 1000 ft^3/min of delivered air, we must first determine the volume of delivered air corresponding to our assumed basis and scale the calculated value of Q by the ratio $(1000\ \text{ft}^3/\text{min})/(V_\text{basis})$. From the psychrometric chart, for humid air saturated at 51°F

$$\hat{V}_\text{H} = 13.0\ \text{ft}^3/\text{lb}_\text{m}\ \text{DA}$$

$$\Downarrow$$

$$V_\text{basis} = \frac{1.0\ \text{lb}_\text{m}\ \text{DA}}{} \left| \frac{13.0\ \text{ft}^3}{\text{lb}_\text{m}\ \text{DA}} \right. = 13.0\ \text{ft}^3$$

$$\Downarrow$$

$$\dot{Q} = \frac{-17.7\ \text{Btu}}{} \left| \frac{1000\ \text{ft}^3/\text{min}}{13.0\ \text{ft}^3} \right. = \boxed{-1360\ \text{Btu/min}}$$

TEST YOURSELF (Answers, p. 660)

Air at 25°C and 1 atm has a relative humidity of 20%. Use the psychrometric chart to estimate the absolute humidity, wet-bulb temperature, dew point, humid volume, and specific enthalpy of the air.

8.4e Adiabatic Cooling

Equipment Encyclopedia
humidifier, dryer, spray dryer

In **adiabatic cooling,** a warm gas is brought into contact with a cold liquid, causing the gas to cool and some of the liquid to evaporate. Heat is transferred from the gas to the liquid but no heat is transferred between the gas–liquid system and its surroundings (hence "adiabatic" cooling). Some common processes of this type are described below.

- ***Spray cooling, spray humidification.*** Liquid water is sprayed into a relatively dry warm air stream. Some of the water evaporates and the temperature of the air and of the unevaporated liquid both decrease. If the object is to cool the water or the air, the operation is called spray cooling; if the point is to increase the moisture content of the air, the operation is spray humidification.[13]
- ***Spray dehumidification.*** Warm humid air is *de*humidified by spraying cold water into it. Provided that the liquid temperature is low enough, the air is cooled below its dew point, causing some of the water vapor in it to condense.
- ***Drying.*** Hot air is blown over wet solids—for example, over a wet cake deposited in a filter or centrifuge. The water evaporates, leaving a dry solid product. Drying is the last step in the production of most crystalline products and powders, including many pharmaceuticals and food products.
- ***Spray drying.*** A suspension of small solid particles in water is sprayed as a fine mist into a stream of hot air. The water evaporates, larger solid particles settle out of the air and are removed by a conveyor, and fine suspended particles are separated from the air by a bag filter or cyclone separator. Dried milk is produced in this manner.

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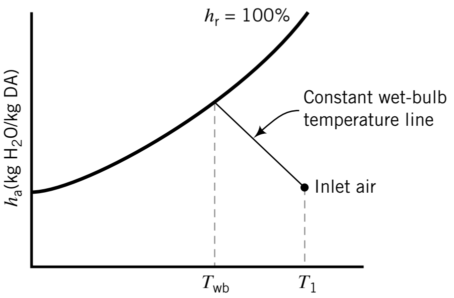
[13] Spraying the water into the air rather than simply blowing air over a water surface provides a large liquid surface-to-volume ratio, greatly increasing the evaporation rate.

Writing material and energy balances on an adiabatic cooling operation is a straightforward but cumbersome procedure. It can be shown, however, that if certain well-justified assumptions are made (we will state them later), *air undergoing adiabatic cooling through contact with liquid water moves along a constant wet-bulb temperature line on the psychrometric chart from its initial condition to the 100% relative humidity curve*. Further cooling of the air below its saturation temperature leads to condensation and hence dehumidification.

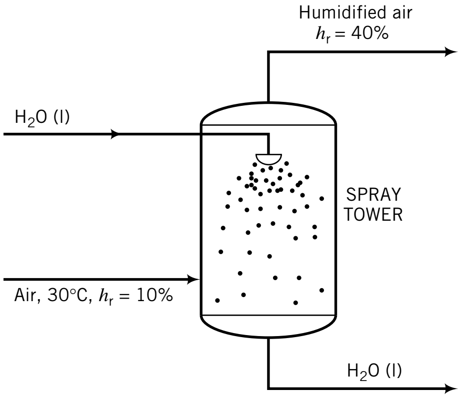


This result (which is far from obvious) allows us to perform adiabatic cooling calculations with relative ease using the psychrometric chart. First locate the initial state of the air on the chart; then locate the final state on the constant wet-bulb temperature line that passes through the initial state (or on the 100% humidity curve if cooling below the adiabatic saturation temperature takes place); and finally perform whatever material and energy balance calculations are required. Example 8.4-7 illustrates such a calculation for an adiabatic humidification operation.

EXAMPLE 8.4-7 *Adiabatic Humidification*

Equipment Encyclopedia
humidifier—water spray

A stream of air at 30°C and 10% relative humidity is humidified in an adiabatic spray tower operating at $P \approx 1$ atm. The emerging air is to have a relative humidity of 40%.



1. Determine the absolute humidity and the adiabatic saturation temperature of the entering air.
2. Use the psychrometric chart to calculate (i) the rate at which water must be added to humidify 1000 kg/h of the entering air, and (ii) the temperature of the exiting air.

SOLUTION We assume that the heat required to raise the temperature of the liquid in the spray tower is negligible compared with the heat of vaporization of water, so that the air follows an adiabatic saturation curve (constant wet-bulb temperature line) on the psychrometric chart.

1. Air at 30°C, 10% relative humidity

$$\Big\Downarrow \text{Figure 8.4-1}$$

$$h_a = 0.0026 \text{ kg H}_2\text{O/kg DA}$$
$$T_{wb} = T_{as} = 13.2°\text{C}$$

2. The state of the outlet air must lie on the $T_{wb} = 13.2°\text{C}$ line. From the intersection of this line with the curve for $h_r = 40\%$, the absolute humidity of the exit gas is determined to be 0.0063 kg H_2O/kg DA. The inlet (and outlet) flow rate of dry air, $\dot{m}_{DA}$, is

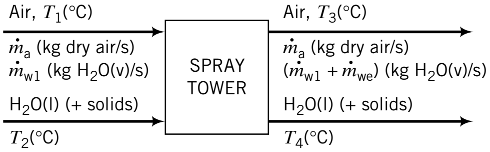
$$\dot{m}_{DA} = (1000 \text{ kg air/h})(1 \text{ kg DA}/1.0026 \text{ kg air}) = 997.4 \text{ kg DA/h}$$

The amount of water that must be evaporated, $\dot{m}_{H_2O}$, may be calculated as the difference between the outlet and inlet water flow rates in the air stream.

$$\dot{m}_{H_2O} = (997.4 \text{ kg DA/h})(0.0063 - 0.0026)\,\frac{\text{kg H}_2\text{O}}{\text{kg DA}}$$
$$= \boxed{3.7 \text{ kg H}_2\text{O/h}}$$

From Figure 8.4-1 the temperature of the exiting air is $\boxed{21.2°\text{C}}$.

A complete justification of the procedure given above is beyond the scope of this text,[14] but we can at least offer a partial explanation. A flowchart of an adiabatic cooling operation is shown below. A stream of warm air and either a stream of liquid water (spray cooling or spray humidification), a wet solid (drying), or a solid suspension (spray drying) are brought into contact. The air enters at T_1 and leaves at T_3, the water and any solids enter at T_2 and leave at T_4, and entering liquid water evaporates at a rate $\dot{m}_{we}$(kg/s).



Let us assume:

1. $(C_p)_{\text{air}}$, $(C_p)_{H_2O}$, and $(\Delta\hat{H}_v)_{H_2O}$ are independent of temperature at the prevailing process conditions.
2. The enthalpy changes undergone by the unevaporated liquid water and the solid (if there is one) in going from T_2 to T_4 are negligible compared to the changes undergone by the entering wet air and the evaporated water.
3. The heat required to raise liquid water from T_2 to T_3 is negligible compared to the heat of vaporization of water.

If the energy balance equation ($\Delta\dot{H} = 0$) is written for this process and these three assumptions are made, the simplified equation becomes

$$\dot{m}_a(C_p)_{\text{air}}(T_3 - T_1) + \dot{m}_{w1}(C_p)_{H_2O(v)}(T_3 - T_1) + \dot{m}_{we}(\Delta\hat{H}_v)_{H_2O} = 0$$
$$\Big\Downarrow$$
$$\frac{\dot{m}_{we}}{\dot{m}_a} = \frac{1}{(\Delta\hat{H}_v)_{H_2O}}\left[(C_p)_{\text{air}} + \frac{\dot{m}_{w1}}{\dot{m}_a}(C_p)_{H_2O(v)}\right](T_1 - T_3) \qquad \textbf{(8.4-9)}$$

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[14] One can be found in W. L. McCabe, J. C. Smith, and P. Harriott, *Unit Operations of Chemical Engineering*, 4th Edition, McGraw-Hill, New York, 1985, Chap. 23.

Suppose now that the temperature T_1 and absolute humidity $\dot{m}_{w1}/\dot{m}_a$ of the inlet air are specified, so that the state of the inlet air is fixed on the psychrometric chart. If we specify in addition the outlet air temperature $T_3(< T_1)$, then $\dot{m}_{we}/\dot{m}_a$ may be calculated from Equation 8.4-9, and it may in turn be used to calculate the absolute humidity of the outlet air, $(\dot{m}_{we} + \dot{m}_{w1})/\dot{m}_a$.

The outlet temperature and humidity determined in this manner are represented by a point on the psychrometric chart. If a lower value of T_3 is assumed, a higher outlet humidity would be calculated, yielding another point on the chart. The set of all such points for a specified T_1 and $\dot{m}_{w1}/\dot{m}_a$ defines a curve on the chart, known as the **adiabatic saturation curve.** *If the three stated assumptions are valid, the final state of air undergoing an adiabatic humidification must lie on the adiabatic saturation curve that passes through the inlet state on the psychrometric chart.*

If the outlet temperature T_3 is low enough, the air leaves saturated with water. The temperature corresponding to this condition is called the **adiabatic saturation temperature** and is found at the intersection of the adiabatic saturation curve with the 100% relative humidity curve.

The psychrometric chart for most gas–liquid systems would show a family of adiabatic saturation curves in addition to the families of curves shown on Figures 8.4-1 and 8.4-2. However, *for the air–water system at 1 atm, the adiabatic saturation curve through a given state coincides with the constant wet-bulb temperature line through that state, so that* $T_{as} = T_{wb}$. The simple material and energy balance procedure for adiabatic cooling outlined in this section is possible only because of this coincidence.

TEST YOURSELF (Answers, p. 660)

1. **(a)** Under what conditions do the temperature and humidity of a gas undergoing adiabatic cooling follow a unique curve on the psychrometric chart, regardless of the entering liquid temperature?
   (b) Does this curve coincide with a constant wet-bulb temperature line if the gas is air and the liquid is water?
   (c) What if they were nitrogen and acetone?
2. Air at 26°C with a relative humidity of 10% undergoes an adiabatic humidification. Use Figure 8.4-1 to estimate the adiabatic saturation temperature of the air. If the exiting air has a dry-bulb temperature of 14°C, determine its absolute humidity, relative humidity, and specific enthalpy.

8.5 MIXING AND SOLUTION

You may have carried out an experiment in a chemistry laboratory in which you mixed two liquids (such as concentrated sulfuric acid and water) or dissolved a solid in a liquid (such as sodium hydroxide in water) and observed that the mixture or solution became quite hot. The question is, why?

When two different liquids are mixed or when a gas or solid is dissolved in a liquid, bonds are broken between neighboring molecules—and possibly between atoms—of the feed materials, and new bonds are formed between neighboring molecules or ions in the product solution. If less energy is required to break the bonds in the feed materials than is released when the solution bonds form, a net release of energy results. Unless this energy is transferred from the solution to its surroundings as heat, it goes into raising the solution temperature, which is what happened in the experiments described in the first paragraph.

Suppose you mix 1 mol of pure liquid sulfuric acid with water at a specified temperature and pressure and then cool the mixture at constant pressure to bring it back to the initial temperature. The energy balance for this constant-pressure process is

$$Q = \Delta H = H_{H_2SO_4(aq)} - (H_{H_2SO_4(l)} + H_{H_2O})$$

where ΔH—the difference between the enthalpy of the solution at the specified temperature and pressure and the total enthalpy of the pure solute and solvent at the same T and P—is the *heat of solution* at that temperature and pressure. For the sulfuric acid dilution, we know $Q < 0$ (the container must be cooled to keep the solution temperature from rising) and so it follows that ΔH—the heat of solution—is negative for this process.

An **ideal mixture** is one for which the heat of mixing or solution is negligible and so $H_{\text{mixture}} \approx \sum n_i \hat{H}_i$, where n_i is the amount of mixture component i and $\hat{H}_i$ is the specific enthalpy of the pure component at the temperature and pressure of the mixture. Up to now in this text, we have assumed ideal mixture behavior for all mixtures and solutions. This assumption works well for nearly all gas mixtures and for liquid mixtures of similar compounds (such as mixtures of paraffins or of aromatics), but for other mixtures and solutions—such as aqueous solutions of strong acids or bases or certain gases (such as hydrogen chloride) or solids (such as sodium hydroxide)—heats of solution should be included in energy balance calculations. This section outlines the required procedures.

8.5a Heats of Solution and Mixing

The **heat of solution** $\Delta\hat{H}_s(T,r)$ is defined as the change in enthalpy for a process in which 1 mole of a solute (gas or solid) is dissolved in r moles of a liquid solvent at a constant temperature T. As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value known as the **heat of solution at infinite dilution.** The **heat of mixing** has the same meaning as the heat of solution when the process involves mixing two fluids rather than dissolving a gas or solid in a liquid.

Perry's Chemical Engineers' Handbook (see footnote 5) on pp. 2-201 through 2-204 gives heats of solution of various substances in water at either 18°C or "room temperature," which is roughly 25°C. *Caution:* The values given in the *Handbook* are *negatives* of the heats of solution $(-\Delta\hat{H}_s)$, although they are not identified as such explicitly.

As an illustration of how to use these data, suppose you wish to calculate ΔH for a process in which 2 mol of potassium cyanide (KCN) is dissolved in 400 mol of water at 18°C. First, calculate the moles of solvent per mole of solute:

$$r = 400/2 = 200 \text{ mol } H_2O/\text{mol KCN}$$

The value of $-\Delta H_s$ (18°C, $r = 200$) is listed as -3.0 kcal/mol (meaning per mol of KCN dissolved). The total enthalpy change is therefore

$$\Delta H = n\,\Delta\hat{H}_s = \frac{2.0 \text{ mol KCN}}{} \left| \frac{3.0 \text{ kcal}}{\text{mol KCN}} \right. = +6.0 \text{ kcal}$$

Table B.11 lists values of the heats of solution at 25°C of HCl(g) and NaOH(s) in water, and the heat of mixing at 25°C of H_2SO_4(l) and water. Heats of solution such as those given in Table B.11 may be used to determine directly the specific enthalpies of solutions at 25°C relative to the pure solute and solvent at this temperature. Another common choice of reference conditions, however, is the pure solvent and an infinitely dilute solution at 25°C.

Consider, for example, a hydrochloric acid solution for which $r = 10$ moles H_2O/mole HCl. From Table B.11, the specific enthalpy of this solution relative to pure HCl(g) and H_2O(l) at 25°C is $\Delta\hat{H}_s(r = 10) = -69.49$ kJ/mol HCl. Now, the enthalpy of the solution relative to H_2O(l) and a highly dilute solution of HCl (say, $r = 10^6$ moles H_2O/mole HCl) is the enthalpy change for the isothermal process

$$\left\{\begin{matrix} 1 \text{ mol HCl} \\ 10^6 \text{ mol } H_2O \end{matrix}\right\} \xrightarrow{25°\text{C}} \left\{\begin{matrix} 1 \text{ mol HCl} \\ 10 \text{ mol } H_2O \end{matrix}\right\} + (10^6 - 10) \text{ mol } H_2O(\text{l})$$

We may evaluate this enthalpy change using any convenient reference state—in particular, taking pure HCl(g) and H_2O(l) at 25°C as references. In view of the latter choice, $\hat{H}$ for the $(10^6 - 10)$ moles of pure water equals zero, and the enthalpy change for the process is therefore

$$\begin{aligned} \Delta\hat{H} &= \Delta\hat{H}_s(r = 10) - \Delta\hat{H}_s(r = \infty) \\ &= (-69.49 + 75.14) \text{ kJ/mol HCl} = 5.65 \text{ kJ/mol HCl} \end{aligned}$$

In general, the enthalpy of a solution containing r moles H_2O/mole solute is for reference states of pure solute and solvent at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r)} \tag{8.5-1}$$

and for reference states of pure solvent and an infinitely dilute solution at 25°C and 1 atm

$$\boxed{\hat{H} = \Delta\hat{H}_s(r) - \Delta\hat{H}_s(\infty)} \tag{8.5-2}$$

Note again that these enthalpies are expressed per mole of *solute,* not per mole of solution.

TEST YOURSELF (Answers, p. 660)

The heat of solution of a solute A in water at 25°C is −40 kJ/mol A for $r = 10$ mol H_2O/mol A and −60 kJ/mol A for infinite dilution.

1. What is the specific enthalpy (kJ/mol A) of an aqueous solution of A for which $r = 10$ mol H_2O/mol A relative to
   (a) pure H_2O and A at 25°C?
   (b) pure H_2O and an infinitely dilute aqueous solution of A?
2. If 5 mol of A is dissolved in 50 mol of H_2O at 25°C, how much heat is evolved or absorbed? (State which, observing that $Q = \Delta H$ for this process.)
3. How much heat is evolved or absorbed if the solution prepared in question 2 is poured into a large tank of water at 25°C?

8.5b Balances on Dissolution and Mixing Processes

When setting up an energy balance on a process that involves forming, concentrating, or diluting a solution for which the heat of solution or mixing cannot be neglected, prepare an inlet–outlet enthalpy table considering the solution as a single substance and the pure components at 25°C as reference states. To calculate the enthalpy of the solution at a temperature $T \neq 25$°C, first calculate its enthalpy at 25°C from tabulated heat of solution data, then add the enthalpy change for the heating or cooling of the solution from 25°C to T. The enthalpy change for the latter step should be calculated from tabulated solution heat capacities if they are available [e.g., if they are listed on pp. 2-184 and 2-185 of *Perry's Chemical Engineers' Handbook* (see footnote 5)]; otherwise, use the average heat capacity determined using Equation 8.3-13 for liquid mixtures or the heat capacity of the pure solvent for dilute solutions.

EXAMPLE 8.5-1 *Production of Hydrochloric Acid*

Equipment Encyclopedia
absorber

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and H_2O(l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.

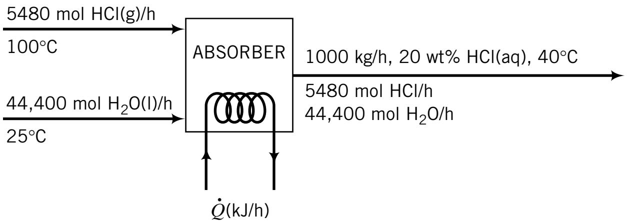
SOLUTION

It is advisable to determine the molar amounts or flow rates of the components of all feed and product solutions before drawing and labeling the flowchart. In this case

$$\text{1000 kg/h of 20.0 wt\% HCl(aq)}$$
$$\Downarrow$$

$$\dot{n}_{\text{HCl}} = \begin{array}{c|c|c} 1000\text{ kg} & 0.200\text{ kg HCl} & 10^3\text{ mol} \\ \hline \text{h} & \text{kg} & 36.5\text{ kg HCl} \end{array} = 5480\text{ mol HCl/h}$$

$$\dot{n}_{H_2O} = \begin{array}{c|c|c} 1000\text{ kg} & 0.800\text{ kg } H_2O & 10^3\text{ mol} \\ \hline \text{h} & \text{kg} & 18.0\text{ kg } H_2O \end{array} = 44{,}400\text{ mol } H_2O\text{/h}$$



The enthalpy table for the process is shown below. As usual, physical property data valid at $P = 1$ atm are used and the effects on enthalpy of any pressure differences that may occur in the process are neglected. Note that the value of $\dot{n}$ for the product solution is the molar flow rate of the *solute* (HCl) rather than the solution, since the enthalpy will be determined in kJ/mol solute.

References: HCl(g), H_2O(l) at 25°C and 1 atm

Substance	$\dot{n}_{in}$	$\hat{H}_{in}$	$\dot{n}_{out}$	$\hat{H}_{out}$
HCl(g)	5480 mol HCl	$\hat{H}_1$ (kJ/mol HCl)	—	—
H_2O(l)	44,400 mol H_2O	0	—	—
HCl(aq)	—	—	5480 mol HCl	$\hat{H}_2$(kJ/mol HCl)

Calculate $\hat{H}_1$ and $\hat{H}_2$

$$\text{HCl(g, 25°C)} \rightarrow \text{HCl(g, 100°C)}$$

$$\hat{H}_1 = \Delta\hat{H} = \int_{25°C}^{100°C} C_p\, dT$$

$$\Big\Downarrow C_p \text{ for HCl(g) from Table B.2}$$

$$\hat{H}_1 = 2.178 \text{ kJ/mol}$$

For the product solution,

$$r = (44{,}400 \text{ mol } H_2O)/(5480 \text{ mol HCl}) = 8.10$$

$$\text{HCl(g, 25°C)} + 8.10\, H_2O\text{(1, 25°C)} \xrightarrow{\Delta\hat{H}_a} \text{HCl(aq, 25°C)} \xrightarrow{\Delta\hat{H}_b} \text{HCl(aq, 40°C)}$$

$$\Delta\hat{H}_a = \Delta\hat{H}_s(25°C, r = 8.1) \xRightarrow{\text{Table B.11}} -67.4 \text{ kJ/mol HCl}$$

The heat capacities of aqueous hydrochloric acid solutions are listed on p. 2-184 of *Perry's Chemical Engineers' Handbook* (see footnote 5) as a function of the mole fraction of HCl in the solution, which in our problem is

$$\frac{5480 \text{ mol HCl/h}}{(5480 + 44{,}400) \text{ mol/h}} = 0.110 \text{ mol HCl/mol}$$

$$\Downarrow$$

$$C_p = \frac{0.73 \text{ kcal}}{\text{kg}\cdot°\text{C}} \left| \frac{1000 \text{ kg solution}}{5480 \text{ mol HCl}} \right| \frac{4.184 \text{ kJ}}{\text{kcal}} = 0.557 \frac{\text{kJ}}{\text{mol HCl}\cdot°\text{C}}$$

$$\Delta\hat{H}_b = \int_{25°C}^{40°C} C_p\, dT = 8.36 \text{ kJ/mol HCl}$$

$$\Downarrow$$

$$\hat{H}_2 = \Delta\hat{H}_a + \Delta\hat{H}_b = (-67.4 + 8.36) \text{ kJ/mol HCl} = -59.0 \text{ kJ/mol HCl}$$

Energy Balance

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

$$= (5480 \text{ mol HCl/h})(-59.0 \text{ kJ/mol HCl}) - (5480 \text{ mol HCl/h})(2.178 \text{ kJ/mol HCl})$$

$$= \boxed{-3.35 \times 10^5 \text{ kJ/h}}$$

Heat must be transferred out of the absorber at a rate of 335,000 kJ/h to keep the product temperature from rising above 40°C.

8.5c Enthalpy–Concentration Charts—Single Liquid Phase

Energy balance calculations on liquid-phase systems involving mixtures can be cumbersome when heats of mixing are significant. The calculations can be simplified for binary (two-component) systems by using an **enthalpy–concentration chart,** a plot of specific enthalpy versus mole fraction (or mole percent) or mass fraction (or weight percent) of one component. An $\hat{H}$-x chart for aqueous solutions of sulfuric acid at several temperatures is shown in Figure 8.5-1. The reference conditions for the plotted enthalpies are pure liquid H_2SO_4 at 77°F and liquid water at 32°F.

The points on the isotherms of Figure 8.5-1 were determined using the procedure outlined in the last section. Suppose, for example, you wish to calculate the specific enthalpy (Btu/lb$_m$) of a 40 wt% sulfuric acid solution at 120°F. If you know the heat of mixing of sulfuric acid at 77°F, the process path you would follow would be to bring pure liquid water from its reference temperature of 32°F to 77°F (the sulfuric acid starts at 77°F and so does not require this step), mix the two liquids at 77°F, bring the product solution to 120°F, and calculate and add the enthalpy changes for each of these steps.

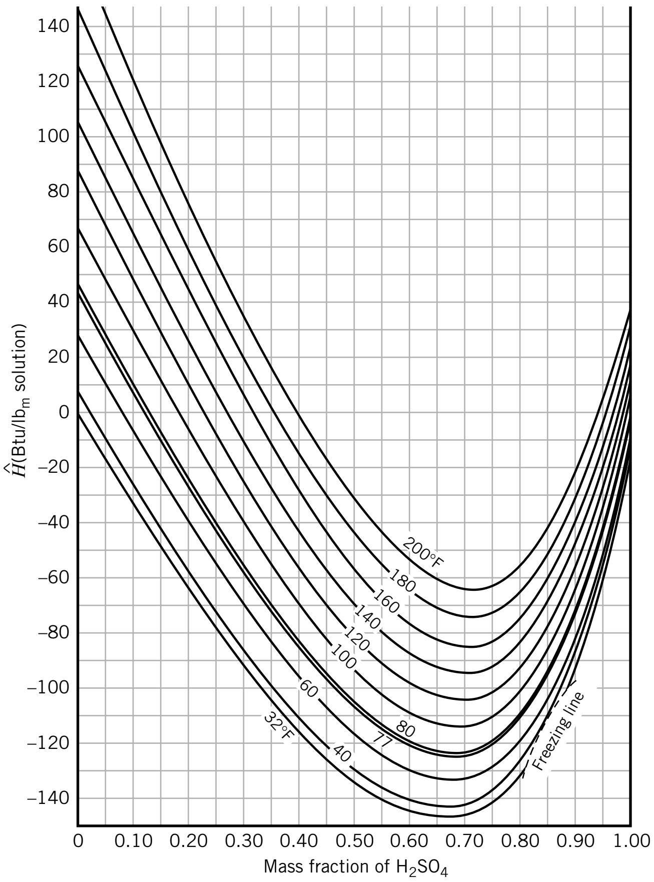


Figure 8.5-1 Enthalpy–concentration chart for H_2SO_4–H_2O. (Redrawn from the data of W. D. Ross, *Chem. Eng. Progr.,* **43**:314, 1952.)

Basis: 1 lb_m solution ($\Longrightarrow$ 0.40 lb_m H_2SO_4 = 4.08×10^{-3} lb-mole, 0.60 lb_m H_2O = 3.33×10^{-2} lb-mole)

- 0.60 lb_m $H_2O(l, 32°F) \longrightarrow$ 0.60 lb_m H_2O (l, 77°F)

$$\Delta H_1(\text{Btu}) = (0.60\ \text{lb}_\text{m}\ H_2O)\left[\int_{32°F}^{77°F} (C_p)_{H_2O}\, dT\right]\left(\frac{\text{Btu}}{\text{lb}_\text{m}}\right)$$

  The heat capacity of liquid water is approximately 1 Btu/(lb_m·°F).

- 0.40 lb_m H_2SO_4(77°F) + 0.60 lb_m H_2O (77°F) $\longrightarrow$ 1.0 lb_m H_2SO_4 solution (aq, 77°F)

$$\Delta H_2(\text{Btu}) = (0.40\ \text{lb}_\text{m}\ H_2SO_4)\left[\Delta\hat{H}_s\left(77°\text{F}, r = 8.2\ \frac{\text{lb-mole } H_2O}{\text{lb-mole } H_2SO_4}\right)\left(\frac{\text{Btu}}{\text{lb}_\text{m}\ H_2SO_4}\right)\right]$$

  The heat of mixing can be determined from the data in Table B.11 to be −279 Btu/lb_m H_2SO_4.

- 1.0 lb_m H_2SO_4 solution (aq, 77°F) $\longrightarrow$ 1.0 lb_m H_2SO_4 solution (aq, 120°F)

$$\Delta H_3(\text{Btu}) = (1.0\ \text{lb}_\text{m})\int_{77°F}^{120°F} (C_p)_{40\%\ H_2SO_4(aq)}\, dT$$

  The heat capacity of the 40% sulfuric acid solution is roughly 0.67 Btu/(lb_m·°F).[15]

- $\hat{H}(40\%\ H_2SO_4, 120°F) = \dfrac{(\Delta H_1 + \Delta H_2 + \Delta H_3)(\text{Btu})}{1.0\ \text{lb}_\text{m}\ \text{solution}} \approx \boxed{-56\ \text{Btu/lb}_\text{m}}$

  (Verify that this is the value shown in Figure 8.5-1.)

If any reference temperature but 77°F had been chosen for sulfuric acid, another step would have been included in which H_2SO_4 was brought from T_ref to 77°F prior to mixing.

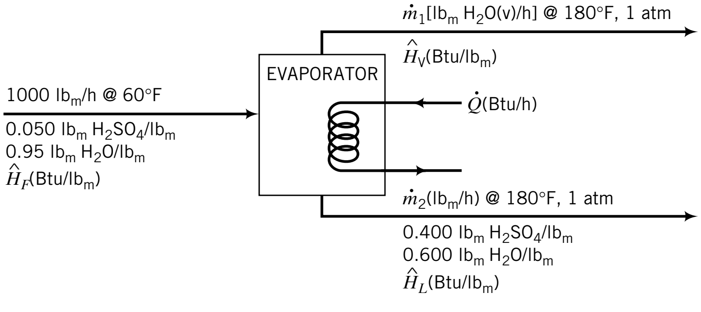
Once someone has gone to the trouble of preparing an enthalpy-concentration chart like that of Figure 8.5-1, energy balance calculations become relatively simple, as shown in Example 8.5-2.

EXAMPLE 8.5-2 *Concentration of an Aqueous H_2SO_4 Solution*

Equipment Encyclopedia
evaporator

A 5.0 wt% H_2SO_4 solution at 60°F is to be concentrated to 40.0 wt% by evaporation of water. The concentrated solution and water vapor emerge from the evaporator at 180°F and 1 atm. Calculate the rate at which heat must be transferred to the evaporator to process 1000 lb_m/h of the feed solution.

Basis: Given Feed Rate of 5% Solution



H_2SO_4 Balance $(0.050)(1000)\ \text{lb}_\text{m}/\text{h} = 0.400\dot{m}_2 \Longrightarrow \dot{m}_2 = 125\ \text{lb}_\text{m}/\text{h}$

Total Mass Balance $1000\ \text{lb}_\text{m}/\text{h} = \dot{m}_1 + \dot{m}_2 \xRightarrow{\dot{m}_2\, =\, 125\ \text{lb}_\text{m}/\text{h}} \dot{m}_1 = 875\ \text{lb}_\text{m}/\text{h}$

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[15] R. H. Perry and D. W. Green, Eds., *Perry's Chemical Engineers' Handbook*, 7th Edition, McGraw-Hill, New York, 1997, p. 2-184.

Reference States for Energy Balance $H_2O(l, 32°F)$, $H_2SO_4(l, 77°F)$

From Figure 8.5-1:

$$\hat{H}_F = 10 \text{ Btu/lb}_m \qquad (5\% \text{ } H_2SO_4 \text{ at } 60°F)$$
$$\hat{H}_L = -17 \text{ Btu/lb}_m \qquad (40\% \text{ } H_2SO_4 \text{ at } 180°F)$$

The enthalpy of water vapor at 180°F and 1 atm relative to liquid water at 32°F may be obtained from the steam tables in *Perry's Chemical Engineers' Handbook* (see footnote 5) as

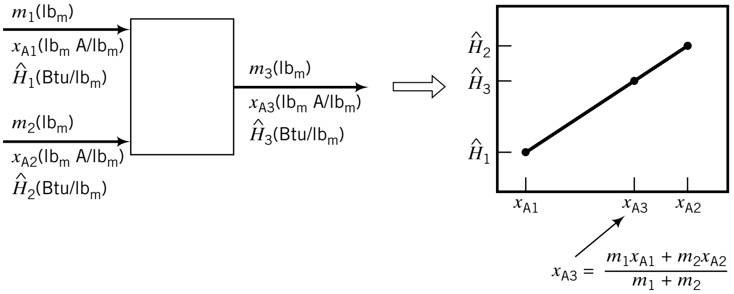
$$\hat{H}_V = 1138 \text{ Btu/lb}_m$$

Energy Balance

$$\begin{aligned}\dot{Q} = \Delta\dot{H} &= \dot{m}_1\hat{H}_V + \dot{m}_2\hat{H}_L - (1000\text{lb}_m/h)\hat{H}_F \\ &= [(875)(1138) + (125)(-17) - (1000)(10)] \text{ Btu/h} \\ &= \boxed{984{,}000 \text{ Btu/h}}\end{aligned}$$

Compare the ease of this computation with that of Example 8.5-1. Having the enthalpy–concentration chart eliminates the need for all of the hypothetical heating, cooling, and isothermal mixing steps that would normally be required to evaluate the total enthalpy change for the process.

Adiabatic mixing processes are particularly simple to analyze when an $\hat{H}$-x chart is available. Suppose x_A is the mass fraction of A in a mixture of two species, A and B, and that a mass m_1 of Solution 1 $(x_{A1}, \hat{H}_1)$ is mixed adiabatically with a mass m_2 of Solution 2 $(x_{A2}, \hat{H}_2)$. We will show that the condition of the product mixture, $(x_{A3}, \hat{H}_3)$, is on a straight line on the $\hat{H}$-x chart between the points corresponding to the feed stream conditions.



To prove this result, we write a total mass balance, a material balance on species A, and an energy balance ($\Delta H = 0$ for this constant-pressure batch process):

Total Mass Balance:

$$m_1 + m_2 = m_3 \tag{a}$$

A Balance:

$$m_1x_{A1} + m_2x_{A2} = m_3x_{A3} \tag{b}$$

$$\Big\Downarrow \text{Substitute for } m_3 \text{ from (a), rearrange}$$

$$m_1(x_{A3} - x_{A1}) = m_2(x_{A2} - x_{A3}) \tag{c}$$

Energy Balance:

$$\Delta H = m_3\hat{H}_3 - m_1\hat{H}_1 - m_2\hat{H}_2 = 0$$

$$\Big\Downarrow \text{Substitute for } m_3 \text{ from (a), rearrange}$$

$$m_1(\hat{H}_3 - \hat{H}_1) = m_2(\hat{H}_2 - \hat{H}_3) \tag{d}$$

Dividing (d) by (c) yields

$$\frac{\hat{H}_3 - \hat{H}_1}{x_{A3} - x_{A1}} = \frac{\hat{H}_2 - \hat{H}_3}{x_{A2} - x_{A3}} \tag{e}$$

Since the slope of the line segment from $(x_{A1}, \hat{H}_1)$ to $(x_{A3}, \hat{H}_3)$ (the left-hand side of this equation) equals the slope of the segment from $(x_{A3}, \hat{H}_3)$ to $(x_{A2}, \hat{H}_2)$ (the right-hand side) and the segments have a point in common, the three points must lie on a straight line. The value of x_{A3} can be calculated from Equations a and b:

$$x_{A3} = \frac{m_1 x_{A1} + m_2 x_{A2}}{m_1 + m_2} \tag{8.5-3}$$

It follows that if two feed solutions of known masses and compositions (m_i, x_i, $i = 1, 2$) are mixed adiabatically and you have an $\hat{H}$-x chart, you may (i) calculate x_3 for the product mixture from Equation 8.5-3, (ii) draw a line connecting the points on the chart corresponding to the two feeds, and (iii) read the enthalpy and temperature of the product mixture from the point on the connecting line for which $x = x_3$.

EXAMPLE 8.5-3 *Adiabatic Mixing*

Pure water at 60°F is mixed with 100 g of an aqueous 80 wt% H_2SO_4 solution, also at 60°F. The mixing vessel is insulated well enough to be considered adiabatic.

1. If 250 g H_2O is mixed with the acid, what will the final solution temperature be?
2. What is the maximum attainable solution temperature and how much water must be added to achieve it?

SOLUTION

1. From Equation 8.5-3, the mass fraction of H_2SO_4 in the product solution is

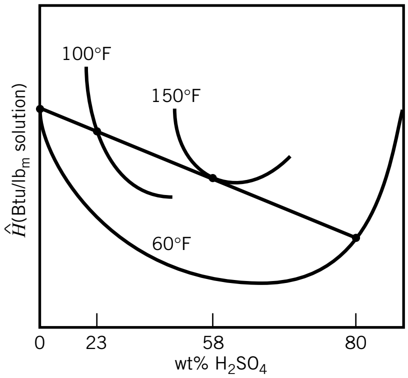
$$x_p = \frac{[(100)(0.80) + (250)(0)]\text{ g } H_2SO_4}{(100 + 250)\text{g}} = 0.23\text{g } H_2SO_4/\text{g}$$

A straight line on Figure 8.5-1 between points at ($x = 0, T = 60$°F) and ($x = 0.80, T = 60$°F) goes through the point ($x = 0.23$, $\boxed{T \approx 100°\text{F}}$). (Verify this result.)

2. The line between ($x = 0, T = 60$°F) and ($x = 0.80, T = 60$° F) passes through a temperature maximum at roughly ($x \approx 0.58$, $\boxed{T \approx 150°\text{F}}$). (*Verify.*) From Equation 8.5-3,

$$0.58 = \frac{(100)(0.80)\text{ g} + (m_w)(0)}{100\text{ g} + m_w} \Longrightarrow \boxed{m_w = 38\text{ g } H_2O}$$

The graphical construction of these solutions is illustrated below.



TEST YOURSELF (Answers, p. 660)

Use Figure 8.5-1 to answer the following questions.

1. What is the specific enthalpy of 80 wt% H_2SO_4(aq, 110°F) relative to pure H_2SO_4 at 77°F and pure water at 32°F?
2. The 100 wt% intercepts of the isotherms on Figure 8.5-1 are difficult to read. Which isotherm must have an intercept of 0 Btu/lb$_m$? (Your answer should be a temperature.)

3. Pure water at 32°F is used to dilute a 90 wt% H_2SO_4 solution (aq, 32°F). Estimate the maximum temperature the product solution can achieve and the concentration of sulfuric acid (wt%) in this solution.
4. Estimate (a) the specific enthalpy of a 30 wt% H_2SO_4 solution (aq, 77°F) and (b) the specific enthalpy of a 30 wt% solution obtained by mixing pure water at 77°F and pure sulfuric acid at 77°F adiabatically. What is the physical significance of the difference between these two enthalpies?

8.5d Using Enthalpy–Concentration Charts for Vapor–Liquid Equilibrium Calculations

Enthalpy–concentration charts are particularly useful for two-component systems in which vapor and liquid phases are in equilibrium. The Gibbs phase rule (Equation 6.2-1) specifies that such a system has $(2 + 2 - 2) = 2$ degrees of freedom. If as before we fix the system pressure, then specifying only one more intensive variable—the system temperature, or the mass or mole fraction of either component in either phase—fixes the values of all other intensive variables in both phases. An $\hat{H}$-x diagram for the ammonia–water system at 1 atm is shown in Figure 8.5-2.

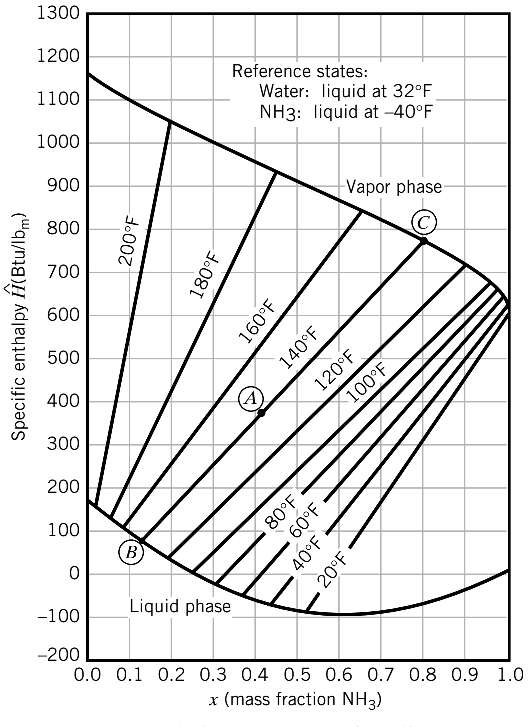


Figure 8.5-2 Enthalpy–concentration diagram for the ammonia–water system at 1 atm. (From G. G. Brown et al., *Unit Operations,* ©1950, Figure 551. Reprinted by permission of John Wiley & Sons.)

The specific enthalpies of aqueous solutions and gaseous mixtures of ammonia and water are shown on the two curves on this figure.

Suppose the mass fraction of ammonia in a liquid solution of NH_3 and H_2O at 1 atm is specified to be 0.25. According to the phase rule, the system temperature and the mass fraction of NH_3 in the vapor phase are uniquely determined by these specifications. (*Verify.*) A **tie line** may therefore be drawn on the enthalpy–concentration chart from $x = 0.25$ on the liquid-phase curve to the corresponding point on the vapor-phase curve, which is at $y = 0.95$; and the tie line may be labeled with the corresponding temperature, 100°F. Several tie lines constructed in this manner are shown in Figure 8.5-2; once drawn, the lines may be used to determine the equilibrium composition and the specific enthalpy of each phase at a specified temperature.

EXAMPLE 8.5-4 Use of the Enthalpy–Concentration Chart for a Two-Phase System

An aqueous ammonia solution is in equilibrium with a vapor phase in a closed system at 160°F and 1 atm. The liquid phase accounts for 95% of the total mass of the system contents. Use Figure 8.5-2 to determine the weight percent of NH_3 in each phase and the enthalpy of the system per unit mass of the system contents.

SOLUTION The mass fractions of ammonia and specific enthalpies of each phase may be read from the intersections of the 160°F tie line with the vapor and liquid equilibrium curves on Figure 8.5-2.

Liquid Phase $\boxed{8\%\ NH_3,\ 92\%\ H_2O}\ ;\quad \hat{H}_L = 110\ \text{Btu/lb}_\text{m}$

Vapor Phase $\boxed{64\%\ NH_3,\ 36\%\ H_2O}\ ;\quad \hat{H}_V = 855\ \text{Btu/lb}_\text{m}$

Basis $1\ \text{lb}_\text{m}$ total mass $\Longrightarrow$ $0.95\ \text{lb}_\text{m}$ liquid, $0.05\ \text{lb}_\text{m}$ vapor

$$\hat{H}(\text{Btu/lb}_\text{m}) = \frac{0.95\ \text{lb}_\text{m}\ \text{liquid}}{\text{lb}_\text{m}}\left|\frac{110\ \text{Btu}}{\text{lb}_\text{m}}\right. + \frac{0.05\ \text{lb}_\text{m}\ \text{vapor}}{\text{lb}_\text{m}}\left|\frac{855\ \text{Btu}}{\text{lb}_\text{m}}\right.$$

$$= \boxed{147\ \text{Btu/lb}_\text{m}}$$

If the overall composition of a two-phase two-component system at a given temperature and pressure is known, the fraction of the system that is liquid or vapor may easily be determined from the enthalpy–concentration chart.

Suppose, for example, that a mixture of ammonia and water that is 40% NH_3 by mass is contained in a closed vessel at 140°F and 1 atm. Point A on Figure 8.5-2 corresponds to this condition. Since this point lies between the vapor and liquid equilibrium curves, the mixture separates into two phases whose compositions are found at the extremities of the 140°F tie line (points B and C).

In general, if F, L, and V are the total mass of the mixture, the mass of the liquid phase and the mass of the vapor phase, respectively, and x_F, x_L, and x_V are the corresponding mass fractions of NH_3, then

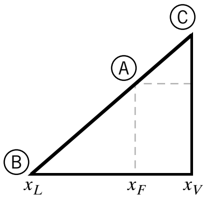
Total balance: $$F = L + V \qquad \textbf{(8.5-4)}$$

NH_3 balance: $$x_F F = x_L L + x_V V \qquad \textbf{(8.5-5)}$$

Substituting the expression of Equation 8.5-4 for F into Equation 8.5-5 and rearranging the result yields

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} \qquad \textbf{(8.5-6)}$$

The tie line in question appears as shown below:



From the properties of similar triangles, the right side of Equation 8.5-6 equals the ratio of distances $\overline{AC}/\overline{AB}$. We have thus proved the following general rule: if A, B, and C are the points on a tie line corresponding to the total mixture, the liquid phase, and the vapor phase, respectively, and if F, L, and V are the corresponding masses, then the liquid-to-vapor mass ratio is

$$\frac{L}{V} = \frac{x_V - x_F}{x_F - x_L} = \frac{\overline{AC}}{\overline{AB}} \tag{8.5-7}$$

This is the *lever rule.* It is also not difficult to prove that the mass fractions of the liquid and vapor phases are

$$\frac{L}{F} = \frac{x_V - x_F}{x_V - x_L} = \frac{\overline{AC}}{\overline{BC}} \tag{8.5-8}$$

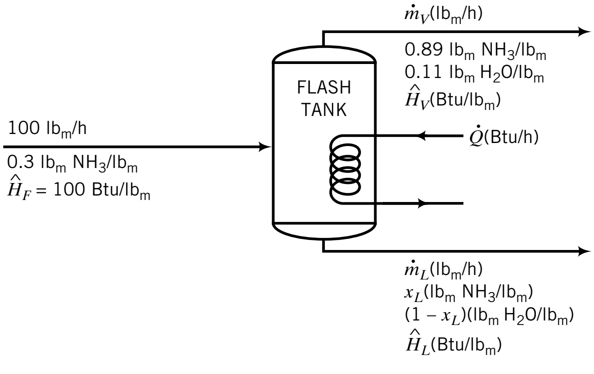
$$\frac{V}{F} = \frac{x_F - x_L}{x_V - x_L} = \frac{\overline{AB}}{\overline{BC}} \tag{8.5-9}$$

Once you have located the total mixture on the chart from a specified set of feed conditions, it becomes a simple matter to determine the compositions, enthalpies, and relative proportions of each phase, calculations that would take much more time in the absence of the chart.

EXAMPLE 8.5-5 *Equilibrium Flash Vaporization*

A 30 wt% NH_3 solution at 100 psia is fed at a rate of 100 lb_m/h to a tank in which the pressure is 1 atm. The enthalpy of the feed solution relative to the reference conditions used to construct Figure 8.5-2 is 100 Btu/lb_m. The vapor composition is to be 89 wt% NH_3. Determine the temperature of the stream leaving the tank, the mass fraction of NH_3 in the liquid product, the flow rates of the liquid and vapor product streams, and the rate at which heat must be transferred to the vaporizer.

SOLUTION ***Basis: 100 lb$_m$/h Feed***



From Figure 8.5-2,

$$x_V = 0.89 \text{ lb}_m \text{ NH}_3/\text{lb}_m$$

$$\boxed{T = 120^\circ\text{F}}$$

$$\boxed{x_L = 0.185 \text{ lb}_m \text{ NH}_3/\text{lb}_m}$$

$$\hat{H}_V = 728 \text{ Btu/lb}_m$$

$$\hat{H}_L = 45 \text{ Btu/lb}_m$$

From Equation 8.5-8

$$\frac{\dot{m}_L}{100\ \mathrm{lb_m/h}} = \frac{x_V - x_F}{x_V - x_L}$$

$$\Downarrow$$

$$\dot{m}_L = (100\ \mathrm{lb_m/h})\frac{0.89 - 0.30}{0.89 - 0.185} = \boxed{84\ \mathrm{lb_m/h}\text{ liquid product}}$$

$$\dot{m}_V = (100 - 84)\ \mathrm{lb_m/h} = \boxed{16\ \mathrm{lb_m/h}\text{ vapor product}}$$

Energy Balance

$$\dot{Q} = \Delta\dot{H} = \dot{m}_V\hat{H}_V + \dot{m}_L\hat{H}_L - 100\hat{H}_F$$

$$= [(16)(728) + (84)(45) - (100)(100)]\ \text{Btu/h} = \boxed{5400\ \text{Btu/h}}$$

TEST YOURSELF (Answers, p. 660)

Use Figure 8.5-2 for the following calculations.

1. Estimate (a) the temperature at which the mass fraction of NH_3 in the vapor phase of a two-phase system equals 0.85, and (b) the corresponding liquid-phase NH_3 mass fraction.
2. What is the heat of vaporization of NH_3 at its normal boiling point?
3. If an NH_3–H_2O mixture whose overall composition is 50% NH_3–50% H_2O is in equilibrium at 120°F, what fraction of the mixture is a vapor?

8.6 SUMMARY

An integral energy balance (the first law of thermodynamics) for a closed constant-volume system with no kinetic or potential energy changes ($\Delta E_k = 0, \Delta E_p = 0$) and no energy transferred in or out as work ($W = 0$) is

$$Q = \Delta U = \sum_{\text{final}} n_i\hat{U}_i - \sum_{\text{initial}} n_i\hat{U}_i$$

For a closed system expanding or contracting against a constant external pressure, the balance is

$$Q = \Delta H = \sum_{\text{final}} n_i\hat{H}_i - \sum_{\text{initial}} n_i\hat{H}_i$$

For an open system at steady state with negligible kinetic and potential energy changes from inlet to outlet and no energy transfer as shaft work, the balance is

$$\dot{Q} = \Delta\dot{H} = \sum_{\text{outlet}} \dot{n}_i\hat{H}_i - \sum_{\text{inlet}} \dot{n}_i\hat{H}_i$$

In these equations n is the amount (mass or moles) of a species in one of its initial or final states in the process, $\dot{n}$ is the flow rate (mass or molar) of a species in a continuous stream entering or leaving the process, and $\hat{U}$ and $\hat{H}$ are respectively the specific internal energy and specific enthalpy of a species in a process state relative to a specified reference state for the same species.

This chapter presents formulas and methods for evaluating $\hat{U}$ and $\hat{H}$ (and hence ΔU, ΔH, and $\Delta\dot{H}$) when tables of internal energies and enthalpies are not readily available. Here is the general procedure:

1. Choose a reference state (phase, temperature, and pressure) for each species involved in a process.
2. Choose a path from the reference state to each initial and final (or inlet and outlet) process state for each species, and evaluate $\hat{U}_i$ (or $\hat{H}_i$) as $\Delta\hat{U}$ (or $\Delta\hat{H}$) for the transition from the reference state to the process state.

3. Once all of the $\hat{U}_i$ (or all $\hat{H}_i$) values are determined in this manner and all of the n_i (or all $\dot{n}_i$) values are determined from material balances, densities or equations of state, and phase equilibrium relations, calculate ΔU, ΔH, or $\Delta \dot{H}$ and substitute the result in the energy balance to determine whichever variable is unknown (usually the heat, Q, or heat transfer rate, $\dot{Q}$).

Following are points regarding the implementation of this procedure for various types of processes.

- Energy balance calculations for a system (a process unit or combination of units) are conveniently organized through the construction of an *inlet–outlet internal energy table* (or *enthalpy table*). The table lists n (or $\dot{n}$) and $\hat{U}$ (or $\hat{H}$) for each species at each state (phase, temperature, pressure) in which the species is found in process streams. Once all of these variable values have been determined and inserted in the table, the subsequent evaluation of ΔU, ΔH, or $\Delta \dot{H}$ is straightforward.
- The fact that internal energy and enthalpy are *state properties* means that any convenient process path from a reference state to a process state may be chosen, even if the actual process proceeds by a different path. As a rule, you would choose a path that allows you to make use of heat capacities, phase transition temperatures, and latent heats tabulated in an available reference (like this text).
- *Changes in pressure at constant temperature.* For a species undergoing an isothermal pressure change, ΔP,

  $\Delta \hat{U} \approx 0$ for solids, liquids, and nearly ideal gases. For ideal gases, $\Delta \hat{U} = 0$.
  $\Delta \hat{H} \approx \hat{V}\Delta P$ for solids and liquids, where $\hat{V}$ is the (presumably constant) specific volume of the solid or liquid.
  $\Delta \hat{H} \approx 0$ for nearly ideal gases or for moderately small pressure changes (on the order of a few atmospheres). For ideal gases, $\Delta \hat{H} = 0$.

  If gases are at conditions at which they are far from ideal or if they undergo large pressure changes, you must either use tables of thermodynamic properties (such as the steam tables for water) or thermodynamic correlations beyond the scope of this text to determine $\Delta \hat{U}$ or $\Delta \hat{H}$.
- *Changes in temperature.* The specific internal energy of a species increases with increasing temperature. If a species is heated at constant volume and $\hat{U}$ is plotted versus T, the slope of the resulting curve is the *heat capacity at constant volume* of the species, $C_v(T)$, or $C_v = (\partial \hat{U}/\partial T)_{\text{constant } \hat{V}}$. If a species undergoes a change in temperature from T_1 to T_2 without changing phase,

  $$\Delta \hat{U} \approx \int_{T_1}^{T_2} C_v(T)\, dT$$

  This equation is

  (a) exact for an ideal gas, even if $\hat{V}$ changes during the heating or cooling process. (For an ideal gas, $\hat{U}$ does not depend on $\hat{V}$.)
  (b) a good approximation for a solid or liquid.
  (c) valid for a nonideal gas only if $\hat{V}$ is constant.

- The specific enthalpy of a species ($\hat{H} = \hat{U} + P\hat{V}$) also increases with increasing temperature. If a species is heated at constant pressure and $\hat{H}$ is plotted versus T, the slope of the resulting curve is the *heat capacity at constant pressure* of the species, $C_p(T)$, or $C_p = (\partial \hat{H}/\partial T)_{\text{constant } P}$. It follows that if a *gas* undergoes a change in temperature from T_1 to T_2, with or without a concurrent change in pressure,

  $$\Delta \hat{H} \approx \int_{T_1}^{T_2} C_p(T)\, dT$$

This equation is

(a) exact for an ideal gas, even if P changes during the heating or cooling process. (For an ideal gas, $\hat{H}$ does not depend on P.)
(b) valid for a nonideal gas only if P is constant.

If a liquid or solid undergoes a temperature change from T_1 to T_2 and a simultaneous pressure change, ΔP, then

$$\Delta\hat{H} \approx \hat{V}\Delta P + \int_{T_1}^{T_2} C_p(T)\, dT$$

- Table B.2 lists coefficients of polynomial expressions for $C_p(T)$[kJ/(mol·°C)] at $P = 1$ atm. The expressions should be accurate for solids, liquids, and ideal gases at any pressure and for nonideal gases only at 1 atm.
- To determine an expression or value for $C_v(T)$ from a known expression or value for $C_p(T)$, use one of the following relationships:

Liquids and Solids: $C_v \approx C_p$

Ideal Gases: $C_v = C_p - R$

where R is the gas constant. Since the degree unit in the denominator of the heat capacity is a temperature interval, R can be subtracted directly from the expressions for C_p in Table B.2.

- The heat capacity of a solid or liquid can be estimated in the absence of tabulated data using *Kopp's rule* (Section 8.3c).
- If only tabulated values of C_p or C_v at discrete temperatures are available, the integrals in the expressions for $\Delta\hat{U}$ and $\Delta\hat{H}$ must be evaluated by *numerical integration,* using formulas such as those given in Appendix A.3.
- *Phase changes at constant temperature and pressure. Latent heats* are changes in specific enthalpy associated with phase changes at constant T and P. For example, the *latent heat of fusion* (more commonly, the *heat of fusion*), $\Delta\hat{H}_m(T, P)$, is the enthalpy change for the process in which a solid at temperature T and pressure P becomes a liquid at the same temperature and pressure, and the *heat of vaporization,* $\Delta\hat{H}_v(T, P)$, is $\Delta\hat{H}$ for the process in which a liquid at T and P becomes a vapor at the same T and P.
- Table B.1 lists *standard heats of fusion and vaporization* for a number of species, or $\Delta\hat{H}_m$ and $\Delta\hat{H}_v$ at the normal melting and boiling point temperatures ($P = 1$ atm), which are also listed in Table B.1. If latent heat data are not available for a species, $\Delta\hat{H}_m$ and $\Delta\hat{H}_v$ may be estimated using formulas given in Section 8.4b.
- You can use the formulas given above to determine the specific enthalpy of any species in one state relative to that species in any other state. For example, to calculate $\hat{H}$ for benzene vapor at temperature 300°C and 15 atm relative to solid benzene at a reference state of −20°C and 1 atm, you would carry out the following steps.

1. Heat the solid from the reference temperature (−20°C) to its normal melting point T_{mp}, which from Table B.1 is 5.53°C.

$$\Delta\hat{H}_1 = \int_{0°C}^{5.53°C} (C_p)_{solid}\, dT$$

$(C_p)_{solid}$ is not listed in Table B.2, so it must either be found elsewhere or estimated using Kopp's rule. The latter provides a crude approximation but a very reasonable one to make in this case, considering how little this step will contribute to the overall enthalpy change.

2. Melt the solid at T_{mp}. $\Delta\hat{H}_2 = \Delta\hat{H}_m(5.53°C)$, which from Table B.1 is 9.837 kJ/mol.
3. Heat the liquid from T_{mp} to the normal boiling point, T_{bp}, which from Table B.1 is 80.10°C.

$$\Delta\hat{H}_3 = \int_{5.53°C}^{80.1°C} (C_p)_{liquid}\, dT$$

A polynomial formula for $(C_p)_{\text{liquid}}$ is given in Table B.2. Since it applies to T expressed in kelvin units, the limits of the integral should be changed to their kelvin equivalents.

4. Vaporize the liquid at T_{bp}. $\Delta\hat{H}_4 = \Delta\hat{H}_{\text{v}}(80.1°\text{C})$, which from Table B.1 is 30.765 kJ/mol.
5. Heat the vapor from T_{bp} to 300°C.

$$\Delta\hat{H}_5 = \int_{80.1°\text{C}}^{300°\text{C}} (C_p)_{\text{vapor}}\, dT$$

A formula for $(C_p)_{\text{vapor}}$ is given in Table B.2.

6. Bring the vapor from 1 atm to 15 atm at 300°C. $\Delta\hat{H}_6 \approx 0$ as long as the vapor behaves like an ideal gas, which it would at this high temperature.
7. Add the enthalpy changes for each of the preceding steps to calculate the desired specific enthalpy.

- The *psychrometric chart* (or *humidity chart*) contains values of a number of process variables for air–water vapor systems at 1 atm. The values listed on the chart include *dry-bulb temperature* (the temperature measured by common temperature-measurement instruments), *moisture content* or *absolute humidity* (mass ratio of water vapor to dry air), *relative humidity, humid volume* (volume per mass of dry air), *wet-bulb temperature* (the temperature reading on a thermometer with a water-saturated wick around the bulb immersed in a flowing stream of humid air), and *enthalpy per mass of dry air.* If you know the values of any two of these variables for humid air at or near 1 atm, you can use the chart to determine the values of the other four, which can greatly simplify material and energy balance calculations.
- In *adiabatic cooling* operations, a stream of warm gas is brought into contact with a stream of cold liquid, causing the gas to cool and some liquid to evaporate. If (a) the gas is dry or humid air, the liquid is water, and the process takes place at about 1 atm, (b) the process is adiabatic, (c) the heat capacities of liquid water, water vapor, and air can be considered constant over the temperature range of the process, and (d) enthalpy changes associated with temperature changes of the liquid may be neglected, then the final state of the air must lie on the same wet-bulb temperature line as the state of the inlet air on the psychrometric chart.
- An enthalpy change known as the *heat of mixing* or *heat of solution* is associated with the mixing of certain liquids (like acids and water) and the dissolving of some gases or solids in a liquid solvent at a given temperature and pressure. An *ideal* solution is one for which the heat of mixing or solution is negligible, so that the enthalpy of the solution is the sum of the enthalpies of the pure solution components at the same temperature and pressure. All gas mixtures are ideal, as are mixtures of structurally similar liquid compounds (like benzene, toluene, and xylene). Table B.11 gives heats of mixing at 25°C and 1 atm for aqueous sulfuric acid solutions and heats of solution at the same temperature and pressure for aqueous solutions of HCl(g) (hydrochloric acid) and NaOH(s) (caustic soda).
- To perform energy balance calculations on processes involving nonideal solutions, take the pure components at 25°C as references. To determine the specific enthalpy of a feed or product solution, look it up on an *enthalpy–concentration chart* if one is available (e.g., Figure 8.5-1 for sulfuric acid solutions or Figure 8.5-2 for aqueous ammonia solutions). Otherwise, form the solution at 25°C [$\Delta\hat{H} = \Delta\hat{H}_{\text{s}}(25°\text{C})$] and heat or cool it to its state in the process ($\Delta\hat{H} = \int_{25°\text{C}}^{T} C_p\, dT$). For the latter step, either find heat capacity data for the solution or (for dilute solutions) assume that the heat capacity is that of the pure solvent.

Interactive Tutorial #5
Questions with Immediate Feedback →

Note: This would be a good time to work through Interactive Tutorial #5.

PROBLEMS

8.1. The specific internal energy of formaldehyde (HCHO) vapor at 1 atm and moderate temperatures is given by the formula

$$\hat{U}(\text{J/mol}) = 25.96T + 0.02134T^2$$

where T is in °C.

(a) Calculate the specific internal energies of formaldehyde vapor at 0°C and 100°C. What reference temperature was used to generate the given expression for $\hat{U}$?

(b) The value of $\hat{U}$ calculated for 100°C is not the true value of the specific internal energy of formaldehyde vapor at this condition. Why not? (*Hint:* Refer back to Section 7.5a.) Briefly state the physical significance of the calculated quantity.

(c) Use the closed system energy balance equation to calculate the heat (J) required to raise the temperature of 3.0 mol HCHO at constant volume from 0°C to 100°C. List all of your assumptions.

(d) From the definition of heat capacity at constant volume, derive a formula for $C_v(T)$[J/mol·°C]. Then use this formula and Equation 8.3-6 to calculate the heat (J) required to raise the temperature of 3.0 mol of HCHO(v) at constant volume from 0°C to 100°C. [You should get the same result you got in part (c).]

8.2. The heat capacity at constant pressure of hydrogen cyanide is given by the expression

$$C_p[\text{J/(mol·°C)}] = 35.3 + 0.0291T(\text{°C})$$

(a) Write an expression for the heat capacity at constant volume for HCN, assuming ideal gas behavior.

(b) Calculate $\Delta\hat{H}$(J/mol) for the constant-pressure process

$$\text{HCN(v, 25°C, 0.80 atm)} \rightarrow \text{HCN(v, 100°C, 0.80 atm)}$$

(c) Calculate $\Delta\hat{U}$(J/mol) for the constant-volume process

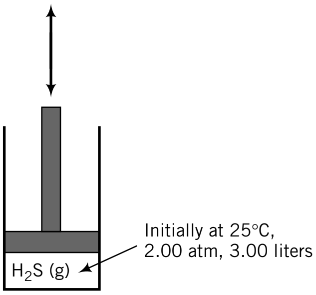
$$\text{HCN(v, 25°C, 50 m}^3\text{/kmol)} \rightarrow \text{HCN(v, 100°C, 50 m}^3\text{/kmol)}$$

(d) If the process of part (b) were carried out in such a way that the initial and final pressures were each 0.80 atm but the pressure varied during the heating, the value of $\Delta\hat{H}$ would still be what you calculated assuming a constant pressure. Why is this so?

8.3. The heat capacity at constant volume of hydrogen sulfide at low pressures is

$$C_v[\text{kJ/(mol·°C)}] = 0.0252 + 1.547 \times 10^{-5}T - 3.012 \times 10^{-9}T^2$$

where T is in °C. A quantity of H_2S is kept in a piston-fitted cylinder with initial temperature, pressure, and volume equal to 25°C, 2.00 atm, and 3.00 liters, respectively.



(a) Calculate the heat (kJ) required to raise the gas temperature from 25°C to 1000°C if the heating takes place at constant volume (i.e., if the piston does not move), retaining successively one term, two terms, and all three terms of the heat capacity formula. (See Example 8.3-1.) Determine the percentage errors in Q that result from retaining only one and two terms of the heat capacity formula, assuming that the full expression yields the correct result.

(b) For a closed system at constant pressure with negligible kinetic and potential energy changes, the energy balance equation is $Q = \Delta H$. Use Equation 8.3-12 to determine an expression for the heat capacity at constant pressure (C_p) for H_2S, assuming ideal gas behavior. Then use it to calculate the heat (J) required to raise the gas from 25°C to 1000°C at constant pressure. What would the piston do during this process?

(c) What is the physical significance of the difference between the values of Q calculated in parts (a) and (b)?

8.4. Use data in Table B.2 to calculate the following:

(a) The heat capacity (C_p) of liquid benzene at 40°C.

(b) The heat capacity at constant pressure of benzene vapor at 40°C.

(c) The heat capacity at constant pressure of solid carbon at 40°C.
(d) $\Delta\hat{H}$(kJ/mol) for benzene vapor going from 40°C to 300°C.
(e) $\Delta\hat{H}$(kJ/mol) for solid carbon going from 40°C to 300°C.

8.5. Estimate the specific enthalpy of steam (kJ/kg) at 350°C and 100 bar relative to steam at 100°C and 1 atm using:
(a) The steam tables.
(b) Table B.2 and assuming ideal gas behavior.
What is the physical significance of the difference between the values of $\hat{H}$ calculated by the two methods?

8.6. Calculate $\Delta\hat{H}$ for each of the following processes. In each case, restate your result as a specific enthalpy relative to a reference state. [The solution—which you should verify—and the restatement for part (a) are given as an illustration.] Assume that the process pressures are low enough for $\hat{H}$ to be considered independent of pressure, so that the formulas of Table B.2 (which strictly apply at 1 atm) can be used.
(a) $CH_3COCH_3(l, 15°C) \longrightarrow CH_3COCH_3(l, 55°C)$.

Solution: $\boxed{\Delta\hat{H} = 5.180 \text{ kJ/mol}}$

The specific enthalpy of liquid acetone at 55°C relative to liquid acetone at 15°C is 5.180 kJ/mol.

(b) $n\text{-}C_6H_{14}(l, 25°C) \longrightarrow n\text{-}C_6H_{14}(l, 80°C)$
(c) $n\text{-}C_6H_{14}(v, 500°C) \longrightarrow n\text{-}C_6H_{14}(v, 0°C)$. (Make statements about both the specific enthalpy of hexane vapor at 500°C relative to hexane vapor at 0°C and the specific enthalpy of hexane vapor at 0°C relative to hexane vapor at 500°C.)

8.7. Two formulas for the heat capacity of CO are given here:

$$C_p[\text{cal/(mol·°C)}] = 6.890 + 0.001436T(°\text{C})$$

$$C_p[\text{Btu/(lb-mole·°F)}] = 6.864 + 0.0007978T(°\text{F})$$

Starting with the first formula, derive the second. (Recall Section 2.5, and remember that the temperature unit in the denominator of C_p refers to a temperature interval.)

8.8. Table B.2 lists values of the heat capacity of liquid ethanol at two temperatures. Use the tabulated values to derive a linear expression for $C_p(T)$; then use the derived expression and data in Table B.1 to calculate the heat transfer rate (kW) required to bring a stream of liquid ethanol flowing at 55.0 L/s from 20°C to the boiling point at 1 atm.

Student Workbook

Physical Property database
Quickly integrates tabulated heat capacities

8.9. Chlorine gas is to be heated from 100°C and 1 atm to 200°C.
(a) Calculate the heat input (kW) required to heat a stream of the gas flowing at 5.0 kmol/s at constant pressure.
(b) Calculate the heat input (kJ) required to raise the temperature of 5.0 kmol of chlorine in a closed rigid vessel from 100°C and 1 atm to 200°C. (Suggestion: Evaluate $\Delta\hat{U}$ directly from the result of the first calculation, so that you do not have to perform another integration.) What is the physical significance of the numerical difference between the values calculated in parts (a) and (b)?
(c) To accomplish the heating of part (b), you would actually have to supply an amount of heat to the vessel greater than the amount calculated. Why?

8.10. The heat required to raise the temperature of m (kg) of a liquid from T_1 to T_2 at constant pressure is

$$Q = \Delta H = m\int_{T_1}^{T_2} C_p(T)\,dT \qquad \textbf{(1)}$$

In high school and in first-year college physics courses, the formula is usually given as

$$Q = mC_p\,\Delta T = mC_p(T_2 - T_1) \qquad \textbf{(2)}$$

(a) What assumption about C_p is required to go from Equation 1 to Equation 2?
(b) The heat capacity (C_p) of liquid n-hexane is measured in a **bomb calorimeter.** A small reaction flask (the bomb) is placed in a well-insulated vessel containing 2.00 L of liquid $n\text{–}C_6H_{14}$ at $T =$ 300 K. A combustion reaction known to release 16.73 kJ of heat takes place in the bomb, and the subsequent temperature rise of the system contents is measured and found to be 3.10 K. In a separate experiment, it is found that 6.14 kJ of heat is required to raise the temperature of

everything in the system except the hexane by 3.10 K. Use these data to estimate C_p[kJ/(mol·K)] for liquid n-hexane at $T \approx 300$ K, assuming that the condition required for the validity of Equation 2 is satisfied. Compare your result with a tabulated value.

8.11. The heat capacities of a substance have been defined as

$$C_v = \left(\frac{\partial \hat{U}}{\partial T}\right)_V, \quad C_p = \left(\frac{\partial \hat{H}}{\partial T}\right)_P$$

Use the defining relationship between $\hat{H}$ and $\hat{U}$ and the fact that $\hat{H}$ and $\hat{U}$ for ideal gases are functions only of temperature to prove that $C_p = C_v + R$ for an ideal gas.

8.12. Ralph Rackstraw, your next-door neighbor, surprised his wife last January by having a hot tub installed in their back yard while she was away on a business trip. It surprised her, all right, but instead of being pleased she was horrified. "Have you lost your mind, Ralph?" she sputtered. "It will cost a fortune to keep this thing hot." "Don't be silly, Josephine," he replied. "It can't cost more than pennies a day, even in the dead of winter." "No way—and when did you become such an expert, anyway?" "I guarantee it will cost nothing—and I don't see your Ph.D. certificate on the kitchen wall either." They argued for awhile and then, remembering your chemical engineering education, came to ask you to settle it for them. You asked a few questions, made several observations, converted everything to metric units, and arrived at the following data, all corresponding to an average outside air temperature of about 5°C.

- The tub holds 1230 liters of water.
- Rackstraw normally keeps the tub temperature at 29°C, raises it to 40°C when he plans to use it, keeps it at 40°C for about one hour, and drops it back to 29°C when he is finished.
- During heating, it takes about three hours for the water temperature to rise from 29°C to 40°C. When the heat is shut off, it takes eight hours for the water temperature to drop back to 29°C.
- Electricity costs 10 cents per kilowatt-hour.

Taking the heat capacity of the tub contents to be that of pure liquid water and neglecting evaporation, answer the following questions.

(a) What is the average rate of heat loss (kW) from the tub to the outside air? (*Hint:* Consider the period when the tub temperature is dropping from 40°C to 29°C.)

(b) At what average rate (kW) does the tub heater deliver energy to the water when raising the water temperature? What is the total quantity of electricity (kW·h) that the heater must deliver during this period? [Consider the result of part (a) when performing the calculation.]

(c) (These answers should settle the argument.) Consider a day in which the tub is used once. Use the results of parts (a) and (b) to estimate the cost ($) of heating the tub from 29°C to 40°C and the cost ($) of keeping the tub at a constant temperature. (There is no cost for the period in which T is dropping.) What is the total daily cost of running the tub? Assume the rate of heat loss is independent of the tub temperature.

(d) The tub lid, which is an insulator, is removed when the tub is in use. Explain how this fact would probably affect your cost estimates in part (c).

8.13. Use tabulated specific enthalpies from Tables B.8 and B.9 to calculate $\Delta\hat{H}$ for the following processes, all taking place at low pressures:

(a) $N_2(25°C) \rightarrow N_2(700°C)$ **(c)** $CO_2(300°C) \rightarrow CO_2(1250°C)$

(b) $H_2(800°F) \rightarrow H_2(77°F)$ **(d)** $O_2(970°F) \rightarrow O_2(0°F)$

8.14. Calculate the rate of cooling (kW) required to bring 300 kg/min of carbon monoxide from 450°C to 50°C, performing the calculation (a) using Table B.2 and (b) using Table B.8. Considering how much simpler the second calculation is, why would you ever use the polynomial formulas of Table B.2 as opposed to tabulated enthalpies to calculate enthalpy changes?

8.15. A stream of water vapor flowing at a rate of 250 mol/h is brought from 600°C and 10 bar to 100°C and 1 atm.

(a) Estimate the required cooling rate (kW) three ways: (i) from the steam tables, (ii) using heat capacity data in Table B.2, and (iii) using specific enthalpy data in Table B.8.

(b) Which of the answers in part (a) is most accurate, and why?

(c) What is the physical significance of the difference between the values calculated with methods (i) and (ii)?

8.16. A stream of air at 77°F and 1.2 atm absolute flowing at a rate of 200 ft^3/h is blown through ducts that pass through the interior of a large industrial motor. The air emerges at 500°F. Using tabulated specific enthalpy data, calculate the rate at which the air is removing heat generated by the motor. What assumption have you made about the pressure dependence of the specific enthalpy of air?

8.17. Calculate the heat required to raise 50 kg of solid sodium carbonate (Na_2CO_3) from 10°C to 50°C at 1 atm using

(a) the true heat capacity of Na_2CO_3, which is 1.14 kJ/(kg·°C).

(b) a heat capacity estimated by Kopp's rule. Calculate the percentage error in the latter calculation.

Student Workbook

8.18. A liquid mixture of 30 wt% acetone and 70 wt% 2-methyl-1-pentanol ($C_6H_{14}O$) is cooled from 45°C to 20°C. Calculate the associated specific enthalpy change in J/g, using Kopp's rule to estimate any heat capacity for which a tabulated value cannot be found. State all assumptions you make.

8.19. A gas mixture contains one-third methane by volume (recall what that means in terms of mole%) and the balance oxygen at 350°C and 3.0 bar. Calculate the specific enthalpy of this stream in kJ/kg (not per kmol) relative to the pure components at 25°C and 1 atm. *State clearly all assumptions.*

8.20. The radiant energy incident on the earth's surface on a sunny day is roughly 900 W/m^2. Collecting and focusing sunlight and using the focused beam to heat a fluid is an old idea, and as the environmental costs of fossil fuel combustion mount, solar heating becomes an increasingly attractive alternative.

Suppose a house is to be designed that will have a circulating forced air central heating unit, and solar energy is contemplated as a heat source (backed up with a conventional furnace to be used on cloudy days). If air is to be fed at a rate of 1000 m^3/min at 30°C and 1 atm, and the air is to be heated to 55°C before being discharged into the living space, what is the required area of the solar collector plates? Assume 30% of the radiant energy incident on the plates is used to heat the air.

8.21. Propane is to be burned with 15.0% excess air. Before entering the furnace, the air is preheated from 32°F to 575°F. At what rate (Btu/h) must heat be transferred to the air if the feed rate of propane is 1.35×10^5 SCFH [ft^3(STP)/h]?

Student Workbook

Equipment Encyclopedia
boiler

8.22. A fuel gas containing 95 mole% methane and the balance ethane is burned completely with 25% excess air. The stack gas leaves the furnace at 900°C and is cooled to 450°C in a **waste heat boiler,** a heat exchanger in which heat lost by cooling gases is used to produce steam from liquid water for heating, power generation, or process applications.

(a) Taking as a basis of calculation 100 mol of the fuel gas fed to the furnace, calculate the amount of heat (kJ) that must be transferred from the gas in the waste heat boiler to accomplish the indicated cooling.

(b) How much saturated steam at 50 bar can be produced from boiler feedwater at 40°C for the same basis of calculation? (Assume all the heat transferred from the gas goes into the steam production.)

(c) At what rate (kmol/s) must fuel gas be burned to produce 1250 kg steam per hour (an amount required elsewhere in the plant) in the waste heat boiler? What is the volumetric flow rate (m^3/s) of the gas leaving the boiler?

(d) Briefly explain how the waste heat boiler contributes to the plant profitability. (Think about what would be required in its absence.)

8.23. Twenty liters of liquid *n*-propyl benzoate ($C_6H_5CO_2C_3H_7$, SG = 1.021) and 15 liters of liquid benzene are mixed and heated from 25°C to 75°C. Calculate the required heat input (kJ), using Kopp's rule when necessary. State all assumptions you make.

Equipment Encyclopedia
heat exchanger

8.24. Propane gas enters a continuous adiabatic heat exchanger[16] at 40°C and 250 kPa and exits at 240°C. Superheated steam at 300°C and 5.0 bar enters the exchanger flowing countercurrently to the propane and exits as a saturated liquid at the same pressure.

(a) Taking as a basis 100 mol of propane fed to the exchanger, draw and label a process flowchart. Include in your labeling the volume of propane fed (m^3), the mass of steam fed (kg), and the volume of steam fed (m^3).

(b) Calculate values of the labeled specific enthalpies in the following inlet–outlet enthalpy table for this process.

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[16] An adiabatic heat exchanger is one for which no heat is exchanged with the surroundings. All of the heat lost by the hot stream is transferred to the cold stream.

References: H_2O(l, 0.01°C), C_3H_8(g, 40°C)

Species	n_{in}	$\hat{H}_{\text{in}}$	n_{out}	$\hat{H}_{\text{out}}$
C_3H_8	100 mol	$\hat{H}_a$(kJ/mol)	100 mol	$\hat{H}_c$(kJ/mol)
H_2O	m_w(kg)	$\hat{H}_b$(kJ/kg)	m_w(kg)	$\hat{H}_d$(kJ/kg)

(c) Use an energy balance to calculate the required mass feed rate of the steam. Then calculate the volumetric feed ratio of the two streams (m^3 steam fed/m^3 propane fed). Assume ideal gas behavior for the propane but not the steam and recall that the exchanger is adiabatic.

(d) Calculate the heat transferred from the water to the propane (kJ/m^3 propane fed). (*Hint:* Do an energy balance on either the water or the propane rather than on the entire heat exchanger.)

(e) Over a period of time, scale builds up on the heat transfer surface, resulting in a lower rate of heat transfer between the propane and the steam. What changes in the outlet streams would you expect to see as a result of the decreased heat transfer?

Equipment Encyclopedia
heat exchanger

8.25. Saturated steam at 300°C is used to heat a countercurrently flowing stream of methanol vapor from 65°C to 260°C in an adiabatic heat exchanger. The flow rate of the methanol is 5500 standard liters per minute, and the steam condenses and leaves the heat exchanger as liquid water at 90°C.

(a) Calculate the required flow rate of the entering steam in m^3/min.

(b) Calculate the rate of heat transfer from the water to the methanol (kW).

Equipment Encyclopedia
membrane

8.26. An adiabatic membrane separation unit is used to dry (remove water vapor from) a gas mixture containing 10.0 mole% H_2O(v), 10.0 mole% CO, and the balance CO_2. The gas enters the unit at 30°C and flows past a semipermeable membrane. Water vapor permeates through the membrane into an air stream. The dried gas leaves the separator at 30°C containing 2.0 mole% H_2O(v) and the balance CO and CO_2. Air enters the separator at 50°C with an absolute humidity of 0.002 kg H_2O/kg dry air and leaves at 48°C. Negligible quantities of CO, CO_2, O_2, and N_2 permeate through the membrane. All gas streams are at approximately 1 atm.

(a) Draw and label a flowchart of the process and carry out a degree-of-freedom analysis to verify that you can determine all unknown quantities on the chart.

(b) Calculate (i) the ratio of entering air to entering gas (kg humid air/mol gas) and (ii) the relative humidity of the exiting air.

(c) List several desirable properties of the membrane. (Think about more than just what it allows and does not allow to permeate.)

8.27. A gas containing water vapor has a dry-basis composition of 8.5 mole% CO, 10.5% CO_2, 0.5% O_2, and 80.5% N_2. The gas leaves a catalyst regeneration unit at 620°C and 1 atm with a dew point of 57°C at a flow rate of 28.5 SCMH [m^3(STP)/h]. Valuable solid catalyst particles entrained in the gas are to be recovered in an electrostatic precipitator, but the gas must first be cooled to 425°C to prevent damage to the precipitator electrodes. The cooling is accomplished by spraying water at 20°C into the gas.

(a) Use simultaneous material and energy balances on the spray cooler to calculate the required water feed rate (kg/h). Treat the spray cooler as adiabatic and neglect the heat transferred from the entrained solid particles as they cool.

(b) In terms that a high school senior could understand, explain the operation of the spray cooler in this problem. (What happens when the cold water contacts the hot gas?)

8.28. On a cold winter day the temperature is 2°C and the relative humidity is 15%. You inhale air at an average rate of 5500 mL/min and exhale a gas saturated with water at body temperature, roughly 37°C. If the mass flow rates of the inhaled and exhaled air (excluding water) are the same, the heat capacities (C_p) of the water-free gases are each 1.05 J/(g·°C), and water is ingested into the body as a liquid at 22°C, at what rate in J/day do you lose energy by breathing? Treat breathing as a continuous process (inhaled air and liquid water enter, exhaled breath exits) and neglect work done by the lungs.

8.29. Seventy-five liters of liquid ethanol at 70.0°C and 55 L of liquid water at 20.0°C are to be mixed in a well-insulated flask. The energy balance for this constant pressure process is $Q = \Delta H$.

(a) Neglecting evaporation and the heat of mixing, estimate the final mixture temperature. (As part of the calculation, use data in Table B.2 to estimate a linear formula for the heat capacity of liquid ethanol.)

(b) If the experiment were actually performed and the final mixture temperature were measured, it would almost certainly not equal the value estimated in part (a). List as many reasons as you can think of. (There are at least seven of them, most involving approximations made in the estimation.)

Student Workbook

8.30. A stream of air at 500°C and 835 torr with a dew point of 30°C flowing at a rate of 1515 L/s is to be cooled in a spray cooler. A fine mist of liquid water at 25°C is sprayed into the hot air at a rate of 110.0 g/s and evaporates completely. The cooled air emerges at 1 atm.

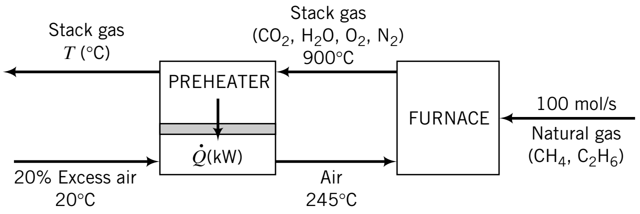
(a) Calculate the final temperature of the emerging air stream, assuming that the process is adiabatic. (*Suggestion*: Derive expressions for the enthalpies of dry air and water at the outlet air temperature, substitute them into the energy balance, and use a spreadsheet to solve the resulting fourth-order polynomial equation.)

(b) At what rate (kW) is heat transferred from the hot air feed stream in the spray cooler? What becomes of this heat?

(c) In a few sentences, explain how this process works in terms that a high school senior could understand. Incorporate the results of parts (a) and (b) in your explanation.

8.31. In the manufacture of nitric acid, ammonia and preheated air are mixed to form a gas containing 10.0 mole% NH_3 at 600°C. The ammonia is then catalytically oxidized to form NO_2, which is absorbed in water to form HNO_3. If ammonia enters the gas blending unit at 25°C at a rate of 520 kg/h and heat is lost from the mixer to its surroundings at a rate of 7.00 kW, determine the temperature to which the air must be preheated. (See Example 8.3-6.)

8.32. A natural gas containing 95 mole% methane and the balance ethane is burned with 20.0% excess air. The stack gas, which contains no unburned hydrocarbons or carbon monoxide, leaves the furnace at 900°C and 1.2 atm and passes through a heat exchanger. The air on its way to the furnace also passes through the heat exchanger, entering it at 20°C and leaving it at 245°C.



(a) Taking as a basis 100 mol/s of the natural gas fed to the furnace, calculate the required molar flow rate of air, the molar flow rate and composition of the stack gas, the required rate of heat transfer in the preheater, $\dot{Q}$ (write an energy balance on the air), and the temperature at which the stack gas leaves the preheater (write an energy balance on the stack gas). *Note*: The problem statement does not give you the fuel feed temperature. Make a reasonable assumption, and state why your final results should be nearly independent of what you assume.

(b) What would $\dot{Q}$ be if the actual feed rate of the natural gas were 350 SCMH [standard cubic meters per hour, m^3(STP)/h]? Scale up the flowchart of part (a) rather than repeating the entire calculation.

8.33. The heat capacity at constant pressure of a gas is determined experimentally at several temperatures, with the following results:

T(°C)	0	100	200	300	400	500	600
C_p[J/(mol·°C)]	33.5	35.1	36.7	38.4	40.2	42.0	43.9

(a) Calculate the heat (kW) required to raise 150 mol/s of the gas from 0°C to 600°C, using Simpson's rule (Appendix A.3) to integrate the tabulated heat capacities.

(b) Use the method of least squares (Appendix A.1) to derive a linear expression for $C_p(T)$ in the range 0°C to 600°C, and use this expression to estimate once again the heat (kW) required to raise 150 mol/s of the gas from 0°C to 600°C. If the estimates differ, in which one would you have more confidence, and why?

***8.34.** As part of a design calculation, you must evaluate an enthalpy change for an obscure organic vapor that is to be cooled from 1800°C to 150°C in a heat exchanger. You search through all the standard references for tabulated enthalpy or heat capacity data for the vapor but have no luck at all, until you finally stumble on an article in the May 1922 *Antarctican Journal of Obscure Organic Vapors* that contains a plot of C_p[cal/(g·°C)] on a logarithmic scale versus $[T\,(°\text{C})]^{1/2}$ on a linear scale. The plot is a straight line through the points ($C_p = 0.329$, $T^{1/2} = 7.1$) and ($C_p = 0.533$, $T^{1/2} = 17.3$).

(a) Derive an equation for C_p as a function of T.

(b) Suppose the relationship of part (a) turns out to be

$$C_p = 0.235 \exp[0.0473T^{1/2}]$$

and that you wish to evaluate

$$\Delta\hat{H}(\text{cal/g}) = \int_{1800°\text{C}}^{150°\text{C}} C_p\, dT$$

First perform the integration analytically, using a table of integrals if necessary; then write a spreadsheet or computer program to do it using Simpson's rule (Appendix A.3). Have the program evaluate C_p at 11 equally spaced points from 150°C to 1800°C, estimate and print the value of ΔH, and repeat the calculation using 101 points. What can you conclude about the accuracy of the numerical calculation?

8.35. A stream of ethylene glycol vapor at its normal boiling point and 1 atm flowing at a rate of 175 kg/min is to be condensed at constant pressure. The product stream from the condenser is liquid glycol at the condensation temperature.

(a) Using data in Table B.1, calculate the rate (kW) at which heat must be transferred from the condenser.

(b) If heat were transferred at a lower rate than that calculated in part (a), what would the state of the product stream be? (Deduce as much as you can about the phase and the temperature of the stream.)

(c) If heat were transferred at a higher rate than that calculated in part (a), what could you deduce about the state of the product stream? Sketch a phase diagram (see Figure 6.1-1 on p. 241) and use it to explain your answer.

Student Workbook

8.36. **(a)** Determine the specific enthalpy (kJ/mol) of n-hexane vapor at 200°C and 2.0 atm relative to n-hexane liquid at 20°C and 1.0 atm, assuming ideal gas behavior for the vapor. Show clearly the process path you construct for this calculation and give the enthalpy changes for each step. State where you used the ideal gas assumption.

(b) What is the enthalpy of n-hexane liquid at 20°C and 1.0 atm relative to n-hexane vapor at 200°C and 2.0 atm? (This part should not take much time to complete.)

(c) Beginning with the value of $\hat{H}$ calculated in part (a) and still assuming ideal gas behavior, determine the specific internal energy of the vapor at 200°C and 2.0 atm. Once again, state where you used the ideal gas assumption.

8.37. Calculate the heat of vaporization of water (kJ/mol) at 50°C and low pressures from the tabulated heat of vaporization in Table B.1 and data in Table B.2 and Table B.8. Show clearly the process path you construct for the calculation. Compare your answer with the value of $\Delta\hat{H}_v(50°\text{C})$ given in Table B.5 (convert it to kJ/mol for the comparison). What might account for the difference between the two values?

Equipment Encyclopedia
condenser

8.38. Benzene vapor at 580°C is cooled and converted to a liquid at 25°C in a continuous condenser. The condensate is drained into 1.75-m^3 drums, each of which takes 2.0 minutes to fill. Calculate the rate (kW) at which heat is transferred from the benzene in the condenser.

Equipment Encyclopedia
adsorption column

8.39. In gas adsorption a vapor is transferred from a gas mixture to the surface of a solid. (See Section 6.7.) An approximate but useful way of analyzing adsorption is to treat it simply as condensation of vapor on a solid surface.

Suppose a nitrogen stream at 35°C and 1 atm containing carbon tetrachloride with a 15% relative saturation is fed at a rate of 10.0 mol/min to a 6-kg bed of activated carbon. The temperature and pressure of the gas do not change appreciably from the inlet to the outlet of the bed, and there

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*Computer problem.

is no CCl_4 in the gas leaving the adsorber. The carbon can adsorb 40% of its own mass of carbon tetrachloride before becoming saturated. Neglecting the effect of temperature on the heat of vaporization of CCl_4, estimate the rate at which heat must be removed from the adsorber (kJ/min) to keep the process isothermal and the time (min) it will take to saturate the bed.

8.40. If carbon dioxide is cooled at 1 atm, it condenses directly to a solid (**dry ice**) at −78.4°C. The heat of sublimation at this temperature is $\Delta\hat{H}_{\text{sub}}(-78.4°\text{C}) = 6030$ cal/mol.

(a) Calculate the heat removal rate (kW) required to produce 300 kg/h of dry ice at 1 atm and −78.4°C if CO_2(v) at 20°C is the feed.

(b) Suppose the process is carried out at 9.9 atm instead of 1 atm with the same initial and final temperatures. Referring to Figure 6.1-1*b* on p. 241, write an expression for the required heat removal rate in terms of heat capacities and latent heats of CO_2 in different phases.

8.41. Molten sodium chloride is to be used as a constant-temperature bath for a high-temperature chemical reactor. Two hundred kilograms of solid NaCl at 300 K is charged into an insulated vessel, and a 3000 kW electrical heater is turned on, raising the salt to its melting point of 1073 K and melting it at a constant pressure of 1 atm.

(a) The heat capacity (C_p) of solid NaCl is 50.41 J/(mol·K) at $T = 300$ K, and 53.94 J/(mol·K) at $T = 500$ K, and the heat of fusion of NaCl at 1073 K is 30.21 kJ/mol. Use these data to determine a linear expression for $C_p(T)$ and to calculate $\Delta\hat{H}$(kJ/mol) for the transition of NaCl from a solid at 300 K to a liquid at 1073 K.

(b) Write and solve the energy balance equation for this closed system isobaric process to determine the required heat input in kilojoules.

(c) If 85% of the full power of 3000 kW goes into heating and melting the salt, how long does the process take?

8.42. Estimate the heat of vaporization of ethyl benzene at its normal boiling point using Trouton's rule and Chen's rule and compare the results with a tabulated value of this quantity. Then estimate $\Delta\hat{H}_{\text{v}}$ at 100°C using Watson's correlation.

8.43. You are writing energy balances for a compound for which you cannot find heat capacity or latent heat data. All you know about the material are its molecular formula ($C_7H_{12}N$) and that it is a liquid at room temperature and has a normal boiling point of 200°C. Use this information to estimate the enthalpy of the vapor of this substance at 200°C relative to the liquid at 25°C. (Recall Section 8.3c.)

8.44. Estimate the heat of vaporization (kJ/mol) of benzene at a pressure of 100 mm Hg, using each of the following correlations and data:

(a) The heat of vaporization at the normal boiling point given in Table B.1, the boiling point at 100 mm Hg as determined from the Antoine equation, and Watson's correlation.

(b) The Clausius–Clapeyron equation and the boiling points at 50 mm Hg and 150 mm Hg as determined from the Antoine equation.

(c) The heat of vaporization at the normal boiling point given in Table B.1, the boiling point at 100 mm Hg as determined from the Antoine equation, and heat capacity data given in Table B. 2.

Equipment Encyclopedia
condenser

8.45. A stream of pure cyclopentane vapor flowing at a rate of 1550 L /s at 150°C and 1 atm enters a cooler in which 55% of the feed is condensed at constant pressure.

(a) What is the temperature at the condenser outlet? Explain how you know (a single sentence should suffice).

(b) Prepare and fill in an inlet–outlet enthalpy table and calculate the required cooling rate in kW.

Student Workbook

Equipment Encyclopedia
condenser

8.46. Humid air at 50°C and 1.0 atm with 2°C of superheat is fed to a condenser. Gas and liquid streams leave the condenser in equilibrium at 20°C and 1 atm.

(a) Assume a basis of calculation of 100 mol inlet air, draw and label a flowchart (including Q in the labeling), and carry out a degree-of-freedom analysis to verify that all labeled variables can be determined.

(b) Write in order the equations you would solve to calculate the mass of water condensed (kg) per cubic meter of air fed to the condenser. Circle the unknown variable for which you would solve each equation. Do not do any of the calculations.

(c) Prepare an inlet–outlet enthalpy table, inserting labels for unknown specific enthalpies ($\hat{H}_1$, $\hat{H}_2, \ldots$). Write expressions for the labeled specific enthalpies, substituting values or formulas for heat capacities and latent heats but not calculating the values of the specific enthalpies. Then write an expression for the rate at which heat must be transferred from the unit (kJ) per cubic meter of air fed to the condenser.

(d) Solve your equations by hand to calculate kg H_2O condensed/m^3 air fed and kJ transferred/m^3 air fed.

*__(e)__ Use an equation-solving program to perform the calculations of part (d).

(f) What cooling rate (kW) would be required to process 250 m^3 air fed/h?

8.47. An air conditioner cools 226 m^3/min of humid air at 36°C and 98% relative humidity to 10°C.

(a) Do a degree-of-freedom analysis to prove that enough information is available to determine the required cooling duty (rate of heat transfer).

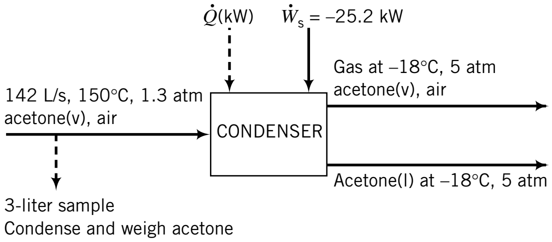
(b) Calculate the rate of condensation of water in the unit and the cooling duty in tons (1 ton = 12,000 Btu/h).

Equipment Encyclopedia
condenser

8.48. A gas stream containing n-hexane in nitrogen with a relative saturation of 90% is fed to a condenser at 75°C and 3.0 atm absolute. The product gas emerges at 0°C and 3.0 atm at a rate of 746.7 m^3/h. Calculate the percentage condensation of hexane (moles condensed/mole fed) and the rate (kW) at which heat must be transferred from the condenser.

Equipment Encyclopedia
condenser

8.49. A gas stream containing acetone in air flows from a solvent recovery unit at a rate of 142 L/s at 150°C and 1.3 atm. The stream flows into a condenser which liquefies most of the acetone, and the liquid and gas outlet streams are in equilibrium at −18°C and 5.0 atm. Shaft work is delivered to the system at a rate of 25.2 kW to achieve the compression from 1.3 atm to 5.0 atm. To determine the condenser feed stream composition, a 3.00-liter sample of the gas is taken and cooled to a temperature at which essentially all the acetone in the sample is recovered as a liquid. The liquid is poured into an empty flask with a mass of 4.017 g. The flask containing the liquid acetone is weighed and found to have a mass of 4.973 g.



(a) Carry out a degree-of-freedom analysis to show that enough information is available to determine the compositions of all streams and the required heat transfer rate.

(b) Write out a complete set of equations for the molar flow rates of all streams, the mole fractions of acetone in the feed and product gas streams, and the rate (kW) at which heat must be removed in the condenser. *Do no calculations.*

(c) Solve the equations of part (b) by hand.

*__(d)__ Solve the equations of part (b) using an equation-solving program.

8.50. A mixture of n-hexane vapor and air leaves a solvent recovery unit and flows through a 70-cm diameter duct at a velocity of 3.00 m/s. At a sampling point in the duct the temperature is 40°C, the pressure is 850 mm Hg, and the dew point of the sampled gas is 25°C. The gas is fed to a condenser in which it is cooled at constant pressure, condensing 60% of the hexane in the feed.

(a) Perform a degree-of-freedom analysis to show that enough information is available to calculate the required condenser outlet temperature (°C) and cooling rate (kW).

(b) Perform the calculations.

(c) If the feed duct diameter were 35 cm for the same molar flow rate of the feed gas, what would the gas velocity be?

Equipment Encyclopedia
evaporator

8.51. An equimolar liquid mixture of n-pentane and n-hexane at 80°C and 5.00 atm is fed into a flash evaporator at a rate of 100.0 mol/s. When the feed is exposed to the reduced pressure in the evaporator, a substantial amount is vaporized. The temperature in the tank is maintained at 65°C by adding heat. The vapor and liquid phases, which are in equilibrium with each other, are separated and discharged

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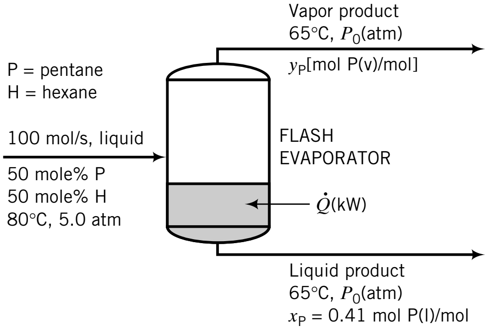
*Computer problems.

as separate streams. The liquid product stream contains 41.0 mole% pentane. A flowchart and an inlet–outlet enthalpy table for the process are given below.



References: P(l, 65°C), H(l, 65°C)

Substance	$\dot{n}_{\text{in}}$	$\hat{H}_{\text{in}}$	$\dot{n}_{\text{out}}$	$\hat{H}_{\text{out}}$
P(l)	$\dot{n}_a$	$\hat{H}_a$	$\dot{n}_c$	$\hat{H}_c$
P(v)	—	—	$\dot{n}_d$	$\hat{H}_d$
H(l)	$\dot{n}_b$	$\hat{H}_b$	$\dot{n}_e$	$\hat{H}_e$
H(v)	—	—	$\dot{n}_f$	$\hat{H}_f$

(a) Using Raoult's law for vapor–liquid equilibrium calculations, calculate (i) the system pressure, P_0(atm), (ii) the mole fraction of pentane in the vapor product, y_P, (iii) the volumetric flow rate of the vapor product, $\dot{V}$(L/s), and (iv) the fractional vaporization of pentane, f(mol vaporized/mol fed).

(b) Determine values for all the $\dot{n}$'s and $\hat{H}$'s in the enthalpy table and calculate the required rate of heat addition to the evaporator, $\dot{Q}$(kW).

Student Workbook

Equipment Encyclopedia
evaporator

8.52. A liquid stream containing 50.0 mole% benzene and the balance toluene at 25°C is fed to a continuous single-stage evaporator at a rate of 1320 mol/s. The liquid and vapor streams leaving the evaporator are both at 95.0°C. The liquid contains 42.5 mole% benzene and the vapor contains 73.5 mole% benzene.

(a) Calculate the heating requirement for this process in kW.

(b) Using Raoult's law (Section 6.4b) to describe the equilibrium between the vapor and liquid outlet streams, determine whether or not the given benzene analyses are consistent with each other. If they are, calculate the pressure (torr) at which the evaporator must be operating; if they are not, give several possible explanations for the inconsistency.

Equipment Encyclopedia
reactor, condenser

8.53. The off-gas from a reactor in a process plant in the heart of an obscure banana republic has been condensing and plugging up the vent line, causing a dangerous pressure buildup in the reactor. Plans have been made to pass the gas directly from the reactor into a cooling condenser in which the gas and liquid condensate will be brought to 25°C.

You have been called in as a consultant to aid in the design of this unit. Unfortunately, the chief (and only) plant engineer has disappeared and nobody else in the plant can tell you what the off-gas is (or what anything else is, for that matter).

However, a job is a job, and you set out to do what you can. You find an elemental analysis in the engineer's notebook indicating that the gas formula is $C_5H_{12}O$. On another page of the notebook, the off-gas flow rate is given as 235 m^3/h at 116°C and 1 atm. You take a sample of the gas and cool it to 25°C, where it proves to be a solid. You then heat the solidified sample at 1 atm and note that it melts at 52°C and boils at 113°C. Finally, you make several assumptions and estimate the heat removal rate in kW required to bring the off-gas from 116°C to 25°C. What is your result?

Equipment Encyclopedia
dryer

8.54. A sheet of cellulose acetate film containing 5.00 wt% liquid acetone enters an adiabatic dryer where 90% of the acetone evaporates into a stream of dry air flowing over the film. The film enters the dryer at $T_{f1} = 35°C$ and leaves at T_{f2}(°C). The air enters the dryer at T_{a1}(°C) and 1.01 atm and exits the dryer at $T_{a2} = 49°C$ and 1 atm with a relative saturation of 40%. C_p may be taken to be 1.33 kJ/(kg·°C) for dry film and 0.129 kJ/(mol·°C) for liquid acetone. Make a reasonable assumption regarding the heat capacity of dry air. The heat of vaporization of acetone may be considered independent of temperature. Take a basis of 100 kg film fed to the dryer for the requested calculations.

(a) Estimate the feed ratio [liters dry air (STP)/kg dry film].

(b) Derive an expression for T_{a1} in terms of the film temperature change, $(T_{f2} - 35)$, and use it to answer parts (c) and (d).

(c) Calculate the film temperature change if the inlet air temperature is 120°C.

(d) Calculate the required value of T_{a1} if the film temperature falls to 34°C, and the value if it rises to 36°C.

(e) If you solved parts (c) and (d) correctly, you found that even though the air temperature is consistently higher than the film temperature in the dryer, so that heat is always transferred from the air to the film, the film temperature can drop from the inlet to the outlet. How is this possible?

Equipment Encyclopedia
heat exchanger

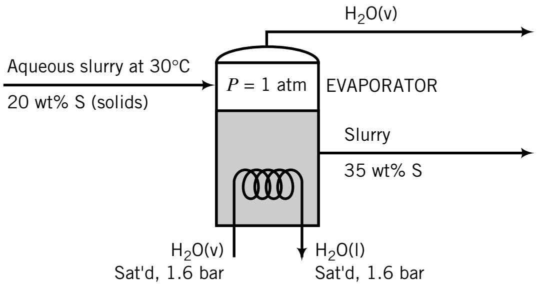
8.55. Saturated propane vapor at 2.00×10^2 psia is fed to a well-insulated heat exchanger at a rate of 3.00×10^3 SCFH (standard cubic feet per hour). The propane leaves the exchanger as a saturated liquid (i.e., a liquid at its boiling point) at the same pressure. Cooling water enters the exchanger at 70°F, flowing cocurrently (in the same direction) with the propane. The temperature difference between the outlet streams (liquid propane and water) is 15°F.

(a) What is the outlet temperature of the water stream? (Use the Cox chart on p. 247.) Is the outlet water temperature less than or greater than the outlet propane temperature? Briefly explain.

(b) Estimate the rate (Btu/h) at which heat must be transferred from the propane to the water in the heat exchanger and the required flow rate (lb_m/h) of the water. (You will need to write two separate energy balances.) Assume the heat capacity of liquid water is constant at 1.00 Btu/($\text{lb}_\text{m}\cdot$°F) and neglect heat losses to the outside and the effects of pressure on the heat of vaporization of propane.

Equipment Encyclopedia
evaporator

8.56. An aqueous slurry at 30°C containing 20.0 wt% solids is fed to an evaporator in which enough water is vaporized at 1 atm to produce a product slurry containing 35.0 wt% solids. Heat is supplied to the evaporator by feeding saturated steam at 1.6 bar absolute into a coil immersed in the liquid. The steam condenses in the coil, and the slurry boils at the normal boiling point of pure water. The heat capacity of the solids may be taken to be half that of liquid water.



(a) Calculate the required steam feed rate (kg/h) for a slurry feed rate of 1.00×10^3 kg/h.

(b) **Vapor recompression** is often used in the operation of an evaporator. Suppose that the vapor (steam) generated in the evaporator described above is compressed to 1.6 bar and simultaneously heated to the saturation temperature at 1.6 bar, so that no condensation occurs. The compressed steam and additional saturated steam at 1.6 bar are then fed to the evaporator coil, in which isobaric condensation occurs. How much additional steam is required?

(c) What more would you need to know to determine whether or not vapor recompression is economically advantageous in this process?

Equipment Encyclopedia
distillation column

8.57. A mixture that contains 46 wt% acetone (CH_3COCH_3), 27% acetic acid (CH_3COOH), and 27% acetic anhydride [$(CH_3CO)_2O$] is distilled at $P = 1$ atm. The feed enters the distillation column at $T = 348$ K at a rate of 15,000 kg/h. The distillate (overhead product) is essentially pure acetone, and the bottoms product contains 1% of the acetone in the feed.

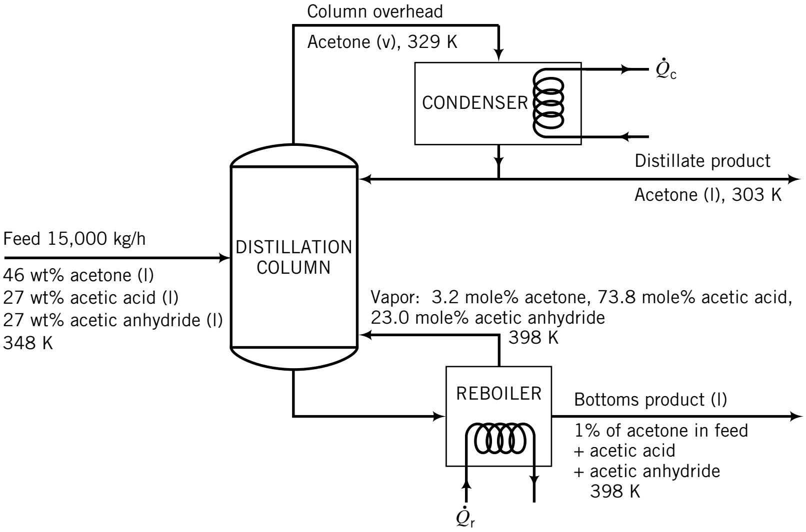
The vapor effluent from the top of the column enters a condenser at 329 K and emerges as a liquid at 303 K. Half of the condensate is withdrawn as the overhead product, and the remainder is refluxed back to the column. The liquid leaving the bottom of the column goes into a steam-heated reboiler, in which it is partially vaporized. The vapor leaving the reboiler is returned to the column at a temperature of 398 K, and the residual liquid, also at 398 K, constitutes the bottoms product. A flowchart of the process and thermodynamic data for the process materials follow.

(a) Calculate the molar flow rates and compositions of the product streams.

(b) Calculate the condenser cooling requirement $\dot{Q}_\text{c}$(kJ/h).

(c) Use an overall energy balance to determine the reboiler heating requirement $\dot{Q}_\text{r}$(kJ/h).

(d) If the reboiler heat is provided by the condensation of saturated steam at 10 bar gauge, at what rate must steam be fed?



Thermodynamic Data (All temperatures are in kelvin)

Acetone: $C_{pl} = 2.30$ kJ/(kg·K)

$C_{pv}[\text{kJ/(kg·K)}] = 0.459 + 3.15 \times 10^{-3}T - 0.790 \times 10^{-6}T^2$

$\Delta\hat{H}_v(329\text{ K}) = 520.6$ kJ/kg

Acetic acid: $C_{pl} = 2.18$ kJ/(kg·K)

$C_{pv}[\text{kJ/(kg·K)}] = 0.688 + 1.87 \times 10^{-3}T - 0.411 \times 10^{-6}T^2$

$\Delta\hat{H}_v(391\text{ K}) = 406.5$ kJ/kg

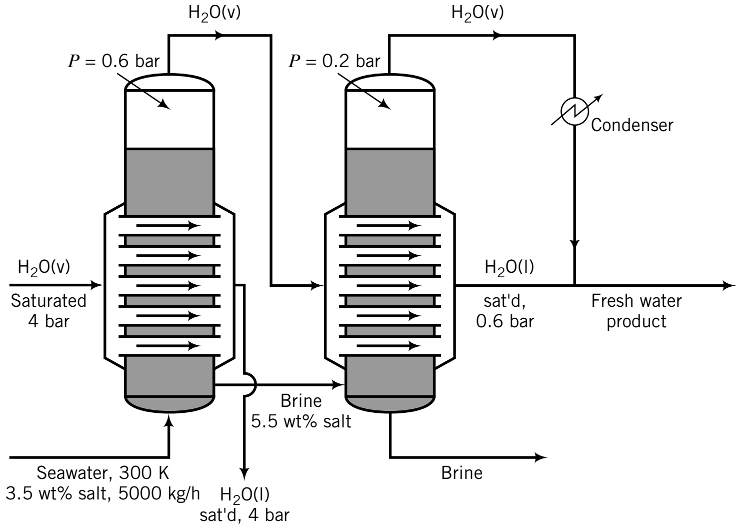
Acetic anhydride: $C_{pl}[\text{kJ/(kg·K)}] = ?$ (Estimate it—see Section 8.3c.)

$C_{pv}[\text{kJ/(kg·K)}] = 0.751 + 1.34 \times 10^{-3}T - 0.046 \times 10^{-6}T^2$

$\Delta\hat{H}_v(413\text{ K}) = ?$ (Estimate it—see Section 8.4b.)

Equipment Encyclopedia
evaporator

8.58. A **double-effect evaporator** (two evaporators in series) is used to produce fresh water from seawater containing 3.5 wt% dissolved salts. A flowchart for the process is shown here.



Seawater enters the first effect at 300 K at a rate of 5000 kg/h, and saturated steam at 4.00 bar absolute is fed into a tube bundle in the first effect. The steam condenses at 4.00 bar, and the condensate is withdrawn at the saturation temperature corresponding to this pressure.

The heat given up by the steam condensing in the tubes causes water to evaporate from the brine solution at the pressure of 0.60 bar maintained in the effect. The exiting brine contains 5.5 wt% salt. The steam generated in the first effect is fed to a tube bundle in the second effect. The condensate from the bundle and the steam generated in the second effect at a pressure of 0.20 bar constitute the fresh water produced in the process.

In solving the problems to be given, assume that the brine solutions in both effects have the physical properties of pure water and that the effects operate adiabatically.

(a) Draw and label a flowchart of this process, giving the temperature and specific enthalpy of each stream.

(b) At what rate must steam be fed to the first effect?

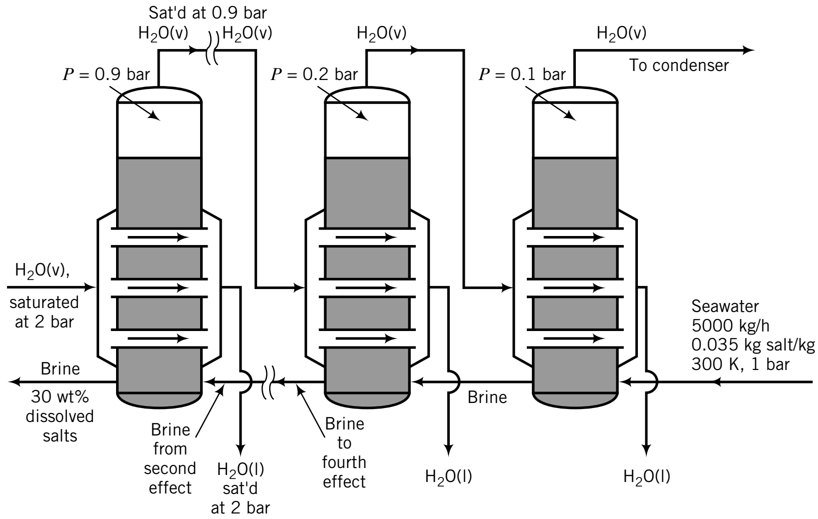
(c) What is the production rate of fresh water? What is the salt concentration (weight percent) of the final brine solution?

(d) Why is it necessary that the pressure decrease from one effect to the next?

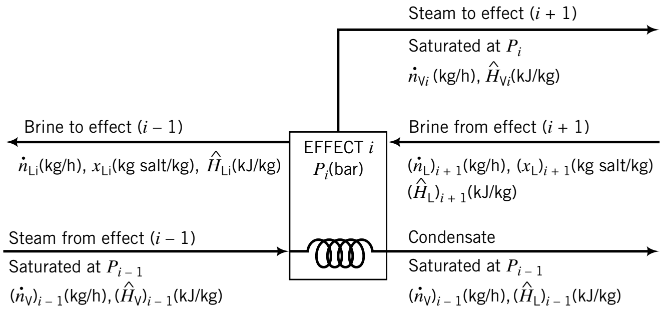
(e) Suppose a single-effect evaporator were used, operating at $P = 0.20$ bar. Calculate the feed rate of saturated steam at $P = 4.00$ bar that would be required to achieve the same production rate of fresh water. What more would you need to know to determine which process is more economical?

Equipment Encyclopedia
evaporator

***8.59.** Seawater containing 3.5 wt% dissolved salts is to be desalinated in an adiabatic six-effect evaporator. (See Problem 8.58.) Backward feed is to be used: the seawater is fed to the last evaporator, and successively concentrated brine solutions flow countercurrent to the direction of flow of steam from one effect to the next. Saturated steam at $P = 2$ bar is fed to the tube bundle in the first effect. The operating pressures in bars of the six effects are, respectively, 0.9, 0.7, 0.5, 0.3, 0.2, and 0.1. The brine leaving the first effect contains 30 wt% salt. The flowchart shows Effects 1, 5, and 6.



Following is a labeled diagram of the *i* th effect:



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*Computer problem.

In terms of the variables defined in this diagram,

$$\dot{n}_{L7} = 5000 \text{ kg/h}$$
$$x_{L7} = 0.035 \text{ kg salt/kg}$$
$$x_{L1} = 0.30 \text{ kg salt/kg}$$
$$\dot{n}_{V0} = \text{ feed rate of steam to the first effect}$$

(a) Use a salt balance to calculate $\dot{n}_{L1}$. Then use this result to determine how much fresh water is produced in the process.

(b) Prepare a table as follows:

	P (bar)	T (K)	$\dot{n}_L$ (kg/h)	x_L	$\hat{H}_L$ (kJ/kg)	$\dot{n}_V$ (kg/h)	$\hat{H}_V$ (kJ/kg)
Fresh steam	2.0		—	—	—		
Effect 1	0.9			0.30			
2	0.7						
3	0.5						
4	0.3						
5	0.2						
6	0.1						
(7)	1.0	300	5000	0.035		—	—

Fill in all *known* variable values (do not calculate any yet), including values obtained from the steam tables, *assuming that the physical properties of the brine solution are those of pure water.*

(c) Show that the following equations can be derived from balances:

$$x_{Li} = (\dot{n}_L)_{i+1}(x_L)_{i+1}/\dot{n}_{Li} \tag{1}$$

$$(\dot{n}_V)_{i-1} = \frac{\dot{n}_{Vi}\hat{H}_{Vi} + \dot{n}_{Li}\hat{H}_{Li} - (\dot{n}_L)_{i+1}(\hat{H}_L)_{i+1}}{(\hat{H}_V)_{i-1} - (\hat{H}_L)_{i-1}} \tag{2}$$

$$(\dot{n}_L)_{i-1} = \dot{n}_{Li} - (\dot{n}_V)_{i-1} \tag{3}$$

(d) The missing entries in the table of part (b) may be determined by solving Equations 1 through 3 for all effects simultaneously, but this is a cumbersome task. Instead, a relatively simple trial-and-error method may be used, which consists of assuming a value for $\dot{n}_{V6}$, calculating $\dot{n}_{L6} = \dot{n}_{L7} - \dot{n}_{V6}$, and successively solving Equations 1 through 3 for x_{L6}, $\dot{n}_{V5}$, $\dot{n}_{L5}$, then x_{L5}, $\dot{n}_{V4}$, $\dot{n}_{L4}$, and so on, until finally x_{L1} is calculated. If the calculated value of x_{L1} is less than the known value of 0.3, a higher value of $\dot{n}_{V6}$ is assumed and the process is repeated; if $x_{L1} > 0.3$, a lower value of $\dot{n}_{V6}$ is assumed. A reasonable first guess for $\dot{n}_{V6}$ is 1/6 of the total rate of evaporation [determined in part (a)].

Construct a spreadsheet program to perform these calculations, using the goalseek tool to carry out the trial-and-error search for the correct value of $\dot{n}_{V6}$. Fill in the table of part (b).

(e) Solve the equations of part (c) for all six effects using an equation-solving program. Fill in the table of part (b).

8.60. A liquid is placed in a well-insulated container, which is then sealed. Initially, the container and its contents (the liquid and pure nitrogen) are at 93°C and 1 atm; the liquid volume is 70 cm^3, and the gas volume is 3.00 L. The liquid partially evaporates, and the system cools down and eventually comes to thermal equilibrium at 85°C with liquid still present. Physical property data for the liquid and its vapor are:

$$\Delta\hat{U}_v = 20 \text{ kcal/mol at } 90°\text{C}$$
$$(C_p)_{\text{liq}} = 20 \text{ cal/(mol·°C)}$$
$$(C_p)_{\text{vap}} = 10 \text{ cal/(mol·°C)}$$
$$(\text{SG})_{\text{liq}} = 0.90$$
$$\text{MW} = 42$$

(a) Determine $(C_v)_{\text{liq}}$ and $(C_v)_{\text{vap}}$. (See Equations 8.3-11 and 8.3-12.)

(b) Draw and label a flowchart for this closed system process, and write and simplify the energy balance equation, assuming adiabatic operation.

(c) Use the energy balance to calculate the mass of liquid that evaporates, taking 4.97 cal/(mol·°C) as the heat capacity of nitrogen.

(d) Calculate the vapor pressure of the liquid at 85°C, assuming that the gas volume remains constant at 3.00 L.

Equipment Encyclopedia
condenser

8.61. A small pharmaceutical firm plans to manufacture a new drug and has hired you as a consultant to design a condenser to remove the drug from a gas–vapor mixture. The mixture, which contains 20 mole% of the drug and the balance nitrogen, will be fed to the condenser at 510 K and 1 atm at a rate of 3.5 L/s. Of the drug fed to the unit, 90% must be condensed. No physical property data are available for the drug, and part of your job is to acquire the data needed to design the condenser. The company has sent you a large sample of the liquid drug for this purpose.

You acquire an insulated 2.000-liter container with a known heat capacity and a built-in electrical heating coil that can deliver a known heat input to the contents of the container. A calibrated thermocouple is used to measure the temperature in the vessel, and the pressure is measured with a mercury manometer.

You carry out a series of experiments on a day when atmospheric pressure is 763 mm Hg.

Experiment 1. Fill the container with the liquid, then seal and weigh.

$$\text{mass of container + liquid} = 4.4553 \text{ kg}$$
$$\text{mass of evacuated container} = 3.2551 \text{ kg}$$

Next, starting at each of two temperatures (T_0), add a fixed quantity of heat to the liquid, observe the final temperature (T_f), and subtract the heat absorbed by the container from the total heat input to determine the amount of the heat added to the liquid, Q_a.

$$T_0 = 283.0 \text{ K}, Q_a = 800.0 \text{ J} \Longrightarrow T_f = 285.4 \text{ K}$$
$$T_0 = 330.0 \text{ K}, Q_a = 800.0 \text{ J} \Longrightarrow T_f = 332.4 \text{ K}$$

Assume that the liquid heat capacity may be expressed as a linear function of temperature ($C_v = aT + b$) when analyzing these results.

Experiment 2. Pour a small quantity of the drug into the container, place the container in a liquid nitrogen bath to freeze the drug, evacuate all of the air, and seal the container. Weigh the container after it comes back to room temperature.

$$\text{mass of container + drug} = 3.2571 \text{ kg}$$

Next heat the sealed container until all of the liquid evaporates, and repeat Experiment 1.

$$T_0 = 363.0 \text{ K}, h_{\text{manometer}} = -500 \text{ mm}, Q_a = 1.30\text{J} \Longrightarrow T_f = 366.9 \text{ K}$$
$$T_0 = 490.0 \text{ K}, h_{\text{manometer}} = -408 \text{ mm}, Q_a = 1.30\text{J} \Longrightarrow T_f = 492.7 \text{ K}$$

Assume that the vapor heat capacity may be expressed as a linear function of temperature when analyzing these results.

Experiment 3. Fill approximately half the container with the drug, freeze, evacuate the air, and seal. Measure the pressure at several temperatures, verifying that liquid is present in the container at each temperature.

$$T = 315.0 \text{ K}, h_{\text{manometer}} = -564 \text{ mm}$$
$$T = 334.0 \text{ K}, h_{\text{manometer}} = -362 \text{ mm}$$
$$T = 354.0 \text{ K}, h_{\text{manometer}} = -2 \text{ mm}$$
$$T = 379.0 \text{ K}, h_{\text{manometer}} = +758 \text{ mm}$$

(a) Using the given data, determine the following physical properties of the drug: (i) liquid specific gravity, (ii) molecular weight, (iii) linear expressions for the heat capacities at constant volume [in J/(mol·K)] for both the liquid and vapor [$C_v = a + bT(\text{K})$], (iv) linear expressions for C_p for both liquid and vapor, (v) a Clausius–Clapeyron expression for $p^*(T)$, (vi) the normal boiling point, and (vii) the heat of vaporization (in J/mol) at the normal boiling point.

(b) Calculate the required condenser temperature, assuming operation at 1 atm.

(c) Calculate the rate at which heat must be removed in the condenser, taking the heat capacity of nitrogen to be constant at 29.0 J/(mol·K).

Equipment Encyclopedia
cryogenics

8.62. **Freeze drying** is a technique for dehydrating substances at low temperatures, thereby avoiding the degradation that may accompany heating. The material to be dried is cooled to a temperature at which all of the water present turns to ice. The frozen substance is then placed in a vacuum chamber and may also be subjected to radiant or microwave heating; the ice in the food sublimates, and the vapor is carried off by the vacuum pump.

Steaks are to be freeze-dried in a heated chamber at 1 torr (1 mm Hg). The steaks, which contain 72% water by mass, enter the chamber at −26°C at a rate of 50 kg/min. Of the water entering with the steaks, 96% leaves as a vapor at 60°C; the remainder leaves as a liquid with the steaks at 50°C.

(a) Use the heat capacity data given below and additional tabulated data for water to calculate the required heat input in kilowatts.

$$(C_p)_{\text{ice}} = 2.17\ \text{J/(g·°C)}$$
$$(C_p)_{\text{dry meat}} = 1.38\ \text{J/(g·°C)}$$

(b) When large temperature changes are not involved in a phase-change operation, a reasonable estimate of the required heat transfer rate may be obtained by neglecting contributions of temperature changes to the overall process enthalpy change (i.e., by taking only phase changes into account). Moreover, it is often reasonable to use any available values of latent heats, neglecting their dependence on temperature and pressure. In the case of the freeze-drying process, the approximation might be to calculate only the heat needed to melt all the water and vaporize 96% of it, using latent heats at the normal melting and boiling points (Table B.1) and neglecting the heat required to raise the temperature of the meat and water. What percentage error in the calculated value of $\dot{Q}$ would result from this approximation? Take the value determined in part (a) to be exact.

Equipment Encyclopedia
cryogenics

8.63. **Freeze concentration** is used to produce a fruit-juice concentrate. A stream of fresh juice containing 12 wt% soluble solids in water at 20°C is combined with a recycle stream to form a preconcentrate, which is fed to a crystallizer. The mixture is cooled in the crystallizer to −7°C, thereby crystallizing 20,000 kg/h of ice. A slurry leaves the crystallizer containing 10 wt% ice and is fed to a filter. The filtrate, which contains 45 wt% dissolved solids, is removed as the process product. The remaining slurry, which contains all the ice and some concentrate (also containing 45% dissolved solids), is sent to a separator that cleanly removes all of the ice. The residual liquid is the recycle stream that combines with the fresh feed to form the preconcentrate.

(a) Determine the rates (kg/h) at which fresh fruit juice is fed and concentrate is produced, and the mass flow rate (kg/h) and solids concentration of the preconcentrate.

(b) Calculate the cooling requirement (kW) for the freezer, assuming that the temperature of the recycle stream is 0°C and the heat capacity of all solutions is 4.0 kJ/(kg·°C).

Equipment Encyclopedia
heat exchanger

8.64. A mixture containing 35.0 mole% n-butane and the balance isobutane at 10°C enters a heat exchanger at a rate of 24.5 kmol/h and a pressure high enough for the mixture to be a liquid. The exchanger has been designed to heat and vaporize the liquid and heat the vapor mixture to 180°C. The heating fluid is a high molecular weight liquid with a constant heat capacity $C_p = 2.62$ kJ/(kg·°C). It enters the exchanger at 215°C and flows countercurrently to the hydrocarbon mixture.

(a) Estimate the minimum pressure (bar) required for the hydrocarbon feed to be a liquid. Use Raoult's law and the Cox chart (Figure 6.1-4) in your calculation.

(b) Assuming that the heat capacities and heats of vaporization of n-butane and isobutane are independent of pressure (so that the values in Tables B.1 and B.2 may be used), calculate the enthalpy change $\Delta\dot{H}$ (kJ/h) undergone by the hydrocarbon mixture in the heat exchanger. Show the process paths you use for n-butane and i-butane in your calculation. (*Hint:* Since you don't have heat capacities for liquid n-butane and i-butane in this text, use process paths that don't require them.)

(c) According to the heat exchanger design calculations, the heating fluid exit temperature should be 45°C. Assuming that all the heat lost by the heating fluid is transferred to the hydrocarbon mixture, what is the required mass flow rate of the heating fluid, $\dot{m}_{\text{hf}}$(kg/h)?

(d) When the heat exchanger is run with $\dot{m}_{\text{hf}}$ equal to the value calculated in part (b), the exit temperature of the hydrocarbon mixture is measured and found to be only 155°C instead of the design value of 180°C. The process operator observes that the outside of the exchanger is hot to the touch, indicating that some of the heat lost by the heating fluid is escaping into the plant instead of being transferred to the hydrocarbon mixture. After discussing the situation with a production engineer, the operator gradually increases the flow rate of the heating fluid while continuing to monitor the outlet temperature of the hydrocarbon. When the flow rate reaches 2540 kg/h, the outlet fluid temperatures level out at their design values (180°C for the hydrocarbon and 45°C for the heating fluid). At what rate (kJ/h) is heat being transferred from the exchanger to the plant air?

(e) When the heating fluid leaves the exchanger, it passes through a heater, which raises its temperature back to 215°C, and is recycled back to the exchanger. How is the profitability of the process being decreased by the heat loss from the exchanger to the surroundings? (Try to think of two costs that result from the heat loss.)

(f) The engineer proposes adding more insulation to the heat exchanger, which would cut down on the heat loss and reduce the required heating fluid flow rate. What are advantages and disadvantages of the two responses to the heat loss problem (adding insulation versus increasing the heating fluid flow rate)? Which would you guess would be the preferable response in the long run, and why?

8.65. A liquid mixture of benzene and toluene containing 50.0 wt% benzene at 90°C and pressure P_0 is fed at a rate of 32.5 m^3/h into a **flash evaporator,** a heated tank maintained at a pressure $P_{tank} \ll P_0$. When the feed is exposed to the reduced pressure in this unit, a portion of it evaporates. The liquid and vapor product streams are in equilibrium at 75°C and P_{tank}. The liquid product contains 43.9 mole% benzene. When carrying out the requested calculations, assume volume additivity of liquid benzene and toluene, use Raoult's law and the Antoine equation where necessary, and neglect the effect of pressure on enthalpy.

(a) Calculate the molar flow rate (mol/s) and molar composition (component mole fractions) of the feed stream. Then calculate the minimum value of P_0(atm) needed to keep the feed stream in the liquid state until it enters the flash tank.

(b) Calculate P_{tank}(atm), the mole fraction of benzene in the vapor, and the molar flow rates of the liquid and vapor products.

(c) Calculate the required heat input rate in kilowatts.

(d) An hour after the system is started up, a chromatographic analysis of the vapor product is run and the benzene mole fraction is found to be 3% higher than the value calculated in part (b). The system temperature and pressure are rechecked and found to have the correct values. Give several possible explanations of the discrepancy between the calculated and measured values.

(e) Briefly explain why the product temperature is lower than the feed temperature. What would be required to run the unit isothermally?

***8.66.** A continuous adiabatic flash tank is to be used to separate a liquid mixture of two substances (A and B). The feed enters at temperature T_F and a high pressure and flashes to a low pressure, P, whereupon its temperature drops to T. For an assumed basis of 1 mol/s of feed, let

$\dot{n}_L, \dot{n}_V$ = molar flow rates of liquid product and vapor product

x_F, x, y = mole fractions of A in the feed, liquid product, and vapor product

$p_A^*(T), p_B^*(T)$ = vapor pressures of A and B

T_{RA}, T_{RB} = reference temperatures for enthalpy calculations

$\left.\begin{matrix}\hat{H}_{AF}(T_F),\ \hat{H}_{AL}(T),\ \hat{H}_{AV}(T)\\ \hat{H}_{BF}(T_F),\ \hat{H}_{BL}(T),\ \hat{H}_{BV}(T)\end{matrix}\right\}$ specific enthalpies of A and B in the feed, liquid product, and vapor product, relative to T_{RA} and T_{RB}

(a) Derive the following relations from Raoult's law and material and energy balances on the flash tank:

$$x = \frac{P - p_B^*(T)}{p_A^*(T) - p_B^*(T)} \tag{1}$$

$$y = x p_A^*(T)/P \tag{2}$$

$$\dot{n}_L = \frac{y - x_F}{y - x} \tag{3}$$

---

*Computer problem.

$$\dot{n}_V = 1 - \dot{n}_L \quad \textbf{(4)}$$

$$\Delta\dot{H} = \dot{n}_L[x\hat{H}_{AL}(T) + (1 - x)\hat{H}_{BL}(T)] + \dot{n}_V[y\hat{H}_{AV}(T) + (1 - y)\hat{H}_{BV}(T)] - [x_F\hat{H}_{AF}(T_F) + (1 - x_F)\hat{H}_{BF}(T_F)] = 0 \quad \textbf{(5)}$$

(b) Write a spreadsheet program to perform flash calculations for a feed mixture of *n*-pentane and *n*-hexane. When calculating enthalpies of these species, the following heat capacity formulas should be used for liquid and vapor, respectively:

$$C_{pl} = a_l$$
$$C_{pv} = a_v + b_v T(^\circ\text{C})$$

The spreadsheet should have the following form. Some values are given, others should be looked up in data tables, and the remainder should be calculated from Equations 1 to 5 and appropriate formulas for specific enthalpies.

Chapter 8—Problem 8.66								
Tref = 25 deg. C								
Compound	A	B	C	al	av	bv	Tbp	DHv
n-pentane	6.84471	1060.793	231.541	0.195	0.115	3.41E-4	36.07	25.77
n-hexane				0.216	0.137	4.09E-4		
xF	0.5	0.5	0.5	0.5				
Tf(deg.C)	110	110	150					
P(mm Hg)	760	1000	1000					
HAF (kJ/mol)								
HBF (kJ/mol)								
T(deg.C)	80.0							
pA* (mm Hg)								
pB* (mm Hg)								
x								
y								
nL (mol/s)								
nV (mol/s)								
HAL (kJ/mol)								
HBL (kJ/mol)								
HAV (kJ/mol)								
HBV (kJ/mol)								
DH (kJ/s)	-51.333							

In this table, A, B, and C are Antoine equation constants, al, av, and bv are the coefficients of the given heat capacity formulas; Tbp(°C) and DHv(kJ/mol) ($\Delta\hat{H}_v$) are the normal boiling point and heat of vaporization, xF(mol pentane/mol) is the mole fraction of pentane in the feed, Tf(°C) is the feed temperature, P(mm Hg) is the system pressure, HAF ($\hat{H}_{AF}$) and HBF ($\hat{H}_{BF}$) are the specific enthalpies of pentane and hexane in the feed stream, pA* is the vapor pressure of *n*-pentane (to be determined using the Antoine equation), x and nL (x and $\dot{n}_L$) are the mole fraction of pentane in the liquid product stream and the molar flow rate of that stream, respectively, y and nV are the corresponding properties of the vapor product stream, HAL is the specific enthalpy of pentane in the liquid product stream, and DH ($\Delta\dot{H}$) is the expression given in Equation 5 for the change in total enthalpy from inlet to outlet.

Enter the appropriate constants and formulas for A, B, C, al, av, bv, Tbp, and DHv for *n*-pentane and *n*-hexane, an initial guess for T in Column 2 (= 80.0), and the appropriate formulas for the rest of the variables in Column 2. Then vary the value of T until the value of $\Delta\dot{H}$ is suitably close to zero, using the goalseek tool if your spreadsheet program provides it. The value of $\Delta\dot{H}$ (-51.33 kJ/s) corresponding to the initial guess of 80°C is shown in the second column of the table. Your spreadsheet should generate the same value.

After completing the calculations in the second column, copy the formulas into the third and fourth columns and perform the calculations for these two sets of input parameter values. State how increasing the system pressure and feed temperature affect the fraction of the feed vaporized (nV) and the final system temperature (T), and briefly explain why your results make sense.

*__(c)__ Write a computer program to read in and print out values of x_F, T_F(°C), and P(mm Hg), and for each of the feed mixture components the Antoine equation coefficients, a reference temperature (e.g., 25°C), the liquid heat capacity (assume constant), normal boiling point, heat of vaporization, and coefficients of a two-term vapor heat capacity formula $C_p = a + bT$. Then have the program carry out a trial-and-error procedure to calculate and print out the flash tank temperature and the flow rates and compositions of the vapor and liquid product streams.

An inefficient but simple procedure is to assume a value of T (T_F is a reasonable first guess), solve Equations 1 through 4 successively, and then evaluate the left side of Equation 5 (which equals $\Delta\dot{H}$ for the assumed temperature and must be positive when $T = T_F$). The value of T is then decreased by a small fixed amount, such as 0.5°C, and the procedure is repeated until the sign of $\Delta\dot{H}$ changes from positive to negative from one T to the next. The true T (for which $\Delta\dot{H} = 0$) must lie between the two last assumed values and may be estimated by linear interpolation. When calculating specific enthalpies, use the heat capacity formulas for pentane and hexane given in part (b).

A flowchart for a program to implement this procedure is shown in Figure P8.1. Write the program and test it by estimating the flash tank temperature and product stream flow rates (mol/s) and compositions (mole fractions) for the flash vaporization of one mol/s of an equimolar mixture of *n*-pentane (A) and *n*-hexane (B), if the feed temperature is 110°C and the tank pressure is 1.0 atm.

Equipment Encyclopedia
distillation column

8.67. A saturated vapor stream containing 10.9 mole% propane, 75.2% isobutane, and 13.9% *n*-butane passes from the top of a distillation column to a total condenser. Seventy-five percent of the condensate is returned to the column as reflux, and the remainder is removed as the overhead column product at a rate of 2500 kmol/h.

A decision must be made on whether to use a refrigerant or cooling water in the condenser. If the refrigerant is used, it will be fed to the condenser as a liquid and vaporized by the heat released by the condensing column vapor. The refrigerant pressure will be such that the vaporization takes place at -6°C, at which temperature $\Delta\hat{H}_v = 151$ kJ/kg. The other option calls for cooling water to be taken from a nearby river at its average summer temperature of 25°C. To avoid environmental problems, the temperature of the water returned to the river can be no greater than 34°C. With either system, the temperature of the condensate should be 6°C greater than the outlet temperature of the coolant, so that if the refrigerant is used the saturated condensate should have a temperature of 0°C, and if cooling water is used the saturated condensate should be at 40°C. The condenser pressure will be set to the minimum value needed to condense all of the vapor, which is to say the condensate

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*Computer problem.

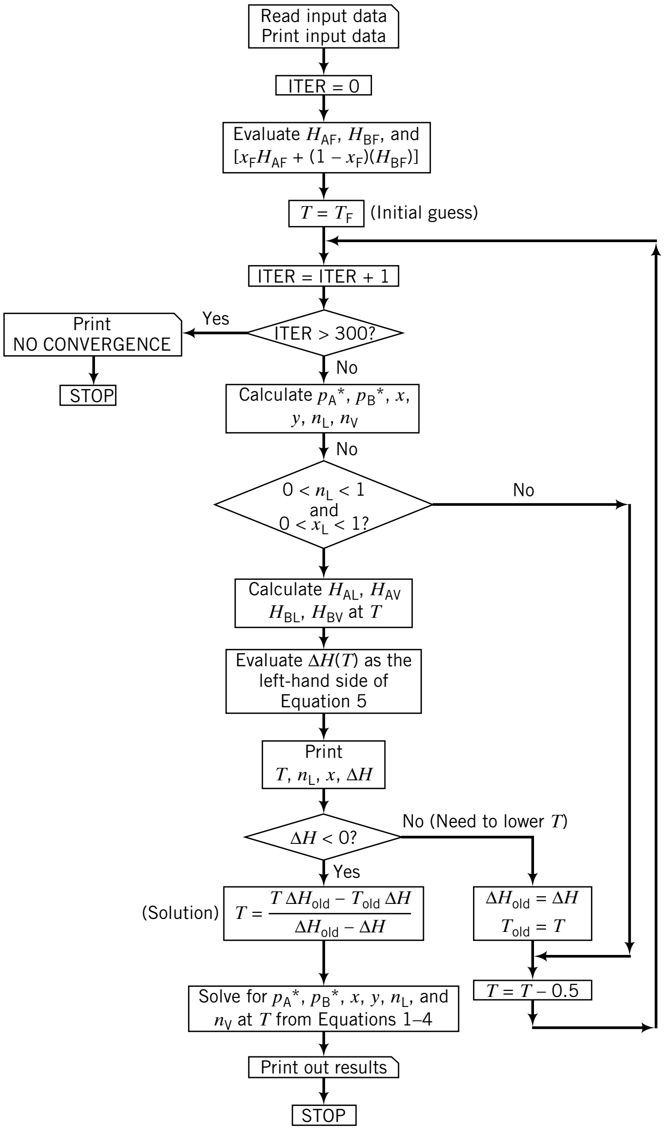


Figure P8.1 Flowchart for program of Problem 8.66.

will be at its bubble-point temperature at the condenser pressure. Raoult's law may be used for all bubble-point and dew-point calculations (see Section 6.4c).

(a) Suppose the refrigerant is used for cooling. Estimate the condenser pressure P(mm Hg); the temperature T_f(°C) of the vapor fed to the condenser, assuming that the vapor is at its dew point at pressure P; and the required coolant flow rate (kg/h).

(b) Repeat part (a) assuming that cooling water is fed to the condenser.

(c) What more would you need to know to be able to choose between the two options?

Equipment Encyclopedia
reactor, boiler,
heat exchanger,
absorption
column

8.68. Formaldehyde is produced from methanol in a catalytic oxidation reactor. The following reactions take place:

$$CH_3OH \rightarrow HCHO + H_2$$
$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

A stream of methanol is joined by a recycle stream, also methanol, and the combined stream is fed to the conversion reactor. Also entering the reactor are air (to oxidize some of the hydrogen produced in the methanol conversion reaction) and steam (to control the reactor temperature). The product gas from the reactor contains 19.9 mole% formaldehyde, 8.34% methanol, 30.3% nitrogen, 0.830% oxygen, 5.0% hydrogen, and 35.6% water vapor and is at 600°C and 1 atm.

The following process is used to separate the formaldehyde from the unreacted methanol and noncondensable gases. The gases leaving the reactor are fed to a waste-heat boiler, in which they are cooled to 145°C, in the process generating steam at 3.1 bar from saturated liquid water (i.e., liquid water at its boiling point) at the same pressure. The gases are cooled further to 100°C in a heat exchanger, where they come into thermal contact with cooling water fed at 30°C. To reduce scaling on the heat exchanger tubes, the temperature increase of the cooling water is limited to 15°C. The cooled gases are fed to an absorption column, where methanol and formaldehyde are absorbed in water. Pure water at 20°C is fed to the top of the column. The gas leaving the absorber is saturated with water vapor at 27°C and 1 atm and contains 200 parts of formaldehyde per million parts (by volume) of total gas. The aqueous solution leaving the bottom of the absorber at 88°C is fed to a distillation column that operates at 1 atm. The final product solution, which contains 37 wt% formaldehyde, 1% methanol, and the balance water, is removed from the reboiler at the bottom of the column, while pure methanol vapor emerges as the overhead product and is condensed at 1 atm. A portion of the condensate is refluxed to the top of the column, and the rest is recycled to the methanol conversion reactor. The reflux ratio, or ratio of methanol refluxed to methanol recycled to the reactor, is 2.5:1.

(a) Taking as a basis of calculation 100 mol of gas leaving the conversion reactor, draw and completely label a flowchart of this process. Then calculate the moles of fresh methanol feed, formaldehyde product solution, recycled methanol, and absorber off-gas, the kg of steam generated in the waste-heat boiler, and the kg of cooling water fed to the heat exchanger between the waste-heat boiler and the absorber. Finally, calculate the heat (kJ) that must be removed in the distillation column overhead condenser, assuming that methanol enters as a saturated vapor at 1 atm and leaves as a saturated liquid at the same pressure.

(b) By what factor must all of the calculated quantities be multiplied to scale the flowchart to a production rate of 3.6×10^4 metric tons per year of formaldehyde solution, assuming that the process is on-stream 350 days per calendar year?

Equipment Encyclopedia
thermometer

8.69. The latest weather report states that the temperature is 24°C and the relative humidity is 50%.

(a) Use the psychrometric chart to estimate the absolute humidity, humid volume, specific enthalpy, wet-bulb temperature, and dew-point temperature of the air.

(b) A thermometer is mounted on the back porch of your house. What temperature would it read?

(c) A sample of outside air is cooled at constant pressure. At what temperature would condensation begin?

(d) You step out of your neighborhood pool and feel quite cold until you dry off. Explain why. Estimate your skin temperature while you were still wet. Explain your answer. What would be different if the relative humidity were 98%?

8.70. An open vessel containing 0.205 lb_m of liquid water is placed in an empty room 5 ft wide, 4 ft deep, and 7 ft high, which initially contains dry air at 90°F. All the water evaporates without changing the room temperature. Use the psychrometric chart to estimate the final relative humidity, wet-bulb temperature, humid volume, dew-point temperature, and specific enthalpy of the room air. Take the molecular weight of dry air to be 29.0, and for simplicity, assume the mass of dry air in the room stays constant at its initial value.

Equipment Encyclopedia
thermometer

8.71. A **sling psychrometer** is a device to measure the humidity of air. A porous cloth (the **wick**) is wrapped around the bulb of a mercury thermometer, which is then whirled around in the air. As the water in the wick evaporates, the temperature of the thermometer bulb drops, and finally stabilizes at the wet-bulb temperature of the air. The dry-bulb temperature is read from a second thermometer mounted on the sling.

One summer day, the weather bureau reports a temperature of 33°C and a relative humidity of 40%. You wipe the sweat from your forehead and remark to a friend that you'd bet \$5 that the report is wrong, and the relative humidity is higher than 80%. He immediately puts a \$5 bill on the table, accepting your challenge. You bring out your sling psychrometer, whirl it around, and read a dry-bulb temperature of 35°C and a wet-bulb temperature of 27°C. Who wins the bet?

Student Workbook

8.72. Humid air is enclosed in a 2.00-liter flask at 40°C. The flask is slowly cooled. When the temperature reaches 20°C, drops of moisture become visible on the flask wall. Although the pressure in the flask changes when the temperature drops, it remains close enough to 1 atm for the psychrometric chart to provide a close representation of the behavior of the system throughout the process. Use the chart to solve the following problems.

(a) What were the relative humidity, absolute humidity, and wet-bulb temperature of the air at 40°C?

(b) Calculate the mass of the water in the flask. (See Example 8.4-5.)

(c) Calculate the enthalpy change in joules undergone by the air in going from 40°C to 20°C.

(d) Write an energy balance for this closed-system process, taking the wet air in the flask as the system, and use it to calculate the heat in joules that must be transferred from the air to accomplish the cooling. (Assume ideal gas behavior, so that $\hat{H} = \hat{U} + RT$.)

Equipment Encyclopedia
dryer

8.73. Wet solids pass through a continuous dryer. Hot dry air enters the dryer at a rate of 400 kg/min and picks up the water that evaporates from the solids. Humid air leaves the dryer at 50°C containing 2.44 wt% water vapor and passes through a condenser in which it is cooled to 10°C. The pressure is constant at 1 atm throughout the system.

(a) At what rate (kg/min) is water evaporating in the dryer?

(b) Use the psychrometric chart to estimate the wet-bulb temperature, relative humidity, dew point, and specific enthalpy of the air leaving the dryer.

(c) Use the psychrometric chart to estimate the absolute humidity and specific enthalpy of the air leaving the condenser.

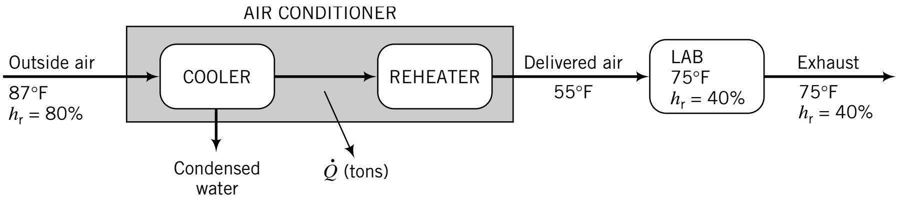
(d) Use the results of parts (b) and (c) to calculate the rate of condensation of water (kg/min) and the rate at which heat must be transferred from the condenser (kW).

(e) If the dryer operates adiabatically, what can you conclude about the temperature of the entering air? Briefly explain your reasoning. What additional information would you need to calculate this temperature?

Equipment Encyclopedia
condenser, heat exchanger

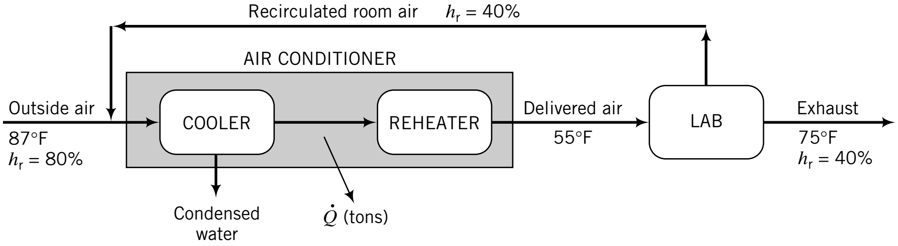
8.74. On an uncomfortable summer day, the air is at 87°F and 80% relative humidity. A laboratory air conditioner is to deliver 1.00×10^3 ft^3/min of air at 55°F in order to maintain the interior air at an average temperature of 75°F and a relative humidity of 40%.

(a) If the vent switch on the air conditioner is turned to the "open" position, outside air enters the unit as shown below.



In the air conditioner, the air is cooled to a temperature low enough to condense the necessary amount of water and reheated to 55°F, at which point it has the same absolute humidity as the room air. Use the psychrometric chart to estimate the rate (lb$_m$/min) at which water is condensed, the temperature to which the air must be cooled to condense water at this rate, and the net tons of cooling required ($\dot{Q}$), where 1 ton of cooling = −12,000 Btu/h. [*Note:* The humid volume of the delivered air (at 55°F), which is difficult to read from the psychrometric chart, is 13.07 ft^3/lb$_m$ dry air, and the heat capacity of liquid water is 1.0 Btu/(lb$_m$·°F).]

(b) If the vent switch is set to the "closed" position (as it normally would be), inside air would be recirculated through the air conditioner as shown in the following diagram.



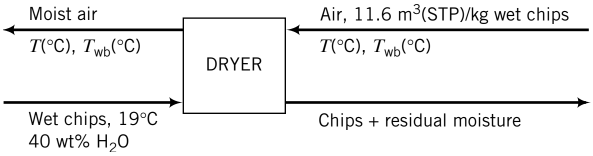
The recycle ratio (ft^3 recirculated/ft^3 exhausted) is 6:1. Calculate the condensation rate and the overall cooling requirement in tons if conditioned air is delivered at the same rate, temperature, and relative humidity as in part (a). What percentage of the cooling load on the air conditioner is saved by recirculating the air? Explain in your own words why the cooling rate is lower when room air is recirculated instead of bringing all the air in from the outside.

(c) An even lower cooling load would be required if *all* of the air passing through the conditioner were recirculated rather than just 6/7 of it, thereby eliminating the need for outside air and exhaust. Why would this be a bad idea? (*Hint:* Think about the people working in the laboratory.)

Equipment Encyclopedia
dryer

8.75. Wet wood chips are dried in a continous rotary dryer that operates at atmospheric pressure. The chips enter at 19°C with a water content of 40 wt% and must leave with a moisture content of less than 15%. Hot air is fed to the dryer at a rate of 11.6 m^3(STP)/kg wet chips.

To monitor the performance of the dryer by sampling the exiting chips and determining their moisture content directly would be a cumbersome procedure and almost impossible to automate. Instead, wet- and dry-bulb thermometers are mounted in both the inlet and outlet air lines, and the moisture content of the exiting chips is determined by a material balance.



After the unit goes on-stream, the inlet dry-bulb temperature is found to be 100°C, and the wet-bulb temperature is low enough so that the moisture content of the air may be neglected. The dry-bulb temperature of the exiting air is found to be 38°C, and the wet-bulb temperature is 29°C.

(a) Use the psychrometric chart to calculate the absolute humidity (kg H_2O/kg dry air) and specific enthalpy (kJ/kg dry air) of the outlet air stream. Then calculate the mass of water in the exiting air per kilogram of wet chips fed, assuming dry air has a molecular weight of 29.0.

(b) Calculate the moisture content of the emerging chips and determine whether the design specification of less than 15% H_2O has been achieved.

(c) If the unit is operating adiabatically and the heat capacity of the dry chips is 2.10 kJ/(kg·°C), what is the exit temperature of the chips? (In estimating the specific enthalpy of the entering air, recall that the reference temperature for dry air used in constructing the psychrometric chart of Figure 8.4-1 is 0°C.)

Equipment Encyclopedia
humidifier

8.76. Air at 45°C (dry bulb) and 10% relative humidity is to be humidified adiabatically to 60% relative humidity.

(a) Use the psychrometric chart to estimate the adiabatic saturation temperature of the air.

(b) Estimate the final temperature of the air and the rate at which water must be added to humidify 15 kg/min of the entering air. (See Example 8.4-7.)

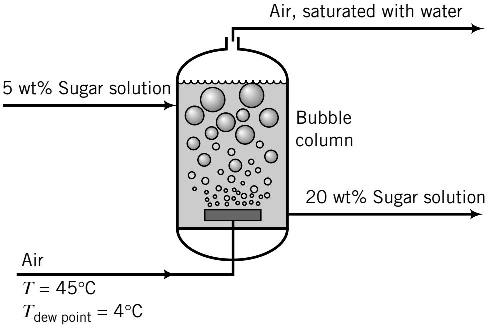
Equipment Encyclopedia
dryer

8.77. Air at 50°C with a dew point of 4°C enters a textile dryer at a rate of 11.3 m^3/min and leaves saturated. The dryer operates adiabatically. Use the psychrometric chart to determine the absolute humidity and humid volume of the entering air, and then use the results to determine the flow rate of *dry* air (kg/min) through the dryer, the final temperature of the air, and the rate (kg/min) at which water is evaporated in the dryer. (*Hint:* Refer to Section 8.4e.)

8.78. A solution of sugar in water is to be concentrated from 5 wt% sugar to 20% sugar. The solution is at about 45°C when it is fed continuously to a bubble column. Air at 45°C with a dew point of 4°C is bubbled through the column and emerges saturated. The humidification of the air may be considered adiabatic. (See figure on next page.) Use the psychrometric chart to solve the following problems:

(a) What are the absolute humidities of the entering and exiting air?

(b) How many kilograms of dry air must be fed per kilogram of the entering sugar solution? What is the corresponding volume of the entering wet air? (Use the chart for the latter problem as well.)



Equipment Encyclopedia
heat exchanger, humidifier

8.79. Cold air at 20°F, 760 mm Hg pressure, and 70% relative humidity is conditioned by being passed through a bank of heating coils, then through a water spray, and finally through a second set of heating coils. In passing through the first coil bank, the air is heated to 75°F. The temperature of the water supplied to the spray chamber is adjusted to the wet-bulb temperature of the air admitted to the chamber, so that the humidifying unit may be assumed to operate adiabatically. It is required that the air emerging from the conditioning unit be at 70°F and 35% relative humidity. Use Figure 8.4-2 to solve the following problems.

(a) Calculate the temperature of the water supplied to the spray chamber and the relative humidity and dry-bulb temperature of the air leaving the spray chamber.

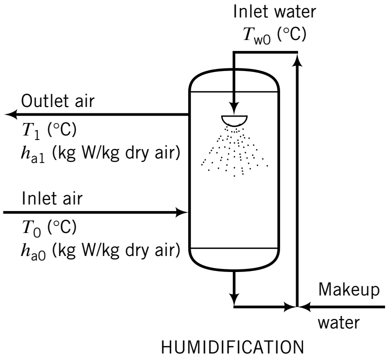
(b) Calculate the mass of water evaporated (lb_m) per cubic foot of air fed to the conditioning unit.

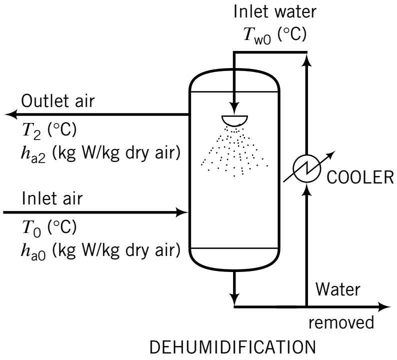
(c) Calculate the required heat transfer rates (Btu/ft^3 entering air) in each of the heating coil banks.

(d) Sketch a psychrometric chart and show the path followed by the air in each of the three steps of this process.

Equipment Encyclopedia
humidifier

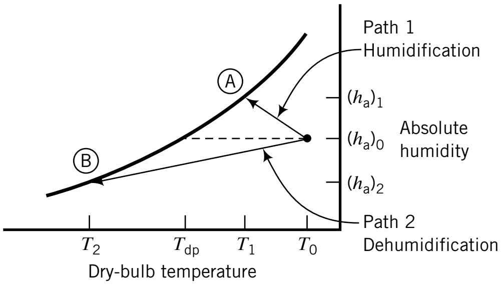
8.80. **Spray cooling** is a technique for cooling and either humidifying or dehumidifying air by contacting it with a liquid water spray.





The liquid water leaving the tower is recirculated and, in the case of dehumidification, cooled before reentering the tower.

Two possible paths on the psychrometric chart corresponding to two different entering liquid temperatures are shown below. On the chart, T_0 and T_{dp} are the entering air dry-bulb temperature and dew point, respectively.



***Path* Ⓐ:** The entering liquid temperature (T_{w0}) is above the dew point of the entering air. Liquid water evaporates into the superheated air, causing the absolute humidity of the air to increase (the path rises) and both the evaporation and the contact with the cold liquid cause the air temperature to decrease (the path moves to the left).

***Path* Ⓑ:** The entering liquid temperature is below the dew point of the entering air. The temperature of the air contacted by the cold spray drops below the dew point (the path again moves to the left), and water vapor condenses out of the air (the path moves down).

We thus arrive at the interesting conclusion that *you can remove water from air by spraying water into the air,* provided that the entering liquid temperature is below the dew point of the entering air.

Use the psychrometric chart to solve the following spray cooling problems.

(a) A spray tower is used to cool and humidify air with dry-bulb and wet-bulb temperatures of 40°C and 18°C, respectively. The air emerges from the tower at 20°C. The tower operation is such that the air follows an adiabatic humidification curve (a constant wet-bulb temperature line on the psychrometric chart). How much water must be added as makeup per kg of dry air treated?

(b) A stream of air at 37°C and 50% relative humidity flowing at a rate of 1250 kg/h is to be cooled to 15°C and dehumidified in a spray tower. The air is saturated as it emerges from the tower. Liquid water leaves the tower at 12°C; some is withdrawn, and the rest is cooled and recirculated. No heat is transferred between the tower and its surroundings. Calculate the rate (kg/h) at which water must be withdrawn from the recirculation loop and the heat duty on the cooler (kW). (*Suggestion:* Use an overall energy balance for the latter calculation.)

8.81. The heat of solution of ammonia in water at 1 atm is

$$\Delta\hat{H}_s(25^\circ\text{C}, r = 2 \text{ mol H}_2\text{O/mol NH}_3) = -78.2 \text{ kJ/mol}$$

Calculate the enthalpy change that accompanies the dissolution of 400 mol of NH_3 in 800 mol of water at 25°C and 1 atm.

8.82. Use Table B.11 to determine the specific enthalpy (kJ/mol HCl) of hydrochloric acid containing 1 mol HCl/5 mol H_2O at 25°C relative to:

(a) HCl(g) and H_2O(l) at 25°C.

(b) H_2O (l) and an infinitely dilute HCl solution at 25°C. (Note Equation 8.5-2.)

8.83. Sodium hydroxide is dissolved in enough water to make up a 20.0 mole% solution. If the NaOH and water are initially at 77°F (25°C), how much heat (Btu/lb product solution) must be removed for the solution also to be at 77°F. Assume the process is carried out at constant pressure, so that $Q = \Delta H$, and use Table B.11 to evaluate $\Delta\hat{H}_s$.

8.84. A sulfuric acid solution is labeled 8N (where 1N = 1 g-equivalent /L, and 1 mol of H_2SO_4 contains two g-equivalents). The specific gravity of the solution is 1.230, and its heat capacity is 3.00 J/(g·°C). Calculate the specific enthalpy of this solution (in kJ/mol H_2SO_4) at 60°C relative to pure H_2O and an infinitely dilute solution at 25°C.

8.85. You are about to dilute 2.00 mol of 100% sulfuric acid with enough water to produce a 30 mole% aqueous solution. The acid and water are initially at 25°C.

(a) How much heat would have to be removed to keep the final solution at 25°C?

(b) Suppose the flask has a mass of 150 g, and that the heat capacity of the flask and its contents is 3.30 J/(g·°C). If the flask is sufficiently insulated to be considered adiabatic, what will be the final solution temperature?

Student Workbook

Equipment Encyclopedia
absorption column

8.86. An 8-molar hydrochloric acid solution [SG = 1.12, C_p = 2.76 J/(g·°C)] is produced by absorbing hydrogen chloride [HCl(g)] in water. Liquid water enters the absorber at 25°C and gaseous HCl is fed at 20°C and 790 torr (absolute). Essentially all of the HCl fed to the column is absorbed. Take one liter of product solution as a basis of calculation.

(a) Estimate the volume (liters) of HCl that must be fed to the absorber.

(b) Estimate the heat (kJ) that must be transferred from the absorber if the product solution is to emerge at 40°C.

(c) Estimate the final solution temperature if the absorber operates adiabatically.

Equipment Encyclopedia
evaporator

8.87. A 0.1 mole% caustic soda (NaOH) solution is to be concentrated in a continuous evaporator. The solution enters the unit at 25°C at a rate of 150 mol/min and is concentrated to 5 mole% at 50°C. Hot dry air at 200°C and 1.1 bar absolute is bubbled through the evaporator and leaves saturated with water at 50°C and 1 atm. Calculate the required volumetric flow rate of the entering air and the rate at which heat must be transferred to or from the unit. Assume that the heat capacity per unit mass of all liquid solutions is that of pure water.

8.88. Water is added to pure sulfuric acid in a well-insulated flask initially at 25°C and 1 atm to produce a 4.00-molar sulfuric acid solution (SG $= 1.231$). The final temperature of the product solution is to be 25°C, so that the water added must be chilled liquid ($T < 25°\text{C}$), or a mixture of liquid water and ice. Take as a basis of calculation one liter of the product solution and assume $Q = \Delta H$ for the process. If you need to know the heat capacity of ice, take it to be half that of liquid water.

(a) If only liquid water is added, what masses (g) of H_2SO_4 and H_2O should be mixed and what should be the initial temperature of the water?

(b) If a mixture of liquid water and ice is added, how many grams of each should be fed?

Equipment Encyclopedia
evaporator

8.89. Ortho-phosphoric acid (H_3PO_4) is produced as a dilute aqueous solution that must be concentrated before further use. In one facility, 100 tons/day of a 28 wt% P_2O_5 solution [see part (a) of this problem] at 125°F is to be concentrated in a single evaporator to 42 wt% P_2O_5. Heat is supplied to the evaporator by condensing saturated steam at 27.5 psia. The evaporator is to operate at 3.7 psia, and there is a boiling point elevation of 37°F for the 42 wt% P_2O_5 solution in the evaporator (see Section 6.5c). The heat of solution of H_3PO_4 at 77°F may be taken to be -5040 Btu/lb-mole H_3PO_4 relative to H_3PO_4 (l) and H_2O(l). The heat capacity of the 28% solution is 0.705 Btu/(lb$_m$·°F) and that of the 42% solution is 0.583 Btu/(lb$_m$·°F).

(a) It is conventional for the compositions of phosphoric acid solutions to be expressed in terms of wt% P_2O_5. Write the stoichiometric equation for the formation of ortho-phosphoric acid (MW $= 98.00$) from phosphorus pentoxide (MW $= 141.96$), and use it to derive the expression

$$\text{wt\% } H_3PO_4 = 1.381(\text{wt\% } P_2O_5)$$

(b) Calculate the ratio (lb$_m$ water evaporated/lb$_m$ feed solution).

(c) Suppose the water evaporated is subsequently condensed at a constant pressure of 3.7 psia. Determine the condensate flow rate in gal/min. How much heat (Btu/min) can be recovered through condensation of this water? At what temperature is this heat available? (To put it another way, if this heat were to be transferred to another stream, what is an upper bound on the temperature of that stream?)

(d) How much steam (lb$_m$/h) must be supplied to the system to evaporate the required amount of water? Recast your answer in terms of lb$_m$ steam per lb$_m$ water evaporated.

Equipment Encyclopedia
crystallizer

8.90. Two hundred kilograms per hour of an aqueous solution containing 20.0 mole% sodium acetate ($NaC_2H_3O_2$) enters an evaporative crystallizer at 60°C. When the solution is exposed to the low pressure in the evaporator, 16.9% of the water evaporates, concentrating the remaining solution and causing crystals of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3\,H_2O$) to form. The product is an equilibrium mixture of crystals and a saturated aqueous solution containing 15.4 mole% $NaC_2H_3O_2$. The effluents (crystals, solution, and water vapor) are all at 50°C.

(a) Calculate the feed rate to the crystallizer in kmol/h.

(b) Calculate the production rate (kg/h) of trihydrate crystals and the mass flow rate (kg/h) of the liquid solution in which the crystals are suspended.

(c) Estimate the rate (kJ/h) at which heat must be transferred to or from the crystallizer (state which), using the following physical property data:

$$(C_p)_{\text{all solutions}} = 3.5 \text{ kJ/(kg·°C)}$$
$$(C_p)_{\text{crystals}} = 1.2 \text{ kJ/(kg·°C)}$$
$$(C_p)_{H_2O(v)} = 32.4 \text{ kJ/(kmol·°C)}$$
$$(\Delta\hat{H}_v)_{H_2O} = 4.39 \times 10^4 \text{ kJ/kmol}$$

Heat of solution of anhydrous sodium acetate:

$$\Delta\hat{H}_s(25°\text{C}) = -1.71 \times 10^4 \text{ kJ/kmol } NaC_2H_3O_2$$

Heat of hydration: $NaC_2H_3O_2(s) + 3\,H_2O(l) \rightarrow NaC_2H_3O_2 \cdot 3\,H_2O(s)$

$$\Delta\hat{H}(25°\text{C}) = -3.66 \times 10^4 \text{ kJ/kmol } NaC_2H_3O_2$$

8.91. Fifty milliliters of 100% H_2SO_4 at 25°C and 84.2 mL of liquid water at 15°C are mixed. The heat capacity of the product solution is 2.43 J/(g·°C). Estimate the maximum temperature attainable by the product solution and state the conditions under which this temperature would be attained, using heat of mixing data from Table B.11.

8.92. Suppose m_A(g) of species A {molecular weight M_A, heat capacity C_{pA} [J/(g·°C)]} at temperature T_{A0} (°C) and m_B(g) of species B (M_B, C_{pB}) at temperature T_{B0} are mixed adiabatically. The heat of mixing of A and B at 25°C is $\Delta\hat{H}_m(r)$ (J/mol A in solution), where $r = (m_B/M_B)/(m_A/M_A)$. The heat capacity of the product solution is C_{ps}[J/(g·°C)]. All heat capacities may be considered independent of temperature.

(a) Derive an expression for T_{max}, the highest temperature attainable by the product solution, in terms of the other quantities defined. State the conditions that would have to be met for this temperature to be approached.

(b) Use your expression to estimate T_{max} for a process in which 100.0 g of sodium hydroxide at 25°C and 225.0 g of water at 40°C are combined to form a product solution with a heat capacity of 3.35 J/(g·°C).

8.93. One g-mole of pure liquid sulfuric acid at temperature T_0 (°C) is mixed with r g-moles of liquid water, also at temperature T_0(°C), in an adiabatic container. The final solution temperature is T_s(°C). The mass heat capacities of the pure acid, pure water, and the product solution [J/(g·°C)] are C_{pa}, C_{pw}, and C_{ps}, respectively, all of which may be taken to be constant (independent of temperature).

(a) Without doing any calculations, sketch the plot of T_s versus r you would expect to obtain for r varying between 0 and ∞. (*Hint:* Think first about what you would expect T_s to be at the extreme values of r.)

(b) Use an energy balance to derive an expression for T_s in terms of the initial acid and water temperatures, the heat capacities, the water/acid mole ratio (r), and the heat of mixing, $\Delta\hat{H}_m(r, 25\,°C)$ (kJ/mol H_2SO_4).

*__(c)__ A series of 1.00 mol samples of pure liquid sulfuric acid are added to 11 insulated flasks containing varying amounts of water. The quantities of water in the flasks and the mass heat capacities of the product solutions are tabulated below:

r (mol H_2O)	0.5	1.0	1.5	2.0	3.0	4.0	5.0	10.0	25.0	50.0	100.0
C_p [J/(g·°C)]	1.58	1.85	1.89	1.94	2.10	2.27	2.43	3.03	3.56	3.84	4.00

The heat capacities of pure sulfuric acid and pure water may be determined from the molar heat capacities in Table B.2 evaluated at 25°C. All heat capacities should be taken to be independent of temperature.

Unfortunately, the laboratory air conditioner has been out of order for three weeks (Physical Plant promises they will get to it any day now) and the temperature on the July afternoon of the experiment (which also equals the initial acid and water temperatures) is an uncomfortable 40°C. Write a spreadsheet to generate a table and then a plot of T_s, the final temperature in each flask, versus r, the water/acid mole ratio of the solution in the flask. (*Suggestion:* Make the r axis logarithmic.) Assume that mixing is adiabatic.

(d) The actual experimental plot of T_s versus r would lie below the one determined in part (c). Why?

***8.94.** A stirred tank with volume V_t(L) is charged with V_l(L) of a liquid, B. The space above the liquid (volume $V_g = V_t - V_l$) is filled with a pure gas, A, at an initial pressure P_0(atm). The initial system temperature is T_0(K). The stirrer in the tank is turned on, and A begins to dissolve in B. The dissolution continues until the liquid is saturated with A at the final system temperature (T) and pressure (P).

The equilibrium solubility of A in B is governed by the following expression, which relates the molar A/B ratio in the liquid to the partial pressure of A in the gas phase (which in turn equals the pressure in the tank, since the gas is pure A):

$$r(\text{mol A/mol B}) = k_s p_A(\text{atm})$$

where

$$k_s[\text{mol A/(mol B·atm)}] = c_0 + c_1 T(\text{K})$$

---

*Computer problems.

When solving the problems to be given, use the following variable definitions:

- M_A, M_B = molecular weights of A and B
- C_{vA}, C_{vB}, C_{vS}[J/(g·K)] =constant-volume heat capacities of A(g), B(l), and solutions of A in B, respectively
- SG_B = specific gravity of B(l)
- $\Delta\hat{U}_s$ (J/mol A dissolved) = internal energy of solution at 298 K (independent of composition over the range of concentrations to be considered)
- n_{A0}, n_{B0} = g-moles of A(g) and B(l) initially charged into the tank
- $n_{A(l)}$, $n_{A(v)}$ = g-moles of A dissolved and remaining in the gas phase at equilibrium, respectively

Make the following assumptions:

- A negligible amount of B evaporates.
- The tank is adiabatic and the work input to the tank from the stirrer is negligible.
- The gas phase behaves ideally.
- The volumes of the liquid and gas phases may be considered constant.
- The heat capacities C_{vA}, C_{vB}, and C_{vs} are constant, independent of temperature and (in the case of C_{vs}) solution composition.

(a) Use material balances, the given equilibrium solubility relation, and the ideal gas equation of state to derive expressions for n_{A0}, n_{B0}, $n_{A(v)}$, $n_{A(l)}$, and P in terms of the final temperature, T, and variables M_A, M_B, SG_B, V_t, V_l, T_0, P_0, c_0, and c_1. Then use an energy balance to derive the following equation:

$$T = 298 + \frac{n_{A(l)}(-\Delta\hat{U}_s) + (n_{A0}M_A C_{vA} + n_{B0}M_B C_{vB})(T_0 - 298)}{n_{A(v)}M_A C_{vA} + (n_{A(l)}M_{A(l)} + n_B M_B)C_{vs}}$$

(b) Write a spreadsheet to calculate T from specified values of $M_A(= 47)$, $M_B(= 26)$, $SG_B(= 1.76)$, $V_t(= 20.0)$, $V_l(= 3.0)$, $c_0(= 1.54 \times 10^{-3})$, $c_1(= -1.60 \times 10^{-6})$, $C_{vA}(= 0.831)$, $C_{vB}(= 3.85)$, $C_{vs}(= 3.80)$, and $\Delta\hat{U}_s(= -1.74 \times 10^5)$, and a number of different values of T_0 and P_0. The spreadsheet should have the structure given below. (Calculated values are shown for one initial temperature and pressure.)

Problem 8.94										
Vt	MA	CvA	MB	CvB	SGB	c0	c1	DUs	Cvs	
20.0	47.0	0.831	26.0	3.85	1.76	0.00154	-1.60E-06	-174000	3.80	
Vl	T0	P0	Vg	nB0	nA0	T	nA(v)	nA(l)	P	Tcalc
3.0	300	1.0								
3.0	300	5.0								
3.0	300	10.0	17.0	203.1	6.906	320.0	5.222	1.684	8.1	314.2
3.0	300	20.0								
3.0	330	1.0								
3.0	330	5.0								
3.0	330	10.0								
3.0	330	20.0								

The values of V_g, n_{B0}, and n_{A0} should first be calculated from the given values of the other variables. Next, a value of T should be guessed (in the example in the table, the guessed value is 320 K), the values of $n_{A(v)}$, $n_{A(l)}$, and P should be calculated from the equations derived in part (a), and the temperature should be recalculated from the energy balance in the column labeled T_{calc} (it equals 314.2 in the example). The value of T should then be varied until it equals the recalculated value of T_{calc}. (*Suggestion:* Create a new cell as $T - T_{calc}$ and use goalseek to find the value of T that drives $T - T_{calc}$ to zero.)

Enter the formulas in the cells for $V_l = 3.0$ L, $T_0 = 300$ K, and $P_0 = 10.0$ atm, and verify that your cell values match those shown above. Then find the correct value of T using the procedure just described, copy the formulas into the other rows of the table, and determine T for each set of initial conditions. Summarize the effects of the initial temperature and pressure on the adiabatic temperature rise and briefly explain why your results make sense.

(c) Write a computer program to perform the same calculations done with the spreadsheet in part (b).

- Define values of V_t, M_A, C_{vA}, M_B, C_{vB}, SG_B, c_0, c_1, $\Delta\hat{U}_s$, and C_{vs}. Use the values shown in the fourth row of the spreadsheet.
- Read in a set of values of V_B, T_0, and P_0. Have the program terminate if $V_B \leq 0.0$.
- If a positive value is read in for V_B, calculate V_G, n_B, and n_{A0}.
- Assume a value of T. (Try $1.1T_0$ as a first guess.)
- Calculate $n_{A(v)}$, $n_{A(l)}$, and P from the equations derived in part (a), then recalculate T from the energy balance. Print out the values of T(assumed), P, $n_{A(v)}$, $n_{A(l)}$, and T (recalculated).
- If the assumed and recalculated values of T are within 0.01 K of each other, end the loop and go back to read the next set of input variables. If they are not and more than 15 iterations have been performed, terminate with an error message. Otherwise, repeat the previous step, using the recalculated value of T as the assumed value for this iteration.

Run the program for the eight sets of conditions shown in the spreadsheet table.

8.95. An aqueous solution containing 85.0 wt% H_2SO_4 at 60°F (specific gravity = 1.78) is diluted with pure liquid water at the same temperature. The feed solution volume is 350 mL. The mixing may be considered adiabatic, and the pressure is constant at 1 atm.

(a) The product solution is to contain 30.0 wt% H_2SO_4. Calculate the volume (mL) of water needed for the dilution, ideally using a single-dimensional equation.

(b) Use the enthalpy–concentration chart of Figure 8.5-1 to estimate the specific enthalpies (Btu/lb$_m$) of the feed solution and the water. Then write an energy balance on this closed system constant-pressure process and solve it for the specific enthalpy of the product solution. Finally, use Figure 8.5-1 to verify your calculated value of $\hat{H}_{product}$ and to estimate the product solution temperature. (See Example 8.5-3.)

(c) Use Figure 8.5-1 to estimate the maximum temperature that could be attained by mixing the feed solution with pure water and the concentration (wt% H_2SO_4) of the product solution.

(d) Good laboratory practice calls for adding acid to water when carrying out dilutions rather than vice versa. Use Figure 8.5-1 to justify this rule for the dilution of the feed solution in this problem.

8.96. Aqueous sulfuric acid solutions containing 15.0 wt% H_2SO_4 and 80.0 wt% H_2SO_4 are mixed to form a 60.0 wt% product solution. The 15% solution was in a laboratory in which the temperature was 77°F. The 80% solution had just been taken from a storage cabinet in an air-conditioned stockroom and was at a temperature of 60°F when the mixing occurred.

(a) The mass of the 15% solution is 2.30 lb$_m$. What mass of 60% solution should be weighed out?

(b) Use Figure 8.5-1 to estimate the product solution temperature if the mixing is adiabatic. (See Example 8.5-3.)

(c) The product solution temperature eventually drops to (77°F). How much heat (Btu) is transferred from the solution to the laboratory air in this constant-pressure cooling process?

(d) Which would be safer—adding the 15% solution slowly to the 80% solution or vice versa? Use Figure 8.5-1 to justify your answer.

8.97. You have analyzed an aqueous ammonia solution and find that it contains 30 wt% NH_3.

(a) Use Figure 8.5-2 to determine the mass fraction of NH_3 in the vapor that would be in equilibrium with this solution in a closed flask at 1 atm and the corresponding system temperature.

(b) If the liquid phase in part (a) accounts for 90% of the total system mass, calculate the overall system composition and specific enthalpy using balances. (See Example 8.5-3.)

8.98. An NH_3–H_2O mixture containing 60 wt% NH_3 is brought to equilibrium in a closed container at 140°F. The total mass of the mixture is 250 g. Use Figure 8.5-2 to determine the masses of ammonia and of water in each phase of the system.

8.99. An ammonia solution at a high pressure is flash-vaporized at a rate of 200 lb_m/h. The solution contains 0.70 lb_m NH_3/lb_m, and its enthalpy relative to H_2O(l, 32°F) and NH_3(l, −40°F) is −50 Btu/lb_m. Liquid and gas streams emerge from the unit at 1 atm and 80°F. Use Figure 8.5-2 to determine the mass flow rates and ammonia mass fractions of the vapor and the liquid product streams and the rate (Btu/h) at which heat must be transferred to the vaporizer. (See Example 8.5-4.)

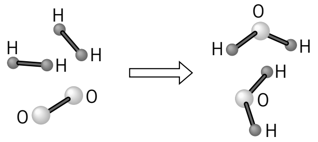
Chapter 9

Balances on Reactive Processes

Consider the familiar reaction in which water is formed from hydrogen and oxygen:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(v)$$

On the molecular level, the reaction might be depicted as follows:



Each time this reaction takes place, three chemical bonds are broken (two between hydrogen atoms and one between oxygen atoms) and four bonds are formed among the atoms of the two water molecules. As it happens, more energy is released when the water molecule bonds form than it takes to break the hydrogen and oxygen molecule bonds. For the reactor temperature to remain constant, the net energy released (about 250 kJ per mol of water formed) must be transferred away from the reactor; otherwise it can raise the reactor temperature by several thousand degrees.

In *any* reaction between stable molecules, energy is required to break the reactant chemical bonds and energy is released when the product bonds form. If the first process absorbs less energy than the second process releases (as in the water formation reaction), the reaction is **exothermic**: the product molecules at a given temperature and pressure have lower internal energies (and hence lower enthalpies) than the reactant molecules at the same temperature and pressure. The net energy released—the **heat of reaction**—must be transferred from the reactor as heat or work, or else the system temperature increases. On the other hand, if less energy is released when the product bonds form than it took to break the reactant bonds, the reaction is **endothermic**: energy must be added to the reactor as heat or work to keep the temperature from decreasing.

The large internal energy and enthalpy changes commonly associated with chemical reactions can play major roles in the design and operation of chemical processes. If a reaction is endothermic, the energy needed to keep the reactor temperature (and hence the reaction rate) from dropping too much may cost enough to turn a profitable process into an unprofitable one. On the other hand, if the reaction is exothermic, heat usually must be transferred away from the reactor to keep the temperature below a value that leads to safety or product quality problems. The heat transferred may be an asset, as when the reactor is a combustion furnace and the heat is used to generate steam in a boiler. It may also be a liability: for example, a momentary failure of the reactor temperature control system can lead to rapid overheating and possibly an explosion.

An energy balance on a reactor tells the process engineer how much heating or cooling the reactor requires in order to operate at the desired conditions. In this chapter we show how enthalpy changes that accompany chemical reactions are determined from tabulated physical properties of the reactants and products and how calculated enthalpies of reaction are incorporated in energy balances on reactive processes.

TEST YOURSELF (Answers, p. 660)

1. Explain in your own words the concepts of exothermic and endothermic reactions. The terms "chemical bonds" and "heat of reaction" should appear in your explanation.
2. The following two sentences seem to contain a self-contradiction.

> *In an exothermic reaction, the products are at a* lower *energy level than the reactants. However, if the reactor is not cooled, the products are hotter than the reactants, which means they must be at a* higher *energy level than the reactants.*

Identify the logical error in this paragraph.

CREATIVITY EXERCISE

Suppose an exothermic reaction takes place in a continuous reactor. Think of several ways the heat of reaction might be removed, illustrating your suggestions with sketches. (For example, pass a cold fluid through a hollow metal tube immersed in the reactor, so that heat is transferred from the hot reacting fluid to the coolant.)

9.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to do the following:

- Explain in your own words the concepts of heat of reaction; exothermic and endothermic reactions; heat of formation; combustion; heat of combustion; standard heats of formation, combustion, and reaction; heating value of a fuel; adiabatic flame temperature; ignition temperature; ignition lag; lower and upper flammability limits and flash point of a fuel; a flame; blue and yellow flames; flashback; and detonation.
- Given (a) the amount of any reactant consumed or any product generated in a reaction at a given temperature and pressure and (b) the heat of the reaction at that temperature and pressure, calculate the total enthalpy change.
- Determine a heat of reaction from heats of other reactions using Hess's law. Determine standard enthalpies and internal energies of reaction from known standard heats of formation and heats of combustion.
- Write and solve an energy balance on a chemical reactor using either the heat of reaction method (taking reactant and product species as references for enthalpy calculations) or the heat of formation method (taking elemental species as references), and specify which method is preferable for a given process. Write the process path implicitly adopted when each method is used.
- Solve reactive-system energy balance problems for (a) the heat transfer required for specified inlet and outlet conditions, (b) the outlet temperature corresponding to a specified heat input (e.g., for an adiabatic reactor), and (c) the product composition corresponding to a specified heat input and a specified outlet temperature.
- Solve energy balance problems for processes involving solutions for which heats of solution are significant.
- Convert a higher heating value of a fuel to a lower heating value and vice versa.

9.1 HEATS OF REACTION

Consider the reaction between solid calcium carbide and liquid water to form solid calcium hydroxide and gaseous acetylene:

$$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g) \qquad \textbf{(9.1-1)}$$

The expression *stoichiometric quantities of reactants* means molar amounts of the reactants numerically equal to their stoichiometric coefficients. For the calcium carbide reaction, stoichiometric quantities of the reactants in the SI system of units would be 1 mol of $CaC_2(s)$ and 2 mol of $H_2O(l)$. If stoichiometric quantities of the reactants are fed and the reaction proceeds to completion, both reactants would be completely consumed and stoichiometric quantities of the products would be formed. (Convince yourself.)

The **heat of reaction** (*or* **enthalpy of reaction**), $\Delta\hat{H}_r(T, P)$, *is the enthalpy change for a process in which stoichiometric quantities of reactants at temperature T and pressure P react completely in a single reaction to form products at the same temperature and pressure.* For example, the heat of the calcium carbide reaction at 25°C and 1 atm is

$$\Delta\hat{H}_r(25°\text{C}, 1\text{ atm}) = -125.4\text{ kJ/mol} \qquad \textbf{(9.1-2)}$$

Equations 9.1-1 and 9.1-2 together signify that if 1 mol of solid calcium carbide reacts completely with 2 mol of liquid water to form 1 mol of solid calcium hydroxide and 1 mol of gaseous acetylene, and the initial and final temperatures are both 25°C and the initial and final pressures are both 1 atm, then $H_{\text{products}} - H_{\text{reactants}} = -125.4$ kJ. If the reaction is run under conditions such that the energy balance reduces to $Q = \Delta H$, then 125.4 kJ of heat must be transferred from the reactor in the course of the reaction. (Recall that a negative Q implies flow of heat out of the system.)

The units of $\Delta\hat{H}_r$ often cause confusion. For example, if the heat of a reaction is reported to be −50 kJ/mol, you might ask "per mol of what?" This difficulty is avoided if you recall that the given $\Delta\hat{H}_r$ applies to stoichiometric quantities of each species. For example,

$$2\text{A} + \text{B} \rightarrow 3\text{C}: \quad \Delta\hat{H}_r(100°\text{C}, 1\text{ atm}) = -50\text{ kJ/mol}$$

means that the enthalpy change for the given reaction is

$$\frac{-50\text{ kJ}}{2\text{ mol A consumed}} = \frac{-50\text{ kJ}}{1\text{ mol B consumed}} = \frac{-50\text{ kJ}}{3\text{ mol C generated}}$$

If you knew, say, that 150 mol of C/s was generated in the given reaction at 100°C and 1 atm, you could calculate the associated enthalpy change as

$$\Delta\dot{H} = \frac{-50\text{ kJ}}{3\text{ mol C generated}} \left| \frac{150\text{ mol C generated}}{\text{s}} \right. = -2500\text{ kJ/s}$$

More generally, if ν_A is the stoichiometric coefficient of a reactant or reaction product A (positive if A is a product, negative if it is a reactant) and $n_{A,r}$ moles of A are consumed or generated at $T = T_0$ and $P = P_0$, then the associated enthalpy change is

$$\Delta H = \frac{\Delta\hat{H}_r(T_0, P_0)}{|\nu_A|} n_{A,r}$$

In Chapter 4, we defined the *extent of reaction*, ξ, as a measure of how far a reaction has proceeded. From Equation 4.6-3, this quantity is

$$\xi = \frac{|n_{A,\text{out}} - n_{A,\text{in}}|}{|\nu_A|} = \frac{n_{A,r}}{|\nu_A|} \qquad \textbf{(9.1-3)}$$

From the preceding two equations, it follows that if a reaction takes place at a temperature T_0 and pressure P_0 and the extent of reaction is ξ, the associated enthalpy change is

$$\boxed{\Delta H = \xi\Delta\hat{H}_r(T_0, P_0)} \qquad \textbf{(9.1-4)}$$

For a continuous process, $n_{\mathrm{A,r}}$(mol) would be replaced by $\dot{n}_{\mathrm{A,r}}$(mol/s) in this expression, ξ(mol) would be replaced by $\dot{\xi}$(mol/s), and ΔH(kJ) would be replaced by $\Delta\dot{H}$(kJ/s).

Following are several important terms and observations related to heats of reaction.

1. If $\Delta\hat{H}_{\mathrm{r}}(T, P)$ is negative the reaction is **exothermic** at temperature T and pressure P, and if $\Delta\hat{H}_{\mathrm{r}}(T, P)$ is positive the reaction is **endothermic** at T and P. These definitions of exothermic and endothermic are equivalent to the ones given earlier in terms of chemical bond strengths. (Convince yourself.)
2. *At low and moderate pressures,* $\Delta\hat{H}_{\mathrm{r}}(T, P)$ *is nearly independent of pressure.* We will presume this independence in the balance of this chapter and write the heat of reaction as $\Delta\hat{H}_{\mathrm{r}}(T)$.
3. *The value of the heat of a reaction depends on how the stoichiometric equation is written.* For example,

$$\begin{aligned} CH_4(g) + 2\,O_2(g) &\longrightarrow CO_2(g) + 2\,H_2O(l): \quad \Delta\hat{H}_{r1}(25°C) = -890.3 \text{ kJ/mol} \\ 2\,CH_4(g) + 4\,O_2(g) &\longrightarrow 2\,CO_2(g) + 4H_2O(l): \quad \Delta\hat{H}_{r2}(25°C) = -1780.6 \text{ kJ/mol} \end{aligned}$$

   This result should seem reasonable to you if you look back at the definition of $\Delta\hat{H}_{\mathrm{r}}$. The first line states that the combined enthalpy of 1 gram-mole of CO_2 plus 2 gram-moles of liquid water is 890.3 kJ lower than the combined enthalpy of 1 gram-mole of methane plus 2 gram-moles of oxygen at 25°C. Doubling the quantity of reactants at a given condition doubles the total enthalpy of the reactants at that condition, and similarly for the products. The difference between the product and reactant enthalpies in the second reaction (by definition, $\Delta\hat{H}_{\mathrm{r2}}$) must therefore be double the enthalpy difference in the first reaction ($\Delta\hat{H}_{\mathrm{r1}}$).
4. *The value of a heat of reaction depends on the states of aggregation (gas, liquid, or solid) of the reactants and products.* For example,

$$\begin{aligned} CH_4(g) + 2\,O_2(g) &\longrightarrow CO_2(g) + 2\,H_2O(l): \quad \Delta\hat{H}_{r}(25°C) = -890.3 \text{ kJ/mol} \\ CH_4(g) + 2\,O_2(g) &\longrightarrow CO_2(g) + 2\,H_2O(g): \quad \Delta\hat{H}_{r}(25°C) = -802.3 \text{ kJ/mol} \end{aligned}$$

   The only difference between the reactions is that the water formed is a liquid in the first one and a vapor in the second. Since enthalpy is a state function, the difference between the two heats of reaction must be the enthalpy change associated with the vaporization of 2 mol of water at 25°C—that is, $2\Delta\hat{H}_{\mathrm{v}}(25°C)$.
5. The **standard heat of reaction,** $\Delta\hat{H}_{\mathrm{r}}^{\circ}$, is the heat of reaction when both the reactants and products are at a specified reference temperature and pressure, usually (and always in this text) 25°C and 1 atm.

EXAMPLE 9.1-1 *Calculation of Heats of Reaction*

1. The standard heat of the combustion of n-butane vapor is

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(l): \quad \Delta\hat{H}_{r}^{\circ} = -2878 \text{ kJ/mol}$$

   Calculate the rate of enthalpy change, $\Delta\dot{H}$(kJ/s), if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.
2. What is the standard heat of the reaction

$$2\,C_4H_{10}(g) + 13\,O_2(g) \longrightarrow 8\,CO_2(g) + 10\,H_2O(l)$$

   Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in *this* reaction and the reactants and products are all at 25°C.
3. The heats of vaporization of n-butane and water at 25°C are 19.2 kJ/mol and 44.0 kJ/mol, respectively. What is the standard heat of the reaction

$$C_4H_{10}(l) + \tfrac{13}{2}O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(v)$$

   Calculate $\Delta\dot{H}$ if 2400 mol/s of CO_2 is produced in this reaction and the reactants and products are all at 25°C.

SOLUTION **1.** From Equation 9.1-3,

$$\dot{\xi} = \frac{(\dot{n}_{CO_2})_r}{|\nu_{CO_2}|} = \frac{2400 \text{ mol/s}}{4} = 600 \text{ mol/s}$$

$$\Big\Downarrow \text{Equation 9.1-4}$$

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ = \left(600\ \frac{\text{mol}}{\text{s}}\right)\left(-2878\ \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

2. Since doubling the stoichiometric coefficients of a reaction must double the heat of reaction,

$$\Delta\hat{H}_{r2}^\circ = 2\Delta\hat{H}_{r1}^\circ = 2(-2878 \text{ kJ/mol}) = -5756 \text{ kJ/mol}$$

The enthalpy change associated with the production of 2400 mol/s of CO_2 at 25°C cannot depend on how the stoichiometric equation is written (the same quantities of reactants and products at the same temperatures must have the same enthalpies), and so $\Delta\dot{H}$ must be the value calculated in part (a). Let us do the calculation and prove it, however. From Equation 9.1-3,

$$\dot{\xi} = \frac{(\dot{n}_{CO_2})_{out}}{|\nu_{CO_2}|} = \frac{2400 \text{ mol/s}}{8} = 300 \text{ mol/s}$$

$$\Big\Downarrow \text{Equation 9.1-4}$$

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ = \left(300\ \frac{\text{mol}}{\text{s}}\right)\left(-5756\ \frac{\text{kJ}}{\text{mol}}\right) = -1.73 \times 10^6 \text{ kJ/s}$$

3. Compare the two reactions:

$$C_4H_{10}(g) + \tfrac{13}{2}O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(l): \quad (\Delta\hat{H}_{r1}^\circ) = -2878 \text{ kJ/mol}$$

$$C_4H_{10}(l) + \tfrac{13}{2}O_2(g) \longrightarrow 4\,CO_2(g) + 5\,H_2O(v): \quad (\Delta\hat{H}_{r2}^\circ) = \ ?$$

The total enthalpy of the products in the second reaction [4 mol $CO_2(g)$ + 5 mol $H_2O(g)$ at 25°C] is greater than that of the products in the first reaction [4 mol $CO_2(g)$ + 5 mol $H_2O(l)$ at 25°C] by five times the heat of vaporization of water. Similarly, the total enthalpy of the reactants in the second reaction is lower than that of the reactants in the first reaction by the heat of vaporization of butane. (Why?) Since $\Delta\hat{H}_r = H_{\text{products}} - H_{\text{reactants}}$, it follows that

$$(\Delta\hat{H}_{r2}^\circ) = (\Delta\hat{H}_{r1}^\circ) + 5(\Delta\hat{H}_v)_{H_2O} + (\Delta\hat{H}_v)_{C_4H_{10}}$$

$$= [-2878 + 5(44.0) + 19.2] \text{ kJ/mol} = \boxed{-2639 \text{ kJ/mol}}$$

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_{r2}^\circ = \left(600\ \frac{\text{mol}}{\text{s}}\right)\left(-2639\ \frac{\text{kJ}}{\text{mol}}\right) = \boxed{-1.58 \times 10^6 \text{ kJ/s}}$$

If a reaction takes place in a closed reactor at constant volume, the heat released or absorbed is determined by the change in internal energy between reactants and products. The **internal energy of reaction,** $\Delta\hat{U}_r(T)$, is the difference $U_{\text{products}} - U_{\text{reactants}}$ if stoichiometric quantities of reactants react completely at temperature T.

Suppose a reaction occurs, and ν_i is the stoichiometric coefficient of the ith gaseous reactant or product. If ideal gas behavior can be assumed and specific volumes of liquid and solid reactants and products are negligible compared with those of the gases, the internal energy of reaction is related to the heat of reaction by

$$\Delta\hat{U}_r(T) = \Delta\hat{H}_r(T) - RT\left(\sum_{\substack{\text{gaseous}\\\text{products}}} |\nu_i| - \sum_{\substack{\text{gaseous}\\\text{reactants}}} |\nu_i|\right) \qquad \textbf{(9.1-5)}$$

For example, for the reaction

$$C_6H_{14}(l) + \tfrac{19}{2}O_2(g) \rightarrow 6\,CO(g) + 7\,H_2O(v)$$

the internal energy of reaction is

$$\begin{aligned}\Delta\hat{U}_r(T) &= \Delta\hat{H}_r(T) - RT(6 + 7 - \tfrac{19}{2})\\ &= \Delta\hat{H}_r(T) - \tfrac{7}{2}RT\end{aligned}$$

If there are no gaseous reactants or products, then to a good approximation $\Delta\hat{U}_r = \Delta\hat{H}_r$.

EXAMPLE 9.1-2 *Evaluation of $\Delta\hat{U}_r$*

The standard heat of the reaction

$$C_2H_4(g) + 2\,Cl_2(g) \rightarrow C_2HCl_3(l) + H_2(g) + HCl(g)$$

is $\Delta\hat{H}_r^\circ = -420.8$ kJ/mol. Calculate $\Delta\hat{U}_r^\circ$ for this reaction.

SOLUTION From the stoichiometric equation

$$\sum \nu_i\,(\text{product gases}) = 1 + 1 = 2$$

$$\sum \nu_i\,(\text{reactant gases}) = 1 + 2 = 3$$

From Equation 9.1-5

$$\begin{aligned}\Delta\hat{U}_r &= \Delta\hat{H}_r - RT(2-3)\\ &= -420.8\text{ kJ/mol} - \frac{8.314\text{ J}}{\text{mol}\cdot\text{K}}\left|\frac{298\text{ K}}{}\right|\frac{-1}{}\left|\frac{1\text{ kJ}}{10^3\text{ J}}\right.\\ &= \boxed{-418.3\text{ kJ/mol}}\end{aligned}$$

TEST YOURSELF (Answers, p. 661)

1. What is a heat of reaction? A standard heat of reaction?
2. Suppose $\Delta\hat{H}_r^\circ$ is −40 kJ/mol for the reaction $2A \rightarrow B$.
   - **(a)** What is the value of the ratio (kJ/mol A reacted)?
   - **(b)** Is the reaction exothermic or endothermic at 25°C and 1 atm?
   - **(c)** If the reactants and products are at the same temperature, must heat be added to or withdrawn from the reactor? (Assume that the energy balance reduces to $Q = \Delta H$.)
   - **(d)** If the reactor is adiabatic ($Q = 0$), would the products leave at a higher or a lower temperature than that of the entering reactants?
3. $C_6H_{14}(l) + \frac{19}{2}O_2 \rightarrow 6\,CO_2 + 7\,H_2O(l)$: $\Delta\hat{H}_r^\circ = -4163$ kJ/mol
   $C_6H_{14}(g) + \frac{19}{2}O_2 \rightarrow 6\,CO_2 + 7\,H_2O(l)$: $\Delta\hat{H}_r^\circ = -4195$ kJ/mol
   The standard state for the heats of reaction is 25° and 1 atm. What is the physical significance of the difference between the two given values of $\Delta\hat{H}_r^\circ$?
4. Write the formula for $\Delta\hat{U}_r(T)$ in terms of $\Delta\hat{H}_r(T)$ for the reaction $A(g) + 2B(g) + C(l) \rightarrow D(g) + 2E(s)$.
5. Derive Equation 9.1-5 from the definition of $\hat{H}$ as $\hat{U} + P\hat{V}$.

9.2 MEASUREMENT AND CALCULATION OF HEATS OF REACTION: HESS'S LAW

A heat of reaction may be measured in a **calorimeter**—a closed reactor immersed in a fluid contained in a well-insulated vessel. The rise or fall of the fluid temperature can be measured and used to determine the energy released or absorbed by the reaction, and the value of $\Delta\hat{H}_r^\circ$ may then be calculated from that energy and known reactant and product heat capacities.

There are serious limitations to this technique, however. Suppose, for example, you wish to determine $\Delta\hat{H}_r^\circ$ for the reaction

$$C(s) + \tfrac{1}{2}\,O_2(g) \rightarrow CO(g)$$

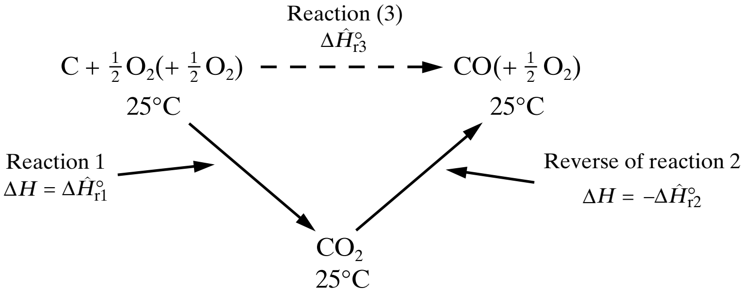
You could put 1 mole of carbon and 0.5 mole of oxygen together in a reactor, but you would never get 1 mole of carbon monoxide as the final product. If the reactants are at or near 25°C or lower, nothing apparent would occur since the rate at which carbon and oxygen react at this temperature is immeasurably low. If, on the other hand, the mixture were heated to a temperature at which C and O_2 react at a measurable rate, the product would be either pure CO_2 or at best a mixture of CO and CO_2, making it impossible to determine the heat of the CO formation reaction alone.

However, you *can* carry out the reactions

1. $C + O_2 \rightarrow CO_2$: $\Delta\hat{H}^\circ_{r1} = -393.51$ kJ/mol
2. $CO + \frac{1}{2}O_2 \rightarrow CO_2$: $\Delta\hat{H}^\circ_{r2} = -282.99$ kJ/mol

and determine their heats of reaction experimentally. You may then construct a process path for the reaction

3. $C + \frac{1}{2}O_2 \rightarrow CO$: $\Delta\hat{H}^\circ_{r3} = ?$



Since $\hat{H}$ is a state function,

$$\Delta\hat{H}^\circ_{r3} = \Delta\hat{H}^\circ_{r1} + (-\Delta\hat{H}^\circ_{r2}) = (-393.51 + 282.99)\text{ kJ/mol} = -110.52\text{ kJ/mol}$$

You have thus calculated the desired heat of reaction, which could not be measured directly, from two measurable heats of reaction.

This result could have been obtained more concisely by treating the stoichiometric equations for reactions 1 and 2 as algebraic equations. If the equation for reaction 2 is subtracted from that for reaction 1, the result is

$$C + O_2 - CO - \tfrac{1}{2}O_2 \rightarrow CO_2 - CO_2$$

$$\Downarrow$$

$$C + \tfrac{1}{2}O_2 \rightarrow CO\ \text{(reaction 3)}$$

The standard heat of reaction 3 may be calculated by applying the same operation to the heats of reactions 1 and 2—that is, $\Delta\hat{H}^\circ_{r3} = \Delta\hat{H}^\circ_{r1} - \Delta\hat{H}^\circ_{r2}$—confirming the result previously obtained.

The general statement of the validity of this procedure is called **Hess's law:** *If the stoichiometric equation for reaction 1 can be obtained by algebraic operations (multiplication by constants, addition, and subtraction) on stoichiometric equations for reactions 2, 3, . . . , then the heat of reaction* $\Delta\hat{H}^\circ_{r1}$ *can be obtained by performing the same operations on the heats of reactions* $\Delta\hat{H}^\circ_{r2}, \Delta\hat{H}^\circ_{r3}, \ldots$.

EXAMPLE 9.2-1 *Hess's Law*

The standard heats of the following combustion reactions have been determined experimentally:

1. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2\,CO_2 + 3\,H_2O$: $\Delta\hat{H}^\circ_{r1} = -1559.8$ kJ/mol
2. $C + O_2 \rightarrow CO_2$: $\Delta\hat{H}^\circ_{r2} = -393.5$ kJ/mol
3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$: $\Delta\hat{H}^\circ_{r3} = -285.8$ kJ/mol

Use Hess's law and the given heats of reaction to determine the standard heat of the reaction

4. $2\,C + 3\,H_2 \rightarrow C_2H_6$: $\Delta H^\circ_{r4} = ?$

SOLUTION Since

$$(4) = 2 \times (2) + 3 \times (3) - (1)$$

(*verify*), from Hess's law

$$\Delta \hat{H}^\circ_{r4} = 2\Delta \hat{H}^\circ_{r2} + 3\Delta \hat{H}^\circ_{r3} - \Delta \hat{H}^\circ_{r1} = -84.6 \text{ kJ/mol}$$

This heat of reaction could not have been measured directly, since you cannot react carbon and hydrogen in such a way that ethane is the only reaction product.

TEST YOURSELF (Answers, p. 661)

1. What is Hess's law?
2. Suppose heats of reaction at 25°C are measured experimentally for the following set of reactions:

$$2\,A + B \rightarrow 2C: \quad \Delta \hat{H}^\circ_{r1} = -1000 \text{ kJ/mol}$$
$$A + D \rightarrow C + 3\,E: \quad \Delta \hat{H}^\circ_{r2} = -2000 \text{ kJ/mol}$$

Use Hess's law to show that for

$$B + 6\,E \rightarrow 2\,D: \quad \Delta \hat{H}^\circ_{r} = +3000 \text{ kJ/mol}$$

9.3 FORMATION REACTIONS AND HEATS OF FORMATION

A **formation reaction** of a compound is the reaction in which the compound is formed from its elemental constituents as they normally occur in nature (e.g., O_2 rather than O). The enthalpy change associated with the formation of 1 mole of the compound at a reference temperature and pressure (usually 25°C and 1 atm) is the **standard heat of formation** of the compound, $\Delta \hat{H}^\circ_f$.

Standard heats of formation for many compounds are listed in Table B.1 of this text and on pp. 2-187 through 2-198 of *Perry's Chemical Engineers' Handbook*.[1] For example, $\Delta \hat{H}^\circ_f$ for crystalline ammonium nitrate is given in Table B.1 as −365.14 kJ/mol, signifying

$$N_2(g) + 2\,H_2(g) + \tfrac{3}{2}O_2(g) \rightarrow NH_4NO_3(c): \quad \Delta \hat{H}^\circ_r = -365.14 \text{ kJ/mol}$$

Similarly, for liquid benzene $\Delta \hat{H}^\circ_f = 48.66$ kJ/mol, or

$$6\,C(s) + 3\,H_2(g) \rightarrow C_6H_6(l): \quad \Delta \hat{H}^\circ_r = +48.66 \text{ kJ/mol}$$

The standard heat of formation of an elemental species (e.g., O_2*) is zero.* (Why?)

It may be shown using Hess's law that *if* ν_i *is the stoichiometric coefficient of the* i^{th} *species participating in a reaction (+ for products, − for reactants) and* $\Delta \hat{H}^\circ_{fi}$ *is the standard heat of formation of this species, then the standard heat of the reaction is*

$$\boxed{\Delta \hat{H}^\circ_r = \sum_i \nu_i \Delta \hat{H}^\circ_{fi} = \sum_{\text{products}} |\nu_i| \Delta \hat{H}^\circ_{fi} - \sum_{\text{reactants}} |\nu_i| \Delta \hat{H}^\circ_{fi}} \quad \textbf{(9.3-1)}$$

The standard heats of formation of all elemental species should be set equal to zero in this formula. The validity of Equation 9.3-1 is illustrated in the next example.

EXAMPLE 9.3-1 *Determination of a Heat of Reaction from Heats of Formation*

Determine the standard heat of reaction for the combustion of liquid *n*-pentane, assuming $H_2O(l)$ is a combustion product.

$$C_5H_{12}(l) + 8\,O_2(g) \rightarrow 5\,CO_2(g) + 6\,H_2O(l)$$

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[1] R. H. Perry and D. W. Green, eds., *Perry's Chemical Engineer's Handbook*, 7th Edition, McGraw-Hill, New York, 1997.

SOLUTION From Equation 9.3-1

$$\Delta\hat{H}_r^\circ = 5(\Delta\hat{H}_f^\circ)_{CO_2(g)} + 6(\Delta\hat{H}_f^\circ)_{H_2O(l)} - (\Delta\hat{H}_f^\circ)_{C_5H_{12}(l)}$$

$$\Big\Downarrow \text{Heats of formation from Table B.1}$$

$$\Delta\hat{H}_r^\circ = [5(-393.5) + 6(-285.84) - (-173.0)]\text{ kJ/mol}$$

$$= \boxed{-3509\text{ kJ/mol}}$$

To verify the formula for $\Delta\hat{H}_r^\circ$, we may write the stoichiometric equations for the formation reactions of the reactants and products:

1. $5\,C(s) + 6\,H_2(g) \rightarrow C_5H_{12}(l)$: $\Delta\hat{H}_{r1}^\circ = (\Delta\hat{H}_f^\circ)_{C_5H_{12}(l)}$
2. $C(s) + O_2(g) \rightarrow CO_2(g)$: $\Delta\hat{H}_{r2}^\circ = (\Delta\hat{H}_f^\circ)_{CO_2(g)}$
3. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$: $\Delta\hat{H}_{r3}^\circ = (\Delta\hat{H}_f^\circ)_{H_2O(l)}$

The desired reaction,

4. $C_5H_{12}(l) + 8\,O_2(g) \rightarrow 5\,CO_2(g) + 6\,H_2O(l)$: $\Delta\hat{H}_r^\circ = ?$

may be obtained as 5 × (2) + 6 × (3) − (1) (*verify*), and the given formula for $\Delta\hat{H}_r^\circ$ then follows from Hess's law.

Techniques for estimating heats of formation of compounds with known molecular structures are given by Reid, Prausnitz, and Poling.[2]

TEST YOURSELF (Answers, p. 661)

1. The standard heat of the reaction

$$2\,CO \rightarrow 2\,C + O_2$$

is $\Delta\hat{H}_r^\circ = +221.0$ kJ/mol. Use this result to calculate the standard heat of formation of CO and check your result with a tabulated value.

2. $\Delta\hat{H}_f^\circ$ is −28.64 kcal/mol for $C_3H_8(l)$ and −24.82 kcal/mol for $C_3H_8(g)$. What is the physical significance of the difference between these values?
3. Consider the reaction

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O(v)$$

Write the formula for $\Delta\hat{H}_r^\circ$ in terms of the standard heats of formation of the reactants and products.

9.4 HEATS OF COMBUSTION

The **standard heat of combustion** of a substance, $\Delta\hat{H}_c^\circ$, is the heat of the combustion of that substance with oxygen to yield specified products [e.g., $CO_2(g)$ and $H_2O(l)$], with both reactants and products at 25°C and 1 atm (the arbitrary but conventional reference state).

Table B.1 lists standard heats of combustion for a number of substances. The given values are based on the following assumptions: (a) all carbon in the fuel forms $CO_2(g)$, (b) all hydrogen forms $H_2O(l)$, (c) all sulfur forms $SO_2(g)$, and (d) all nitrogen forms $N_2(g)$. The standard heat of combustion of liquid ethanol, for example, is given in Table B.1 as $\Delta\hat{H}_c^\circ = -1366.9$ kJ/mol, which signifies

$$C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(l): \quad \Delta\hat{H}_r(25^\circ\text{C, 1 atm}) = -1366.9\text{ kJ/mol}$$

Additional heats of combustion are given on pp. 2-195 through 2-199 of *Perry's Chemical Engineers' Handbook* (see footnote 1).

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[2] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th Edition, McGraw-Hill, New York, 1987.

Standard heats of reactions that involve only combustible substances and combustion products can be calculated from tabulated standard heats of combustion, in another application of Hess's law. A hypothetical reaction path may be constructed in which (a) all combustible reactants are burned with O_2 at 25°C and (b) CO_2 and H_2O combine to form the reaction products plus O_2. Step (b) involves the reverse of the combustion reactions of the reaction products. Since both steps involve only combustion reactions, the total enthalpy change—which equals the desired heat of reaction—can be determined entirely from heats of combustion as

$$\boxed{\Delta\hat{H}_r^\circ = -\sum_i \nu_i(\Delta\hat{H}_c^\circ)_i = \sum_{\text{reactants}} |\nu_i|(\Delta\hat{H}_c^\circ)_i - \sum_{\text{products}} |\nu_i|(\Delta\hat{H}_c^\circ)_i} \qquad \textbf{(9.4-1)}$$

If any of the reactants or products are themselves combustion products [$CO_2, H_2O(l), SO_2, \ldots$], their $\Delta\hat{H}_c^\circ$ terms in Equation 9.4-1 should be set equal to 0.

Note that this formula is similar to that used to determine $\Delta\hat{H}_r^\circ$ from heats of formation, except that in this case the negative of the sum is taken. The validity of this formula is illustrated in the next example.

EXAMPLE 9.4-1 ***Calculation of a Heat of Reaction from Heats of Combustion***

Calculate the standard heat of reaction for the dehydrogenation of ethane:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

SOLUTION

From Table B.1,

$$\begin{aligned}(\Delta\hat{H}_c^\circ)_{C_2H_6} &= -1559.9 \text{ kJ/mol}\\ (\Delta\hat{H}_c^\circ)_{C_2H_4} &= -1411.0 \text{ kJ/mol}\\ (\Delta\hat{H}_c^\circ)_{H_2} &= -285.84 \text{ kJ/mol}\end{aligned}$$

From Equation 9.4-1, therefore,

$$\Delta\hat{H}_r^\circ = (\Delta\hat{H}_c^\circ)_{C_2H_6} - (\Delta\hat{H}_c^\circ)_{C_2H_4} - (\Delta\hat{H}_c^\circ)_{H_2} = \boxed{136.9 \text{ kJ/mol}}$$

As an illustration, let us demonstrate the validity of this formula using Hess's law. The combustion reactions are

1. $C_2H_6 + \frac{7}{2}O_2 \rightarrow 2\,CO_2 + 3\,H_2O$
2. $C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$
3. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

It is easy to show that

4. $C_2H_6 \rightarrow C_2H_4 + H_2$

is obtained as (1) − (2) − (3). (Show it.) The desired result follows from Hess's law.

One of the principal applications of Equation 9.4-1 is to determine heats of formation for combustible substances whose formation reactions do not occur naturally. For example, the formation reaction of pentane

$$5\,C(s) + 6\,H_2(g) \rightarrow C_5H_{12}(l): \quad \Delta\hat{H}_f^\circ = ?$$

cannot be carried out in a laboratory, but carbon, hydrogen, and pentane can all be burned and their standard heats of combustion determined experimentally. The heat of formation of pentane may then be calculated from Equation 9.4-1 as

$$(\Delta\hat{H}_f^\circ)_{C_5H_{12}(l)} = 5(\Delta\hat{H}_c^\circ)_{C(s)} + 6(\Delta\hat{H}_c^\circ)_{H_2(g)} - (\Delta\hat{H}_c^\circ)_{C_5H_{12}(l)}$$

CREATIVITY EXERCISE

When an exothermic reaction takes place, the energy released raises the temperature of the reactor contents unless the reactor is cooled. Suppose such a reaction occurs in a batch reactor.

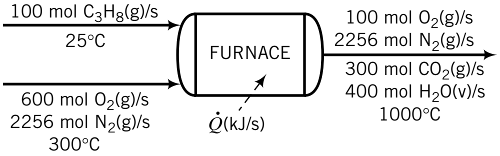
1. Think of as many reasons as you can why you might not want the reactor temperature to increase. (*Example:* The product might degrade or decompose at higher temperatures.)
2. Think of as many ways as you can to keep the reactor temperature from increasing as the reaction proceeds. (*Example:* Throw in some ice.)

9.5 ENERGY BALANCES ON REACTIVE PROCESSES

9.5a General Procedures

To perform energy balance calculations on a reactive system, proceed much as you did for nonreactive systems: (a) draw and label a flowchart; (b) use material balances and phase equilibrium relationships such as Raoult's law to determine as many stream component amounts or flow rates as possible; (c) choose reference states for specific enthalpy (or internal energy) calculations and prepare and fill in an inlet–outlet enthalpy (or internal energy) table; and (d) calculate $\Delta\dot{H}$ (or ΔU or ΔH), substitute the calculated value in the appropriate form of the energy balance equation, and complete the required calculation.

Two methods are commonly used to choose reference states for enthalpy calculations and to calculate specific enthalpies and $\Delta\dot{H}$[3]. We outline the two approaches below, using a propane combustion process to illustrate them. For simplicity, the material balance calculations for the illustrative process have been performed and the results incorporated into the flowchart.



$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l): \quad \Delta\hat{H}_r^\circ = -2220\ \text{kJ/mol}$$

Heat of Reaction Method. This method is generally preferable when there is a single reaction for which $\Delta\hat{H}_r^\circ$ is known.

1. *Complete the material balance calculations on the reactor to the greatest extent possible.*
2. *Choose reference states for specific enthalpy calculations.* The best choices are generally reactant and product species at 25°C and 1 atm in the states for which the heat of reaction is known [$C_3H_8(g)$, $O_2(g)$, $CO_2(g)$, and $H_2O(l)$ in the example process], and nonreacting species at any convenient temperature, such as the reactor inlet or outlet temperature or the reference condition used for the species in an available enthalpy table [$N_2(g)$ at 25°C and 1 atm, the reference state for Table B.8].
3. *For a single reaction in a continuous process, calculate the extent of reaction, $\dot{\xi}$, from Equation 9.1-3.*[4] When writing the equation, choose as species A any reactant or product for

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[3] In what follows, we presume that the value of $\Delta\dot{H}$ is needed for the energy balance. If ΔU or ΔH is required, replace each $\dot{H}$ that appears with U or H.

[4] If multiple reactions occur you would calculate the extents of each independent reaction, $\dot{\xi}_1, \dot{\xi}_2, \ldots$ (Equation 4.6-6 on p. 123), but for such processes you are generally better off using the heat of formation method to be described.

which the feed and product flow rates are known. In the example, we may choose any reactant or product since we know all inlet and outlet species flow rates and calculate the rate of consumption or generation of A ($\dot{n}_{A,r}$ in Equation 9.1-3) as $|(\dot{n}_A)_{out} - (\dot{n}_A)_{in}|$. If A is propane,

$$\dot{\xi} = \frac{|(\dot{n}_{C_3H_8})_{out} - (\dot{n}_{C_3H_8})_{in}|}{|\nu_{C_3H_8}|} = \frac{|0 - 100|\ \text{mol/s}}{1} = 100\ \text{mol/s}$$

As an exercise, let A be O_2, CO_2, or H_2O and verify that the value of $\dot{\xi}$ is independent of the species chosen.

4. *Prepare the inlet–outlet enthalpy table, inserting known molar amounts (n_i) or flow rates ($\dot{n}_i$) for all inlet and outlet stream components.* If any of the components is at its reference state, insert 0 for the corresponding $\hat{H}_i$. For the example process, the table would appear as follows:

References: C_3H_8(g), O_2(g), N_2(g), CO_2(g), H_2O(l) at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
C_3H_8	100	0	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

5. *Calculate each unknown stream component enthalpy, $\hat{H}_i$, as $\Delta\hat{H}$ for the species going from its reference state to the process state, and insert the enthalpies in the table.* In the example,

$$\hat{H}_2 = \Delta\hat{H} \text{ for } O_2(25°\text{C}) \rightarrow O_2(300°\text{C}) = 8.47 \text{ kJ/mol (from Table B.8)}$$

We proceed in the same manner to calculate $\hat{H}_3 = 8.12$ kJ/mol, $\hat{H}_4 = 32.47$ kJ/mol, $\hat{H}_5 = 30.56$ kJ/mol, $\hat{H}_6 = 48.60$ kJ/mol, and $\hat{H}_7 = 81.71$ kJ/mol.

Consider the last result. By definition

$$\hat{H}_7 = \Delta\hat{H} \text{ for } H_2O(\text{l}, 25°\text{C}) \rightarrow H_2O(\text{g}, 1000°\text{C})$$

We could either use steam tables to determine $\Delta\hat{H}$ in one step or heat the liquid water from 25°C to 100°C, vaporize it, heat the vapor from 100°C to 1000°C, and calculate $\hat{H}_7 = \int_{25°\text{C}}^{100°\text{C}} C_{pl}\,dT + \Delta\hat{H}_v(100°\text{C}) + \int_{100°\text{C}}^{1000°\text{C}} C_{pv}\,dT$.

6. *Calculate $\Delta\dot{H}$ for the reactor.* Use one of the following formulas:

$$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} \quad \text{(single reaction)} \qquad \textbf{(9.5-1a)}$$

$$\Delta\dot{H} = \sum_{\text{reactions}} \dot{\xi}_j\,\Delta\hat{H}_{rj}^\circ + \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in} \quad \text{(multiple reactions)} \qquad \textbf{(9.5-1b)}$$

A derivation of these equations is outlined following the presentation of the heat of formation method. Substitution of the previously calculated values into Equation 9.5-1a yields $\Delta\dot{H} = -1.26 \times 10^5$ kJ/s.

7. Substitute the calculated value of $\Delta\dot{H}$ in the energy balance ($\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p$ for an open system) and complete the required calculations.

Heat of Formation Method: This method is generally preferable for multiple reactions and single reactions for which $\Delta\hat{H}_r$ is not readily available.

1. *Complete the material balance calculations on the reactor to the greatest extent possible.*
2. *Choose reference states for enthalpy calculations.* (This is the step that distinguishes the preceding method from this one.) The choices should be the elemental species that con-

stitute the reactants and products in the states in which the elements are found at 25°C and 1 atm [C(s), H_2(g), etc.] and nonreacting species at any convenient temperature. In the example, the reference states would be C(s), H_2(g), and O_2(g) at 25°C (the elemental species constituting the reactants and products), and N_2 at 25°C (the reference temperature of Table B.8).

3. *Prepare the inlet–outlet enthalpy table, inserting known molar amounts (n_i) or flow rates ($\dot{n}_i$) for all inlet and outlet stream components.* For the example process, the table would appear as follows:

References: C(s), H_2(g), O_2(g), N_2(g) at 25°C and 1 atm

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\hat{H}_{\text{out}}$ (kJ/mol)
C_3H_8	100	$\hat{H}_1$	—	—
O_2	600	$\hat{H}_2$	100	$\hat{H}_4$
N_2	2256	$\hat{H}_3$	2256	$\hat{H}_5$
CO_2	—	—	300	$\hat{H}_6$
H_2O	—	—	400	$\hat{H}_7$

4. *Calculate each unknown specific enthalpy.* For a reactant or product, start with the elemental species at 25°C and 1 atm (the references) and form 1 mol of the process species at 25°C and 1 atm ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$ from Table B.1). Then bring the species from 25°C and 1 atm to its process state, calculating $\Delta\hat{H}$ using the appropriate heat capacities from Table B.2, specific enthalpies from Table B.8 or B.9, and latent heats from Table B.1. The specific enthalpy that goes in the inlet–outlet table is the sum of the enthalpy changes for each step in the process path.

   In the example, we would first calculate the specific enthalpy of the entering propane ($\hat{H}_1$) as follows:

$$3\,C(s)(25°C,\ 1\ \text{atm}) + 4\,H_2(g)(25°C,\ 1\ \text{atm}) \rightarrow C_3H_8(g)(25°C,\ 1\ \text{atm})$$

$$\Downarrow$$

$$\hat{H}_1 = (\Delta\hat{H}_f^\circ)_{C_3H_8(g)} = -103.8\ \text{kJ/mol (from Table B.1)}$$

   This is the enthalpy of propane at 25°C (the process state) relative to C(s) and H_2(g) at 25°C (the reference states). If the propane had entered at a temperature T_0 other than 25°C, a term of the form $\int_{25°C}^{T_0} C_p\,dT$ would be added to the heat of formation of propane.

   Next, we calculate the specific enthalpy of O_2 at 300°C (the process state) relative to O_2 at 25°C(the reference state) as $\hat{H}_2 = 8.47$ kJ/mol (from Table B.8). There is no heat of formation term, since O_2 is an elemental species. We proceed in the same manner to calculate $\hat{H}_3 = 8.12$ kJ/mol, $\hat{H}_4 = 32.47$ kJ/mol, $\hat{H}_5 = 30.56$ kJ/mol, $\hat{H}_6 = -344.9$ kJ/mol, and $\hat{H}_7 = -204.1$ kJ/mol. To calculate $\hat{H}_6$ and $\hat{H}_7$, we form the corresponding species [CO_2(g) and H_2O(v)] at 25°C from their elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$), then heat them from 25°C to 1000°C ($\Delta\hat{H} = \hat{H}_{1000°C}$ from Table B.8), and add the formation and heating terms.

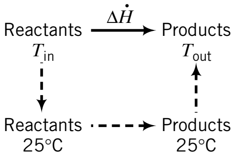
5. *Calculate $\Delta\dot{H}$ for the reactor.* For both single and multiple reactions, the formula is

$$\Delta\dot{H} = \sum \dot{n}_{\text{out}}\hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}}\hat{H}_{\text{in}} \qquad \textbf{(9.5-2)}$$

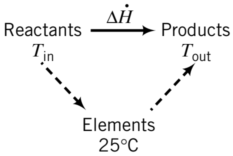
   Note that heat of reaction terms are not required if the elements are chosen as references. The heats of reaction are implicitly included when the heats of formation of the reactants (included in the $\hat{H}_{\text{in}}$ terms) are subtracted from those of the products (in the $\hat{H}_{\text{out}}$ terms) in the expression for $\Delta\dot{H}$. Substituting the calculated $\dot{n}$ and $\hat{H}$ values into Equation 9.5-2 yields $\Delta\dot{H} = -1.26 \times 10^5$ kJ/s.

6. ***Substitute the calculated value of $\Delta\dot{H}$ in the energy balance equation and complete the required calculations.***

The process paths that correspond to the heat of reaction and heat of formation methods are shown below.



(*a*) Process path for heat of reaction method



(*b*) Process path for heat of formation method

The heat of reaction method amounts to bringing the reactants from their inlet conditions to their reference states at 25°C ($\Delta\dot{H} = -\sum \dot{n}_{in}\hat{H}_{in}$), carrying out the reaction at 25°C (from Equation 9.1-3, $\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ$ or the summation of such terms for multiple reactions), bringing the products from their reference states at 25°C to their outlet states ($\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out}$), and summing the enthalpy changes for these three steps to calculate $\Delta\dot{H}$ for the overall process. The heat of formation method amounts to bringing the reactants from their inlet conditions to their constituent elements at 25°C ($\Delta\dot{H} = -\sum \dot{n}_{in}\hat{H}_{in}$), taking the elements to the products at their outlet states ($\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out}$), and summing the enthalpy changes for these two steps to calculate $\Delta\dot{H}$ for the overall process.

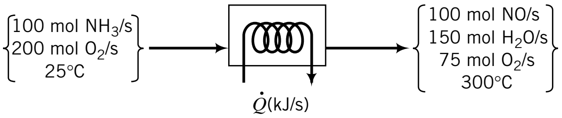
EXAMPLE 9.5-1 *Energy Balance About an Ammonia Oxidizer*

The standard heat of reaction for the oxidation of ammonia is given below:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(v): \quad \Delta\hat{H}_r^\circ = -904.7 \text{ kJ/mol}$$

One hundred mol NH_3/s and 200 mol O_2/s at 25°C are fed into a reactor in which the ammonia is completely consumed. The product gas emerges at 300°C. Calculate the rate at which heat must be transferred to or from the reactor, assuming operation at approximately 1 atm.

SOLUTION ***Basis: Given Feed Rates***



(Verify the product flow rates.) Since only one reaction takes place and $\Delta\hat{H}_r^\circ$ is known, we will use the heat of reaction method for the energy balance, choosing as references the reactant and product species in the states for which the heat of reaction is given. The enthalpy table appears as follows:

References: $NH_3(g)$, $O_2(g)$, $NO(g)$, $H_2O(v)$ at 25°C and 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
NH_3	100	0	—	—
O_2	200	0	75	$\hat{H}_1$
NO	—	—	100	$\hat{H}_2$
H_2O	—	—	150	$\hat{H}_3$

Calculate Unknown Enthalpies

O_2(g, 300°C): From Table B.8, $\hat{H}_1 = 8.470$ kJ/mol (Insert value in enthalpy table)

$$\text{NO(g, 300°C):}\quad \hat{H}_2 = \int_{25°\text{C}}^{300°\text{C}} (C_p)_{\text{NO}}\,dT \xrightarrow{\text{Table B.2}} \hat{H}_2 = 8.453 \text{ kJ/mol} \quad \text{(Insert in table)}$$

H_2O(v, 300°C): From Table B.8, $\hat{H}_3 = 9.570$ kJ/mol (Insert in table)

Calculate $\dot{\xi}$ and $\Delta\dot{H}$

Since 100 mol NH_3/s is consumed in the process (A = NH_3, $\dot{n}_{\text{A,r}} = 100$ mol NH_3 consumed/s), Equation 9.1-3 becomes

$$\dot{\xi} = \frac{\dot{n}_{\text{NH}_3,\text{r}}}{|\nu_{\text{NH}_3}|} = \frac{100 \text{ mol/s}}{4} = 25 \text{ mol/s}$$

$$\Big\Downarrow \text{Equation 9.5-1a}$$

$$\Delta\dot{H} = \dot{\xi}\Delta\hat{H}_\text{r}^\circ + \underbrace{\sum \dot{n}_{\text{out}}\hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}}\hat{H}_{\text{in}}}_{\text{from table}}$$

$$= (25 \text{ mol/s})(-904.7 \text{ kJ/mol}) + [(75)(8.470) + (100)(8.453)$$
$$+ (150)(9.570) - (100)(0) - (200)(0)] \text{ kJ/s} = -19{,}700 \text{ kJ/s}$$

Energy Balance

For this open system,

$$\dot{Q} - \dot{W}_\text{s} = \Delta\dot{H} + \Delta\dot{E}_\text{k} + \Delta\dot{E}_\text{p}$$

$$\Big\Downarrow \begin{array}{ll} \dot{W}_\text{s} = 0 & \text{(no moving parts)} \\ \Delta\dot{E}_\text{p} = 0 & \text{(horizontal unit)} \\ \Delta\dot{E}_\text{k} \approx 0 & \text{(neglect kinetic energy changes)} \end{array}$$

$$\dot{Q} \approx \Delta\dot{H} = -19{,}700 \text{ kJ/s} = \boxed{-19{,}700 \text{ kW}}$$

Thus, 19,700 kW of heat must be transferred from the reactor to maintain the product temperature at 300°C. If less heat were transferred, more of the heat of reaction would go into the reaction mixture and the outlet temperature would increase.

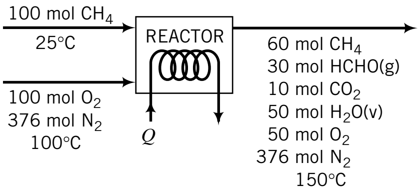
The heat of formation method, which involves taking elemental constituents of the reactants and products in their naturally occurring states as references for enthalpy calculations, is usually convenient for processes that involve several simultaneous reactions. The next example illustrates this approach.

EXAMPLE 9.5-2 *Energy Balance on a Methane Oxidation Reactor*

Methane is oxidized with air to produce formaldehyde in a continuous reactor. A competing reaction is the combustion of methane to form CO_2.

1. $CH_4(g) + O_2 \rightarrow HCHO(g) + H_2O(v)$
2. $CH_4(g) + 2\,O_2 \rightarrow CO_2 + 2\,H_2O(v)$

A flowchart of the process for an assumed basis of 100 mol of methane fed to the reactor is shown here.



SOLUTION

Basis: 100 mol CH_4 Fed

Since the component amounts of all streams are known, we may proceed directly to the energy balance. We choose as references the elemental species that form the reactants and products at 25°C and 1 atm (the state for which heats of formation are known) and the nonreactive species—$N_2(g)$—also at 25°C and 1 atm (the reference state for Table B.8). The inlet–outlet enthalpy table is shown below.

References: C(s), $O_2(g)$, $H_2(g)$, $N_2(g)$ at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{in}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{out}$ (kJ/mol)
CH_4	100	$\hat{H}_1$	60	$\hat{H}_4$
O_2	100	$\hat{H}_2$	50	$\hat{H}_5$
N_2	376	$\hat{H}_3$	376	$\hat{H}_6$
HCHO	—	—	30	$\hat{H}_7$
CO_2	—	—	10	$\hat{H}_8$
H_2O	—	—	50	$\hat{H}_9$

Calculate Unknown Enthalpies

In the following calculations, values of $\Delta\hat{H}_f^\circ$ come from Table B.1, formulas for $C_p(T)$ come from Table B.2, and values of $\hat{H}(T)$ for O_2 and N_2 are specific enthalpies relative to the gaseous species at 25°C taken from Table B.8. Effects of any pressure changes on enthalpies are neglected, and the details of the calculations are not shown.

$$\text{CH}_4(25°\text{C}):\quad \hat{H}_1 = (\Delta\hat{H}_f^\circ)_{CH_4} = -74.85 \text{ kJ/mol}$$

$$\text{O}_2(100°\text{C}):\quad \hat{H}_2 = \hat{H}_{O_2}(100°\text{C}) = 2.235 \text{ kJ/mol}$$

$$\text{N}_2(100°\text{C}):\quad \hat{H}_3 = \hat{H}_{N_2}(100°\text{C}) = 2.187 \text{ kJ/mol}$$

$$\text{CH}_4(150°\text{C}):\quad \hat{H}_4 = (\Delta\hat{H}_f^\circ)_{CH_4} + \int_{25°\text{C}}^{150°\text{C}} (C_p)_{CH_4}\, dT$$

$$= (-74.85 + 4.90) \text{ kJ/mol} = -69.95 \text{ kJ/mol}$$

$$\text{O}_2(150°\text{C}):\quad \hat{H}_5 = \hat{H}_{O_2}(150°\text{C}) = 3.758 \text{ kJ/mol}$$

$$\text{N}_2(150°\text{C}):\quad \hat{H}_6 = \hat{H}_{N_2}(150°\text{C}) = 3.655 \text{ kJ/mol}$$

$$\text{HCHO}(150°\text{C}):\quad \hat{H}_7 = (\Delta\hat{H}_f^\circ)_{HCHO} + \int_{25°\text{C}}^{150°\text{C}} (C_p)_{HCHO}\, dT$$

$$= (-115.90 + 4.75) \text{ kJ/mol} = -111.15 \text{ kJ/mol}$$

$$\text{CO}_2(150°\text{C}):\quad \hat{H}_8 = (\Delta\hat{H}_f^\circ)_{CO_2} + \hat{H}_{CO_2}(150°\text{C})$$

$$= (-393.5 + 4.75) \text{ kJ/mol} = -388.6 \text{ kJ/mol}$$

$$\text{H}_2\text{O}(\text{v}, 150°\text{C}):\quad \hat{H}_9 = (\Delta\hat{H}_f^\circ)_{H_2O(v)} + \hat{H}_{H_2O(v)}(150°\text{C})$$

$$= (-241.83 + 4.27) \text{ kJ/mol} = -237.56 \text{ kJ/mol}$$

As each of these values is calculated, it should be substituted in the inlet–outlet enthalpy table. The table finally appears as follows:

References: C(s), O_2(g), H_2(g), N_2(g) at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{\text{in}}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{\text{out}}$ (kJ/mol)
CH_4	100	–74.85	60	−69.95
O_2	100	2.235	50	3.758
N_2	376	2.187	376	3.655
HCHO	—	—	30	–111.15
CO_2	—	—	10	–388.6
H_2O	—	—	50	–237.56

Evaluate ΔH
From Equation 9.5-2,

$$\Delta H = \sum n_{\text{out}}\hat{H}_{\text{out}} - \sum n_{\text{in}}\hat{H}_{\text{in}} = -15{,}300 \text{ kJ}$$

If molecular species had been chosen as references for enthalpy calculations, the extents of each reaction (ξ_1 and ξ_2) would have had to be calculated and Equation 9.5-1b used to determine ΔH. When more than one reaction occurs in a process, you are advised to choose elemental species as references and avoid these complications.

Energy Balance
Remember that we are dealing with a continuous process and hence an open system. [The reason we use n(mol) and not $\dot{n}$(mol/s) is that we took 100 mol CH_4 as a basis of calculation.] With ΔE_k, ΔE_p, and W_s neglected, the open system energy balance yields

$$\boxed{Q = \Delta H = -15{,}300 \text{ kJ}}$$

9.5b Processes with Unknown Outlet Conditions: Adiabatic Reactors

In the reactive systems we have looked at so far, the inlet and outlet conditions were specified and the required heat input could be determined from an energy balance.

In another important class of problems, the input conditions, heat input, and product composition are specified, and the outlet temperature is to be calculated. To solve such problems, you must evaluate the enthalpies of the products relative to the chosen reference states in terms of the unknown final temperature, and then substitute the resulting expressions into the energy balance ($\dot{Q} = \Delta\dot{H}$, or $\Delta\dot{H} = 0$ for an adiabatic reactor) to calculate T_{out}.

EXAMPLE 9.5-3 *Energy Balance on an Adiabatic Reactor*

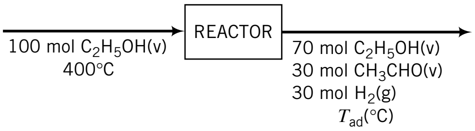
The dehydrogenation of ethanol to form acetaldehyde

$$C_2H_5OH(v) \rightarrow CH_3CHO(v) + H_2(g)$$

is carried out in a continuous adiabatic reactor. Ethanol vapor is fed to the reactor at 400°C, and a conversion of 30% is obtained. Calculate the product temperature.

SOLUTION ***Basis: 100 mol Feed***

Material balances lead to the information on the flowchart shown here.



Since only one reaction occurs, we could equally well choose the reactants and products [$C_2H_5OH(v)$, $CH_3CHO(v)$, $H_2(g)$] or their elemental constituents [$C(s)$, $H_2(g)$, $O_2(g)$] as references for enthalpy calculations. Let us choose the molecular species.

References: $C_2H_5OH(v)$, $CH_3CHO(v)$, $H_2(g)$ at 25°C and 1 atm

Substance	n_{in} (mol)	$\hat{H}_{\text{in}}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{\text{out}}$ (kJ/mol)
C_2H_5OH	100.0	$\hat{H}_1$	70.0	$\hat{H}_2$
CH_3CHO	—	—	30.0	$\hat{H}_3$
H_2	—	—	30.0	$\hat{H}_4$

The open system energy balance neglecting kinetic and potential energy changes and shaft work and setting $Q = 0$ for this adiabatic reactor is

$$\Delta H = \xi\,\Delta\hat{H}_r^\circ + \sum n_{\text{out}}\hat{H}_{\text{out}} - \sum n_{\text{in}}\hat{H}_{\text{in}} = 0$$

The expression for ΔH is that of Equation 9.5-1a.

Calculate Extent of Reaction

We could use any reactant or product as a basis for calculating ξ. Let us use acetaldehyde. From Equation 9.1-3,

$$\xi = \frac{|(n_{CH_3CHO})_{\text{out}} - (n_{CH_3CHO})_{\text{in}}|}{|\nu_{CH_3CHO}|} = \frac{|30.0 \text{ mol} - 0 \text{ mol}|}{1} = 30.0 \text{ mol}$$

Calculate Standard Heat of Reaction

From Equation 9.3-1 and Table B.1 (heats of formation),

$$\begin{aligned}\Delta\hat{H}_r^\circ &= \sum \nu_i\,\Delta\hat{H}_f^\circ = (-1)(\Delta\hat{H}_f^\circ)_{C_2H_5OH(v)} + (1)(\Delta\hat{H}_f^\circ)_{CH_3CHO(v)} + (1)(\Delta\hat{H}_f^\circ)_{H_2(g)} \\ &= [(-1)(-235.31) + (1)(-166.2) + (1)(0)] \text{ kJ/mol} = 69.11 \text{ kJ/mol}\end{aligned}$$

Calculate Inlet Enthalpy

$$\hat{H}_1 = \int_{25°C}^{400°C} (C_p)_{C_2H_5OH} \xrightarrow{C_p \text{ from Table B.2}} \hat{H}_1 = 33.79 \text{ kJ/mol}$$

Calculate Outlet Enthalpies

The heat capacities of ethanol vapor and hydrogen are given in Table B.2. For acetaldehyde vapor, the heat capacity is given by Reid, Prausnitz, and Poling[5]:

$$(C_p)_{CH_3CHO}\left(\frac{\text{kJ}}{\text{mol·°C}}\right) = 0.05048 + 1.326 \times 10^{-4}T - 8.050 \times 10^{-8}T^2 + 2.380 \times 10^{-11}T^3$$

where T is in °C. For the three species in the product stream,

$$\hat{H}_i = \int_{25°C}^{T_{\text{ad}}} C_{pi}(T)\,dT, \quad i = 1, 2, 3$$

If the heat capacity formulas for the three species are substituted in this expression and the integrals are evaluated, the results are three fourth-order polynomial expressions for $\hat{H}_2(T_{\text{ad}})$, $\hat{H}_3(T_{\text{ad}})$, and $\hat{H}_4(T_{\text{ad}})$:

C_2H_5OH:
$$\begin{aligned}\hat{H}_2(\text{kJ/mol}) &= 4.958 \times 10^{-12}T_{\text{ad}}^4 - 2.916 \times 10^{-8}T_{\text{ad}}^3 \\ &\quad + 7.860 \times 10^{-5}T_{\text{ad}}^2 + 0.06134T_{\text{ad}} - 1.582\end{aligned}$$

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[5] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids,* 4th Edition, McGraw-Hill, New York, 1987. The formula given has been derived from the one shown in this reference, which is for the heat capacity in J/(mol·K) with the temperature expressed in kelvin.

$$\textit{CH}_3\textit{CHO:}\qquad \hat{H}_3(\text{kJ/mol}) = 5.950\times10^{-12}T_{\text{ad}}^4 - 2.683\times10^{-8}T_{\text{ad}}^3 + 6.630\times10^{-5}T_{\text{ad}}^2 + 0.05048T_{\text{ad}} - 1.303$$

$$\textit{H}_2\textit{:}\qquad \hat{H}_4(\text{kJ/mol}) = -0.2175\times10^{-12}T_{\text{ad}}^4 + 0.1096\times10^{-8}T_{\text{ad}}^3 + 0.003825\times10^{-5}T_{\text{ad}}^2 + 0.02884T_{\text{ad}} - 0.7210$$

Solve the Energy Balance for T_{ad}

$$\Delta H = \xi\,\Delta\hat{H}_{\text{r}}^{\circ} + (70.0\text{ mol})\hat{H}_2 + (30.0\text{ mol})\hat{H}_3 + (30.0\text{ mol})\hat{H}_4 - (100.0\text{ mol})\hat{H}_1 = 0$$

$$\Big\Downarrow \text{Substitute for } \xi\ (= 30.0\text{ mol}),\ \Delta\hat{H}_{\text{r}}^{\circ}\ (= 69.11\text{ kJ/mol}),\ \hat{H}_1\ (= 33.79\text{ kJ/mol}),\text{ and } \hat{H}_2 \text{ through } \hat{H}_4$$

$$\Delta H = 5.190\times10^{-10}T_{\text{ad}}^4 + 2.813\times10^{-6}T_{\text{ad}}^3 + 7.492\times10^{-3}T_{\text{ad}}^2 + 6.673T_{\text{ad}} - 1477 = 0$$

This equation can be solved using an equation-solving program or a spreadsheet.[6] The solution is

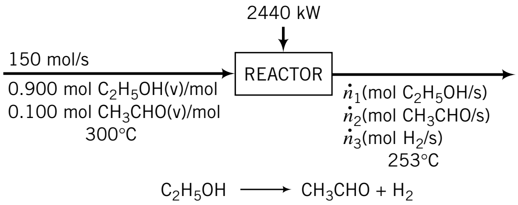
$$\boxed{T_{\text{ad}} = 185^{\circ}\text{C}}$$

Another class of problems involves processes for which the heat input and outlet temperature are specified but the extent of reaction and product composition are not. Solving such problems requires the simultaneous solution of material and energy balance equations, as the next example illustrates.

EXAMPLE 9.5-4 *Simultaneous Material and Energy Balances*

The ethanol dehydrogenation reaction of Example 9.5-3 is carried out with the feed entering at 300°C. The feed contains 90.0 mole% ethanol and the balance acetaldehyde and enters the reactor at a rate of 150 mol/s. To keep the temperature from dropping too much and thereby decreasing the reaction rate to an unacceptably low level, heat is transferred to the reactor. When the heat addition rate is 2440 kW, the outlet temperature is 253°C. Calculate the fractional conversion of ethanol achieved in the reactor.

SOLUTION



A degree-of-freedom analysis based on atomic species balances (see Section 4.7) is as follows:

3 unknown labeled variables ($\dot{n}_1$, $\dot{n}_2$, $\dot{n}_3$)
− 2 independent atomic species balances (C and H)
− 1 energy balance
= 0 degrees of freedom

(Convince yourself that there are only two independent atomic balances by writing the C and O balances and observing that they yield the same equation.)

---

[6] To obtain the solution using a spreadsheet, put a guessed value of T_{ad} in one cell and the expression for ΔH in an adjacent cell, and use the goalseek tool to determine the value of T_{ad} for which the expression for ΔH equals zero. A first guess might be the value of T_{ad} obtained by dropping all higher-order terms in the expression, leaving $6.673T_{\text{ad}} - 1134 = 0 \Longrightarrow T_{\text{ad}} \approx 170^{\circ}\text{C}$.

Balance on C

$$\frac{150\text{ mol}}{\text{s}}\left|\frac{0.900\text{ mol }C_2H_5OH}{\text{mol}}\right|\frac{2\text{ mol C}}{1\text{ mol }C_2H_5OH}+\frac{150\text{ mol}}{\text{s}}\left|\frac{0.100\text{ mol }CH_3CHO}{\text{mol}}\right|\frac{2\text{ mol C}}{1\text{ mol }CH_3CHO}$$

$$=\frac{\dot{n}_1(\text{mol }C_2H_5OH)}{\text{s}}\left|\frac{2\text{ mol C}}{1\text{ mol }C_2H_5OH}\right.+\frac{\dot{n}_2(\text{mol }CH_3CHO)}{\text{s}}\left|\frac{2\text{ mol C}}{1\text{ mol }CH_3CHO}\right.$$

$$\Downarrow$$

$$\dot{n}_1+\dot{n}_2=150\text{ mol/s} \tag{1}$$

Balance on H

$$[(150)(0.900)(6)+(150)(0.100)(4)]\text{ mol H/s}=6\dot{n}_1+4\dot{n}_2+2\dot{n}_3 \quad \text{(Convince yourself)}$$

$$\Downarrow$$

$$3\dot{n}_1+2\dot{n}_2+\dot{n}_3=435\text{ mol H/s} \tag{2}$$

Energy Balance

In the last example we used molecular species as references for specific enthalpy calculations. This time we will use elemental species [$C(s)$, $H_2(g)$, $O_2(g)$] at 25°C and 1 atm. (For a single reaction both choices require about the same computational effort.) The energy balance neglecting shaft work and kinetic and potential energy changes becomes

$$\dot{Q}=\Delta\dot{H}=\sum\dot{n}_{\text{out}}\hat{H}_{\text{out}}-\sum\dot{n}_{\text{in}}\hat{H}_{\text{in}}$$

The value of $\dot{Q}$ is 2440 kJ/s and the expression for $\Delta\dot{H}$ is that of Equation 9.5-2. The specific enthalpies of the species at the inlet and outlet of the process relative to their elemental constituents are calculated as

$$\hat{H}_i=\Delta\hat{H}_{\text{f}i}^{\circ}+\int_{25^\circ\text{C}}^{T}C_{pi}(T)\,dT$$

where T is 300°C at the inlet and 253°C at the outlet. Taking standard heats of formation from Table B.1 and formulas for C_p from Table B.2 and (for acetaldehyde vapor) Example 9.5-3, we calculate the values of $\hat{H}_i$ shown in the inlet–outlet enthalpy table.

References: $C(s)$, $H_2(g)$, $O_2(g)$ at 25°C and 1 atm

Substance	$\dot{n}_{\text{in}}$ (mol/s)	$\hat{H}_{\text{in}}$ (kJ/mol)	$\dot{n}_{\text{out}}$ (mol/s)	$\hat{H}_{\text{out}}$ (kJ/mol)
C_2H_5OH	135	−212.19	$\dot{n}_1$	−216.81
CH_3CHO	15	−147.07	$\dot{n}_2$	−150.90
H_2	—	—	$\dot{n}_3$	6.595

The energy balance ($\dot{Q}=\sum\dot{n}_{\text{out}}\hat{H}_{\text{out}}-\sum\dot{n}_{\text{in}}\hat{H}_{\text{in}}$) becomes

$$2440\text{ kJ/s}=[-216.81\dot{n}_1-150.90\dot{n}_2+6.595\dot{n}_3-(135)(-212.19)-(15)(-147.07)]\text{ kJ/s}$$

$$\Downarrow$$

$$216.81\dot{n}_1+150.90\dot{n}_2-6.595\dot{n}_3=28{,}412\text{ kJ/s} \tag{3}$$

Solving Equations 1 through 3 simultaneously yields

$$\dot{n}_1=92.0\text{ mol }C_2H_5OH/\text{s}$$
$$\dot{n}_2=58.0\text{ mol }CH_3CHO/\text{s}$$
$$\dot{n}_3=43.0\text{ mol }H_2/\text{s}$$

The fractional conversion of ethanol is

$$x = \frac{(\dot{n}_{C_2H_5OH})_{in} - (\dot{n}_{C_2H_5OH})_{out}}{(\dot{n}_{C_2H_5OH})_{in}} = \frac{(135 - 92.0)\text{ mol/s}}{135\text{ mol/s}} = \boxed{0.319}$$

9.5c Thermochemistry of Solutions[7]

The enthalpy change associated with the formation of a solution from the solute elements and the solvent at 25°C is called the **standard heat of formation of the solution**. If a solution contains n moles of solvent per mole of solute, then

$$\boxed{(\Delta\hat{H}_f^\circ)_{\text{solution}} = (\Delta\hat{H}_f^\circ)_{\text{solute}} + \Delta\hat{H}_s^\circ(n)} \qquad \textbf{(9.5-3)}$$

where $\Delta\hat{H}_s^\circ$ is the heat of solution at 25°C (Section 8.5). From the definitions of $\Delta\hat{H}_f^\circ$ and $\Delta\hat{H}_s^\circ$, the dimensions of the heat of formation of the solution are (energy)/(mole of solute).

The standard heat of a reaction involving solutions may be calculated from heats of formation of the solutions. For example, for the reaction

$$2\,HNO_3(aq, r = 25) + Ca(OH)_2(aq, r = \infty) \rightarrow Ca(NO_3)_2(aq, r = \infty) + 2\,H_2O(l)$$

the standard heat of reaction is

$$\begin{aligned}\Delta\hat{H}_r^\circ &= (\Delta\hat{H}_f^\circ)_{Ca(NO_3)_2(aq)} + 2(\Delta\hat{H}_f^\circ)_{H_2O(l)} - 2(\Delta\hat{H}_f^\circ)_{HNO_3(aq,\, r=25)} - (\Delta\hat{H}_f^\circ)_{Ca(OH)_2(aq,\, r=\infty)} \\ &= -114.2\text{ kJ/mol}\end{aligned}$$

The last equation signifies that if a solution containing 2 mol of HNO_3 in 50 mol of H_2O($r = 25$) is neutralized at 25°C with 1 mol of $Ca(OH)_2$ dissolved in enough water so that the addition of more water would not cause a measurable enthalpy change ($r = \infty$), the enthalpy change is −114.2 kJ.

If a standard heat of formation is tabulated for a solution involved in a reaction, the tabulated value may be substituted directly into the expression for $\Delta\hat{H}_r$; otherwise, $(\Delta\hat{H}_f^\circ)_{soln}$ must first be calculated by adding the standard heat of formation of the pure solute to the standard heat of solution.

EXAMPLE 9.5-5 ***Standard Heat of a Neutralization Reaction***

1. Calculate $\Delta\hat{H}_r^\circ$ for the reaction

$$H_3PO_4(aq, r = \infty) + 3\,NaOH(aq, r = 50) \rightarrow Na_3PO_4(aq, r = \infty) + 3\,H_2O(l)$$

2. If 5.00 mol of NaOH dissolved in 250 mol of water is neutralized completely at 25°C with dilute phosphoric acid, what is the attendant enthalpy change?

SOLUTION

1. H_3PO_4(aq): $\Delta\hat{H}_f^\circ = -309.3$ kcal/mol $= -1294$ kJ/mol [from p. 2-189 of *Perry's Chemical Engineers' Handbook* (see footnote 1)].

$$NaOH(aq, r = 50):\quad (\Delta\hat{H}_f^\circ)_{NaOH(aq)} = (\Delta\hat{H}_f^\circ)_{NaOH(s)} + \Delta\hat{H}_s^\circ(r = 50)$$

$$\Big\Downarrow \begin{array}{l}\text{Table B.1 } (\Delta\hat{H}_f^\circ) \\ \text{Table B.11 } (\Delta\hat{H}_s^\circ)\end{array}$$

$$= (-426.6 - 42.51)\text{ kJ/mol} = -469.1\text{ kJ/mol}$$

Na_3PO_4(aq): $\Delta\hat{H}_f^\circ = -471.9$ kcal/mol $= -1974$ kJ/mol (from p. 2-193 of *Perry's Chemical Engineers' Handbook*).

---

[7] Reviewing Sections 8.5a and 8.5b before reading this section might prove helpful.

$$H_2O(l)\text{: } \Delta\hat{H}_f^\circ = -285.8 \text{ kJ/mol (from Table B.1)}$$

$$\Delta\hat{H}_r^\circ = (\Delta\hat{H}_f^\circ)_{Na_3PO_4(aq)} + 3(\Delta\hat{H}_f^\circ)_{H_2O(l)} - (\Delta\hat{H}_f^\circ)_{H_3PO_4(aq)} - 3(\Delta\hat{H}_f^\circ)_{NaOH(aq,\, r=50)}$$

$$= \boxed{-130.1 \text{ kJ/mol}}$$

2. If 5 mol of dissolved NaOH is neutralized, then

$$\Delta H(25^\circ C) = \frac{-\ 130.1 \text{ kJ}}{3.00 \text{ mol NaOH}} \left| \frac{5.00 \text{ mol NaOH}}{} \right. = \boxed{-217 \text{ kJ}}$$

When you calculate ΔH for a reactive process as

$$\sum_{\text{products}} n_i\hat{H}_i - \sum_{\text{reactants}} n_i\hat{H}_i$$

and one of the reactant or product species is a solution, its specific enthalpy usually has the dimensions (energy)/(mole of solute), so that the corresponding value of n_i must be moles or molar flow rate of the *solute*, and not of the total solution. A complicating factor may be that while the heat of formation of a solution is always obtained in the desired units, solution heat capacities are normally based on a unit mass of the total solution rather than of the solute. To calculate the specific enthalpy of a solution at a temperature T in (energy)/(mole of solute), you must first calculate m, the mass of solution corresponding to 1 mole of dissolved solute, and then add

$$m\int_{25^\circ C}^{T} (C_p)_{\text{solution}}\, dT$$

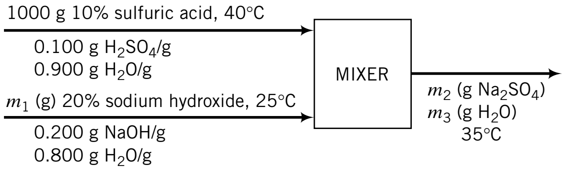
to the standard heat of formation of the solution. The next example illustrates this calculation.

EXAMPLE 9.5-6 *Energy Balance on a Neutralization Process*

A 10.0 wt% aqueous solution of H_2SO_4 at 40°C is to be neutralized with a 20.0 wt% aqueous solution of NaOH at 25°C in a continuous reactor. At what rate in kJ/kg H_2SO_4 solution must heat be removed from the reactor if the product solution emerges at 35°C?

SOLUTION ***Basis: 1 kg H_2SO_4 Solution***

$$H_2SO_4(aq, 10\%) + 2\ NaOH(aq, 20\%) \rightarrow Na_2SO_4(aq) + 2\ H_2O(l)$$



This is a straightforward problem, but the number of intermediate calculations required to solve it might make it appear more difficult than it is. Let us summarize what must be done.

1. Solve for m_1, m_2, and m_3 by material balances.
2. Calculate the solvent-to-solute mole ratios of all solutions. (The quantities are needed to determine the solution enthalpies from tabulated heats of solution.)
3. Calculate the enthalpies of the solutions. (This will require additional composition calculations to allow the use of tabulated solution heat capacities.)
4. Write the energy balance equation and solve it for the heat removal rate.

Observe that nothing here is really new, and, as we work our way through to the final result, recognize that most of the calculations are simply conversions of solution compositions from mass fractions to mole ratios back to mass ratios—conversions required by the nature of the available data for properties of solutions.

1. ***Solve for m_1, m_2, and m_3 by material balances, and calculate the amount of water formed.***

S balance:

$$\begin{array}{c|c} 100\text{ g H}_2\text{SO}_4 & 32.0\text{ g S} \\ \hline & 98.1\text{ g H}_2\text{SO}_4 \end{array} = \begin{array}{c|c} m_2(\text{g Na}_2\text{SO}_4) & 32.0\text{ g S} \\ \hline & 142\text{ g Na}_2\text{SO}_4 \end{array}$$

$$\Downarrow$$

$$m_2 = 145\text{ g Na}_2\text{SO}_4$$

Na balance:

$$\begin{array}{c|c} 0.200\,m_1(\text{g NaOH}) & 23.0\text{ g Na} \\ \hline & 40.0\text{ g NaOH} \end{array} = \begin{array}{c|c} 145\text{ g Na}_2\text{SO}_4 & 46.0\text{ g Na} \\ \hline & 142\text{ g Na}_2\text{SO}_4 \end{array}$$

$$\Downarrow$$

$$m_1 = 408\text{ g NaOH(aq)}$$

Total mass balance: $1000\text{ g} + 408\text{ g} = 145\text{ g} + m_3 \Longrightarrow m_3 = 1263\text{ g H}_2\text{O(l)}$

Mass of product solution: $m = m_2 + m_3 = 1408\text{ g}$

$$\text{Water formed by reaction} = \begin{array}{c|c|c} 145\text{ g Na}_2\text{SO}_4\text{ formed} & 1\text{ mol} & 2\text{ mol H}_2\text{O} \\ \hline & 142\text{ g} & 1\text{ mol Na}_2\text{SO}_4 \end{array}$$

$$= 2.04\text{ mol H}_2\text{O}$$

2. ***Calculate solvent/solute mole ratios*** (needed to determine heats of solution).

H_2SO_4 (aq):

$$(900\text{ g H}_2\text{O})/(18.0\text{ g/mol}) = 50.0\text{ mol H}_2\text{O}$$

$$(100\text{ g H}_2\text{SO}_4)/(98.1\text{ g/mol}) = 1.02\text{ mol H}_2\text{SO}_4$$

$$\Downarrow$$

$$r = 50.0\text{ mol H}_2\text{O}/1.02\text{ mol H}_2\text{SO}_4 = 49.0\text{ mol H}_2\text{O/mol H}_2\text{SO}_4$$

NaOH (aq):

$$[(0.800 \times 408)\text{g H}_2\text{O}]/(18.0\text{ g/mol}) = 18.1\text{ mol H}_2\text{O}$$

$$[(0.200 \times 408)\text{g NaOH}]/(40.0\text{ g/mol}) = 2.04\text{ mol NaOH}$$

$$\Downarrow$$

$$r = 18.1\text{ mol H}_2\text{O}/2.04\text{ mol NaOH} = 8.90\text{ mol H}_2\text{O/mol NaOH}$$

Na_2SO_4 (aq):

$$(1263\text{ g H}_2\text{O})/(18.0\text{ g/mol}) = 70.2\text{ mol H}_2\text{O}$$

$$(145\text{ g Na}_2\text{SO}_4)/(142\text{ g/mol}) = 1.02\text{ mol Na}_2\text{SO}_4$$

$$\Downarrow$$

$$r = 70.2\text{ mol H}_2\text{O}/1.02\text{ mol Na}_2\text{SO}_4 = 68.8\text{ mol H}_2\text{O/mol Na}_2\text{SO}_4$$

3. *Calculate extent of reaction.* To calculate ξ, we note that 1.02 mol H_2SO_4 reacted. From Equation 9.1-3,

$$\xi = \frac{(n_{\text{H}_2\text{SO}_4})_{\text{reacted}}}{|\nu_{\text{H}_2\text{SO}_4}|} = \frac{1.02\text{ mol}}{1} = 1.02\text{ mol}$$

4. ***Calculate ΔH.*** This problem is made tricky by the fact that water is not just the solvent in the solutions involved but is also formed as a reaction product. We will take as references the reactant and product solutions at 25°C and evaluate ΔH using Equation 9.5-1a:

$$\Delta H = \xi\,\Delta\hat{H}_r^\circ + \sum n_{\text{out}}\hat{H}_{\text{out}} - \sum n_{\text{in}}\hat{H}_{\text{in}}$$

It is convenient in solution chemistry calculations to tabulate the products $n\hat{H}$ rather than n and $\hat{H}$ separately. The completed enthalpy table is shown below, followed by the calculations that led to the entries.

References: H_2SO_4(aq, $r = 49$),
NaOH(aq, $r = 8.9$), Na_2SO_4(aq, $r = 69$) at 25°C

Substance	$n_{in}\hat{H}_{in}$	$n_{out}\hat{H}_{out}$	
H_2SO_4(aq)	57.8	—	$n\hat{H}$ in kJ
NaOH(aq)	0	—	
Na_2SO_4(aq)	—	58.9	

H_2SO_4(aq, $r = 49$, 40°C): From Table 2.217, p. 2-185 of *Perry's Chemical Engineers' Handbook* (see footnote 1), the heat capacity of a sulfuric acid solution with the given composition is 3.85 J/(g·°C).

$$n\hat{H} = m\int_{25^\circ\text{C}}^{40^\circ\text{C}} C_p\,dT$$

$$= \frac{1000\text{ g}}{} \left| \frac{3.85\text{ J}}{\text{g}\cdot{}^\circ\text{C}} \right| \frac{(40-25)^\circ\text{C}}{} \left| \frac{1\text{ kJ}}{1000\text{ J}} \right. = 57.8\text{ kJ}$$

NaOH(aq, $r = 8.9$, 25°C): $n\hat{H} = 0$

Na_2SO_4(aq, $r = 69$, 35°C): In the absence of better information, we will assume that the heat capacity of the solution is that of pure water, 4.184 J/(g·°C).

$$n\hat{H} = m\int_{25^\circ\text{C}}^{35^\circ\text{C}} C_p\,dT$$

$$= \frac{1408\text{ g}}{} \left| \frac{4.184\text{ J}}{\text{g}\cdot{}^\circ\text{C}} \right| \frac{(35-25)^\circ\text{C}}{} \left| \frac{1\text{ kJ}}{1000\text{ J}} \right. = 58.9\text{ kJ}$$

The heats of formation of H_2SO_4(l) and NaOH(c) are given in Table B.1, and the heats of solution of these species are given in Table B.11. *Perry's Chemical Engineers' Handbook* (see footnote 1) on p. 2-193 gives the standard heat of formation of Na_2SO_4(aq, $r = 1100$) as -330.82 kcal/mol $Na_2SO_4 = -1384$ kJ/mol Na_2SO_4. In the absence of heat of solution data, we will assume that this value also applies to the solution for which $r = 69$ moles of water per mole of solute. The standard heats of formation of the species involved in the reaction

$$H_2SO_4(\text{aq}, r = 49) + 2\,NaOH(\text{aq}, r = 8.9) \rightarrow Na_2SO_4(\text{aq}) + 2\,H_2O(\text{l})$$

are obtained from Equation 9.5-4 (heat of formation of the solution equals heat of formation of the solute plus heat of solution) as

$$\begin{aligned} H_2SO_4(\text{aq}):\quad \Delta\hat{H}_f^\circ &= [(-811.3) + (-73.3)]\text{ kJ/mol } H_2SO_4 = -884.6\text{ kJ/mol } H_2SO_4 \\ NaOH(\text{aq}):\quad \Delta\hat{H}_f^\circ &= [(-426.6) + (-41.5)]\text{ kJ/mol NaOH} = -468.1\text{ kJ/mol NaOH} \\ Na_2SO_4(\text{aq}):\quad \Delta\hat{H}_f^\circ &= -1384\text{ kJ/mol } Na_2SO_4 \\ H_2O(\text{l}):\quad \Delta\hat{H}_f^\circ &= -285.84\text{ kJ/mol } H_2O \end{aligned}$$

and the standard heat of reaction is therefore

$$\begin{aligned} \Delta\hat{H}_r^\circ &= [(-1384)(1) + (-285.84)(2) - (-884.6)(1) - (-468.1)(2)]\text{ kJ/mol} \\ &= -134.9\text{ kJ/mol} \end{aligned}$$

5. ***Energy balance.***

$$\begin{aligned} Q = \Delta H &= \xi\,\Delta\hat{H}_r^\circ + \sum n_{out}\hat{H}_{out} - \sum n_{in}\hat{H}_{in} \\ &= (1.02\text{ mol})(-134.9\text{ kJ/mol}) + (58.9 - 57.8)\text{ kJ} = \boxed{-136\text{ kJ}} \end{aligned}$$

When a strong acid or base is dissolved in water, it dissociates into ionic species; for example, dissolved NaOH exists as Na^+ and OH^- in a dilute solution. **Heats of formation of ions** may be determined from heats of solutions of such substances and may be used to calculate heats of formation of dilute solutions of highly dissociated materials. A good discussion of this topic and a table of heats of formation of ions is given by Hougen, Watson, and Ragatz.[8]

TEST YOURSELF (Answers, p. 661)

The heat of formation of A(s) is $(\Delta\hat{H}_f^\circ)_A = -100$ kJ/mol; heats of solution of A in a solvent B are $\Delta\hat{H}_s^\circ(r = 50 \text{ mol B/mol A}) = -10$ kJ/mol and $\Delta\hat{H}_s^\circ(r = \infty) = -15$ kJ/mol.

1. **(a)** What is the standard heat of formation of A(soln, $r = 50$) relative to B and the elements of A(s)?
   (b) What is $\Delta\hat{H}_f^\circ$ for A(soln, $r = \infty$) relative to the same references?
2. **(a)** What is the enthalpy (kJ/mol A) of a solution of A in B at 25°C for which $r = 50$, relative to B and the elements of A at 25°C?
   (b) What is the enthalpy (kJ) of a solution containing 5 mol of A in 250 mol of B at 25°C, relative to A(s) and B(l) at 25°C? What is it relative to B(l) and the elements of A at 25°C?

9.6 FUELS AND COMBUSTION

The use of heat generated by a combustion reaction to produce steam, which drives turbines to produce electricity, may be the single most important commercial application of chemical reactions. (See Chapter 14.)

The analysis of fuels and combustion reactions and reactors has always been an important activity for chemical engineers. In this section, we review the properties of the fuels most often used for power generation and outline techniques for energy balances on combustion reactors.

9.6a Fuels and Their Properties

Fuels burned in power-plant furnaces may be solids, liquids, or gases. Some of the more common fuels are:

Solid fuels: Principally coal (a mixture of carbon, water, noncombustible ash, hydrocarbons, and sulfur), coke (primarily carbon—the solid residue left after coal or petroleum is heated, driving off volatile substances and decomposing hydrocarbons), and to a small extent wood and solid waste (garbage).

Liquid fuels: Principally hydrocarbons obtained by distilling crude oil (petroleum); also coal tars and shale oil. There is also a strong worldwide interest in the use of alcohols obtained by fermenting grains.

Gaseous fuels: Principally natural gas (80% to 95% methane, the balance ethane, propane, and small quantities of other gases); also light hydrocarbons obtained from petroleum or coal treatment, acetylene, and hydrogen (the latter two are relatively expensive to produce).

QUESTIONS FOR DISCUSSION

Coal contains primarily carbon and combustible hydrocarbons, but also contains substantial amounts of noncombustible ash and as much as 5% sulfur by weight.

1. What becomes of the sulfur when coal is burned? What about the ash? (Suggest two possibilities for the ash.)

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[8] O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles,* Part I, Wiley, New York, 1954, pp. 315–317.

2. In view of the answer to the preceding question, why might coal be less desirable as a fuel than natural gas?
3. What might prompt a power company to use coal as its primary fuel despite its drawbacks relative to liquid or gaseous fuels?

The **heating value** of a combustible material is the negative of the standard heat of combustion. The **higher heating value** (or **total heating value** or **gross heating value**) is $-\Delta\hat{H}_c^\circ$ with $H_2O(l)$ as a combustion product, and the **lower heating value** (or **net heating value**) is the value based on $H_2O(v)$ as a product. Since $\Delta\hat{H}_c^\circ$ is always negative, the heating value is positive.

To calculate a lower heating value of a fuel from a higher heating value or vice versa, you must determine the moles of water produced when one mole of the fuel is burned. If this quantity is designated n, then

$$HHV = LHV + n\,\Delta\hat{H}_v(H_2O,\ 25°C) \qquad \textbf{(9.6-1)}$$

(Try to prove this relationship from the definitions of LHV and HHV and Hess's law.) The heat of vaporization of water at 25°C is

$$\Delta\hat{H}_v(H_2O,\ 25°C) = 44.013\ \text{kJ/mol} \qquad \textbf{(9.6-2a)}$$

$$= 18{,}934\ \text{Btu/lb-mole} \qquad \textbf{(9.6-2b)}$$

If a fuel contains a mixture of combustible substances, its heating value (lower or higher) is

$$HV = \sum x_i (HV)_i \qquad \textbf{(9.6-3)}$$

where $(HV)_i$ is the heating value of the ith combustible substance. If the heating values are expressed in units of (energy)/(mass), then the x_is are the mass fractions of the fuel components, while if the dimensions of the heating values are (energy)/(mole) then the x_is are mole fractions.

EXAMPLE 9.6-1 *Calculation of a Heating Value*

A natural gas contains 85% methane and 15% ethane by volume. The heats of combustion of methane and ethane at 25°C and 1 atm with water *vapor* as the assumed product are given below:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(v): \quad \Delta\hat{H}_c^\circ = -802\ \text{kJ/mol}$$

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2\,CO_2(v) + 3\,H_2O(v): \quad \Delta\hat{H}_c^\circ = -1428\ \text{kJ/mol}$$

Calculate the higher heating value (kJ/g) of the natural gas.

SOLUTION

Since the heating value per unit mass of the fuel is desired, we will first calculate the composition on a mass basis:

$$1\ \text{mol fuel} \Longrightarrow \begin{array}{lcl} 0.85\ \text{mol } CH_4 & \Longrightarrow & 13.6\ \text{g } CH_4 \\ 0.15\ \text{mol } C_2H_6 & \Longrightarrow & \underline{\ 4.5\ \text{g } C_2H_6} \\ & & 18.1\ \text{g total} \end{array}$$

Thus

$$x_{CH_4} = 13.6\ \text{g } CH_4/18.1\ \text{g} = 0.751\ \text{g } CH_4/\text{g fuel}$$

$$x_{C_2H_6} = 1 - x_{CH_4} = 0.249\ \text{g } C_2H_6/\text{g fuel}$$

The higher heating values of the components are calculated from the given heats of combustion (which are the negatives of the lower heating values) as follows:

$$\begin{aligned}(HHV)_{CH_4} &= (LHV)_{CH_4} + n_{H_2O}(\Delta\hat{H}_v)_{H_2O} \\ &= \left[802\,\frac{\text{kJ}}{\text{mol } CH_4} + \frac{2\ \text{mol } H_2O}{\text{mol } CH_4}\left(44.013\,\frac{\text{kJ}}{\text{mol } H_2O}\right)\right]\frac{1\ \text{mol}}{16.0\ \text{g } CH_4} \\ &= 55.6\ \text{kJ/g}\end{aligned}$$

$$\begin{aligned}(HHV)_{C_2H_6} &= \left[1428\,\frac{\text{kJ}}{\text{mol } C_2H_6} + \frac{3\ \text{mol } H_2O}{\text{mol } C_2H_6}\left(44.013\,\frac{\text{kJ}}{\text{mol } H_2O}\right)\right]\frac{1\ \text{mol}}{30.0\ \text{g } C_2H_6} \\ &= 52.0\ \text{kJ/g}\end{aligned}$$

The higher heating value of the mixture is from Equation 9.6-3:

$$HHV = x_{CH_4}(HHV)_{CH_4} + x_{C_2H_6}(HHV)_{C_2H_6}$$

$$= [(0.751)(55.6) + (0.249)(52.0)]\ \text{kJ/g} = \boxed{54.7\ \text{kJ/g}}$$

Higher heating values for common solid, liquid, and gaseous fuels are tabulated in Section 27 of *Perry's Chemical Engineers' Handbook* (see footnote 1). Representative values are given in Table 9.6-1. From the standpoint of heating value per unit mass, hydrogen is clearly the best fuel; however, it does not occur naturally in appreciable quantities and the current cost of producing it makes it less economical than the other fuels in Table 9.6-1.

Table 9.6-1 Typical Heating Values of Common Fuels

	Higher Heating Value	
Fuel	kJ/g	Btu/lb$_m$
Wood	17	7700
Soft coal	23	10,000
Hard coal	35	15,000
Fuel oil, gasoline	44	19,000
Natural gas	54	23,000
Hydrogen	143	61,000

TEST YOURSELF (Answers, p. 661)

1. The standard heat of the reaction

$$n\text{-}C_4H_{10}(v) + \tfrac{13}{2}\,O_2 \longrightarrow 4\,CO_2 + 5\,H_2O(v)$$

is −2658 kJ/mol. What is the lower heating value per mol of n-butane vapor? The higher heating value?

2. A gas mixture contains 40.0 wt% H_2 (HHV = 143 kJ/g) and 60.0 wt% CH_4 (HHV = 55 kJ/g). Calculate the higher heating value of this mixture in kJ/g.
3. In 1998, bituminous coal for residential heating use cost roughly \$150 per ton. What would natural gas have to cost (\$/ton) to be as economical as coal on a \$/Btu basis? (Use Table 9.6-1.)

9.6b Adiabatic Flame Temperature

When a fuel is burned, a considerable amount of energy is released. Some of this energy is transferred as heat through the reactor walls, and the remainder raises the temperature of the reaction products; the less heat transferred, the higher the product temperature. The highest achievable temperature is reached if the reactor is adiabatic and all of the energy released by the combustion goes to raise the temperature of the combustion products. This temperature is called the **adiabatic flame temperature,** T_{ad}.

The calculation of an adiabatic flame temperature follows the general procedure outlined in Section 9.5b. Unknown stream flow rates are first determined by material balances. Reference conditions are chosen, specific enthalpies of feed components are calculated, and specific enthalpies of product components are expressed in terms of the product temperature, T_{ad}. Finally, $\Delta\dot{H}(T_{ad})$ for the process is evaluated and substituted into the energy balance equation ($\Delta\dot{H} = 0$), which is solved for T_{ad}.

Suppose $\dot{n}_f$(mol/s) of a fuel species with heat of combustion $\Delta\hat{H}_c^\circ$ is burned completely with pure oxygen or air in a continuous adiabatic reactor. If the reference states of the molecular feed and product species are those used to determine $\Delta\hat{H}_c^\circ$, the enthalpy change from inlet to outlet is determined from Equation 9.5-2a to be[9]

$$\Delta\dot{H} = \dot{n}_\mathrm{f}\,\Delta\hat{H}_\mathrm{c}^\circ + \sum_\mathrm{out} \dot{n}_i\hat{H}_i(T_\mathrm{ad}) - \sum_\mathrm{in} \dot{n}_i\hat{H}_i(T_\mathrm{feed})$$

Since the reactor is adiabatic, $\dot{Q} = 0$ in the energy balance. If shaft work and kinetic and potential energy changes ($\dot{W}_\mathrm{s}, \Delta\dot{E}_\mathrm{k}, \Delta\dot{E}_\mathrm{p}$) are negligible compared to each of the first two terms in the expression for $\Delta\dot{H}$, the energy balance simplifies to $\Delta\dot{H} = 0$, which in turn leads to

$$\sum_\mathrm{out} \dot{n}_i\hat{H}_i(T_\mathrm{ad}) = -\dot{n}_\mathrm{f}\,\Delta\hat{H}_\mathrm{c}^\circ + \sum_\mathrm{in} \dot{n}_i\hat{H}_i(T_\mathrm{feed}) \qquad \textbf{(9.6-4)}$$

Once again, the reference states for determination of the specific enthalpies in this equation must be those used to determine the value of $\Delta\hat{H}_\mathrm{c}^\circ$. If the heats of combustion in Table B.1 are used, the reference states would be the fuel, combustion products (including liquid water), and inert species at 25°C and 1 atm. The fuel would be in whichever state (solid, liquid, or gas) Table B.1 specifies.

If the third-order polynomial heat capacity formulas in Table B.2 are used to determine $\hat{H}_i(T_\mathrm{ad})$ for each product species, Equation 9.6-4 becomes a fourth-order polynomial equation. Solving this equation for T_ad is easily accomplished with a spreadsheet or equation-solving program. The next example illustrates the procedure.

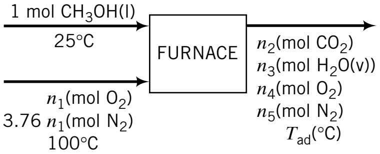
EXAMPLE 9.6-2 *Calculation of an Adiabatic Flame Temperature*

Liquid methanol is to be burned with 100% excess air. The engineer designing the furnace must calculate the highest temperature that the furnace walls will have to withstand so that an appropriate material of construction can be chosen. Perform this calculation, assuming that the methanol is fed at 25°C and the air enters at 100°C.

SOLUTION ***Basis: 1 mol CH_3OH Burned***

Assume complete combustion. From Table B.1,

$$CH_3OH(l) + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O(l): \quad \Delta\hat{H}_\mathrm{c}^\circ = -726.6 \text{ kJ/mol}$$



Calculate Component Amounts

$$(n_{O_2})_\mathrm{theoretical} = 1.50 \text{ mol}$$

$$n_1 = (2)(1.50 \text{ mol}) = 3.00 \text{ mol } O_2 \text{ fed}$$

$$\Downarrow$$

$$(3.76 \text{ mol } N_2/\text{mol } O_2)(3.00 \text{ mol } O_2) = 11.28 \text{ mol } N_2 \text{ fed}$$

Material balances yield

$$n_2 = 1.00 \text{ mol } CO_2$$
$$n_3 = 2.00 \text{ mol } H_2O$$
$$n_4 = 1.50 \text{ mol } O_2$$
$$n_5 = 11.28 \text{ mol } N_2$$

---

[9] In the equation that follows, we make use of the fact that the tabulated values of $\Delta\hat{H}_\mathrm{c}^\circ$ presume a stoichiometric coefficient of 1 for the fuel species, so that $\dot{n}_\mathrm{f}$ may be substituted for $\dot{\xi} = \dot{n}_\mathrm{f}/|\nu_\mathrm{f}|$ in Equation 9.5-2a.

Calculate Feed Component Enthalpies

References: $CH_3OH(l),\ O_2,\ N_2$ at 25°C
$CH_3OH(l, 25°C)$: $\hat{H} = 0$
Air (100°C): $\hat{H} = 2.191$ kJ/mol (from Table B.8)

Evaluate the Right Side of Equation 9.6-4

$$\begin{aligned}-n_f\Delta\hat{H}_c^\circ + \sum_{\text{in}} n_i\hat{H}_i &= -(1.00 \text{ mol CH}_3\text{OH})\left(-726.6\ \frac{\text{kJ}}{\text{mol}}\right)\\ &\quad + (1.00 \text{ mol CH}_3\text{OH})\left(0\ \frac{\text{kJ}}{\text{mol}}\right) + (14.28 \text{ mol air})\left(2.191\ \frac{\text{kJ}}{\text{mol}}\right)\\ &= 757.9 \text{ kJ}\end{aligned}$$

Calculate Enthalpy of Product Stream

References: $CO_2(g), O_2(g), N_2(g)$, and $H_2O(l)$ at 25°C. (Liquid water is assumed since this is the state for which $\Delta\hat{H}_c$ is known.)

From Table B.2, the heat capacities of the product gases in kJ/(mol·°C) in terms of T(°C) are

$$\begin{aligned}(C_p)_{CO_2} &= 0.03611 + 4.233 \times 10^{-5}T - 2.887 \times 10^{-8}T^2 + 7.464 \times 10^{-12}T^3\\ (C_p)_{H_2O(g)} &= 0.03346 + 0.688 \times 10^{-5}T + 0.7604 \times 10^{-8}T^2 - 3.593 \times 10^{-12}T^3\\ (C_p)_{O_2} &= 0.02910 + 1.158 \times 10^{-5}T - 0.6076 \times 10^{-8}T^2 + 1.311 \times 10^{-12}T^3\\ (C_p)_{N_2} &= 0.02900 + 0.2199 \times 10^{-5}T + 0.5723 \times 10^{-8}T^2 - 2.871 \times 10^{-12}T^3\end{aligned}$$

We could integrate each of these formulas from the reference temperature of 25°C to the unknown T_{ad} to obtain expressions for each $(\hat{H}_i)_{out}$, and then substitute in $\sum_{out} n_i\hat{H}_i$; however, we can save some calculation time by summing before integrating. Substituting the values of n_i calculated previously and the tabulated heat capacities, and recalling that to calculate $(\hat{H})_{H_2O(g)}$ we must first vaporize the liquid at 25°C (using Equation 9.6-2a for $\Delta\hat{H}_v$), we obtain

$$\sum n_iC_{pi} = 0.4378 + 9.826 \times 10^{-5}T + 4.178 \times 10^{-8}T^2 - 30.14 \times 10^{-12}T^3$$

$$\Downarrow$$

$$\begin{aligned}\sum_{\text{out}} n_i\hat{H}_i &= n_3(\Delta\hat{H}_v)_{H_2O} + \int_{25°C}^{T_{ad}} \left(\sum n_iC_{pi}\right) dT\\ &= 88.026 + 0.4378T_{ad} + 4.913 \times 10^{-5}T_{ad}^2 + 1.393 \times 10^{-8}T_{ad}^3\\ &\quad - 7.535 \times 10^{-12}T_{ad}^4 - 11.845\end{aligned}$$

$$\Downarrow$$

$$\begin{aligned}\sum_{\text{out}} n_i\hat{H}_i &= 76.18 + 0.4738T_{ad} + 4.913 \times 10^{-5}T_{ad}^2 + 1.393 \times 10^{-8}T_{ad}^3\\ &\quad - 7.535 \times 10^{-12}T_{ad}^4\end{aligned}$$

Energy Balance

From Equation 9.6-4

$$\sum_{\text{out}} n_i\hat{H}_i = -n_f\ \Delta\hat{H}_c^\circ + \sum_{\text{in}} n_i\hat{H}_i = 757.9 \text{ kJ}$$

$$\Downarrow$$

$$7.535 \times 10^{-12}T_{ad}^4 - 1.393 \times 10^{-8}T_{ad}^3 - 4.913 \times 10^{-5}T_{ad}^2 - 0.4738T_{ad} + 681.7 = 0$$

This quartic equation may be solved using a spreadsheet, an equation-solving program, or a calculator programmed to solve polynomial equations. The solution is

$$\boxed{T_{ad} = 1256°C}$$

The furnace walls will therefore never be exposed to a temperature greater than 1256°C as long as the feed and air properties remain the same.

The adiabatic flame temperature is much greater when pure oxygen rather than air is fed to the reactor and is greatest when the fuel and oxygen are fed in stoichiometric proportion.

TEST YOURSELF (Answers, p. 661)

1. What is the adiabatic flame temperature of a fuel?
2. Suppose T_{ad} is the adiabatic flame temperature calculated for a given fuel + air feed to a furnace. Give two reasons why the actual furnace temperature might be less than T_{ad}.
3. Why should the adiabatic flame temperature be much higher for a pure oxygen feed than for an air feed?

9.6c Flammability and Ignition

In this section and the one that follows, we discuss qualitatively what happens during the rapid chemical reaction between a fuel and oxygen. Along the way, we provide answers to the following questions:

1. What is a flame? Why are some flames blue and some yellow?
2. If you light a match in a mixture of methane and air that contains 10% CH_4 by volume, the mixture will burn explosively, but if the mixture contains 20% CH_4 nothing will happen. Why?
3. What is an explosion? What is the loud noise you hear when something explodes?
4. Hydrogen and oxygen react explosively to form water, yet if you mix these two gases in a flask, nothing happens. Why not?

We have so far in this text only considered the initial and final conditions in a chemical reactor, and not how long it may have taken to get from one to the other. When you study **chemical reaction kinetics,** you will learn that the rate of a reaction depends strongly on the reaction temperature; for many reactions, a temperature rise of only 10°C is enough to double the rate.

Suppose a mixture of methane and air containing 10 mole% CH_4 is heated by a central heat source (e.g., an electrical coil) at atmospheric pressure, beginning at room temperature. Although methane reacts with oxygen

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$$

the reaction proceeds at an immeasurably low rate at room temperature, and to an observer nothing would seem to be happening in the reactor.

As the temperature increases, the rate of the oxidation reaction also increases, and measurable amounts of CO_2 and H_2O appear. However, if the heat source is turned off, the reactor temperature drops again—the rate at which heat is generated by the reaction alone is not enough to compensate for the rate at which heat is lost from the reaction zone.

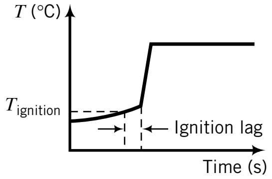
However, if the temperature at any point in the reactor reaches about 640°C or higher, the rate of heat generation by the reaction exceeds the rate of heat loss from the reaction zone. The gas adjacent to this zone is then heated above 640°C, causing the zone of rapid reaction to spread. The temperature of the gas rapidly rises by several hundred or even a thousand degrees in a fraction of a second; even if the heating source is turned off, the rate of heat generation by the now rapidly occurring reaction is enough to maintain the system at its high temperature until the reactants are exhausted.

Combustion is defined as a rapid, high-temperature oxidation reaction. What happens in the reactor just described after the reaction rate accelerates dramatically is combustion, whereas the initial slow oxidation reaction between methane and oxygen to form CO_2 and H_2O and other reactions between these species, such as the formation reaction of formaldehyde

$$CH_4 + O_2 \rightarrow HCHO + H_2O$$

are not classified as combustion reactions.

The rapid increase in the rate of an oxidation reaction when the reaction mixture exceeds a certain temperature is called **ignition**; the temperature at which this phenomenon occurs is called the **ignition temperature,** and the time between the instant when the mixture reaches the ignition temperature and the moment of ignition is the **ignition lag.** The ignition temperature and lag are shown here on a representative plot of the temperature of a fuel mixture that is being heated.



The value of the ignition temperature depends on a number of things for a given fuel, including the fuel-to-air ratio, the total pressure in the reactor, and even the reactor geometry. For any given fuel, there is a lower limit to this quantity called the **autoignition temperature.** Representative values of this quantity for stoichiometric fuel–air mixtures at 1 atm are 400°C for H_2, 540°C for CH_4, and 515°C for C_2H_6. Ignition lags are typically 0.1–10 s in duration and decrease with increasing temperature above the autoignition temperature.

We saw in Section 9.6b that the highest attainable temperature in a combustion reaction—the adiabatic flame temperature—depends on the fuel-to-air ratio, and we stated but did not prove that this upper temperature limit is a maximum when the fuel and oxygen are present in stoichiometric proportion. If the mixture is either **rich** (fuel in excess) or **lean** (O_2 in excess), the adiabatic flame temperature decreases.

There exist two values of the mole percent of fuel in a fuel-air mixture—the **lower** or **lean flammability limit** and the **upper** or **rich flammability limit**—that define a range within which self-sustaining combustion can occur. *A fuel–air mixture whose composition falls outside these limits is incapable of igniting or exploding, even if exposed to a spark or flame.* The composition range between the two flammability limits is called the **explosive range** of the mixture.

For example, the stoichiometric percentage of methane in a methane–air mixture is 9.5 mole%. (Prove it.) Experimentally, it is found that the lower flammability limit of CH_4–air mixtures at 1 atm is approximately 5% CH_4 and the upper flammability limit is approximately 15% CH_4. Thus, a CH_4–air mixture containing between 5% CH_4 and 15% CH_4 must be considered a fire or explosion hazard, while a mixture containing 3% CH_4 may be considered safe, and a mixture containing 18% CH_4 may also be considered safe as long as it is not brought into contact with additional oxygen.

Flammability limits of a number of hydrocarbon–air mixtures are listed in tables on pp. 26-53 and 26-54 of *Perry's Chemical Engineers' Handbook* (see footnote 1). The given values apply to an initial temperature of roughly 25°C and a pressure of 1 atm.

EXAMPLE 9.6-3 Ignition Temperature and Flammability Limits

Propane gas and air are to be mixed and fed to a combustion reactor. The combustion is to be initiated with a gas torch. Determine the minimum and maximum percentages of propane in the feed to the reactor and the minimum required temperature of the torch flame.

SOLUTION From Table 26-10 of *Perry's Chemical Engineer's Handbook* (see footnote 1),

$$\text{Minimum mole\% } C_3H_8 \text{ for combustion} = 2.1\%$$

$$\text{Maximum mole\% } C_3H_8 \text{ for combustion} = 9.5\%$$

The torch flame temperature must be at least as high as the autoignition temperature of a propane–air mixture, which from Table 26-10 is $\boxed{450°\text{C}}$.

If a liquid (or a volatile solid) is exposed to air, the vapor given off could form a combustible mixture with the air adjacent to it, and a spark or match lit in the vicinity of the liquid could cause the mixture to ignite or explode. The **flash point** of a liquid is the temperature at which the liquid gives off enough vapor to form an ignitable mixture with the air above the liquid surface. The flash point of gasoline, for example, is roughly −42°C, and that of ethanol is 13°C, so that these liquids constitute fire hazards at room temperature, while the flash points of fuel oils vary from 38°C to 55°C, making the hazards associated with these materials considerably less.

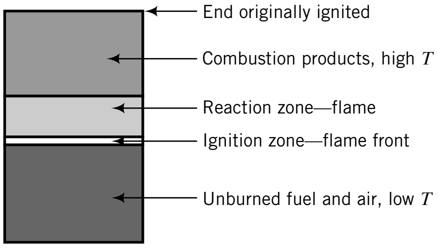
TEST YOURSELF (Answers, p. 661)

1. Briefly define the following terms: (a) ignition, (b) autoignition temperature, (c) ignition lag, (d) flammability limits of a fuel–air mixture, and (e) flash point of a liquid.
2. The flammability limits of methane–air mixtures are 5% CH_4 and 15% CH_4 at 1 atm, and the autoignition temperature is 540°C.
   - **(a)** What would happen if a spark were struck in a methane–air mixture containing 10% CH_4? What about a mixture containing 20% CH_4?
   - **(b)** If a methane–air mixture containing 20% CH_4 were heated to 700°C, would the combustion reaction take place? What would happen if the heat source were turned off?
   - **(c)** Pure methane is clearly not within the explosive range of methane–air mixtures, yet if pure methane is blown out of a cylinder into a room and a match is lit nearby, a flame is observed that persists after the match is withdrawn. How is this possible?

9.6d Flames and Detonations

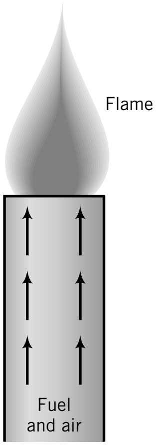
Suppose a combustible gas–air mixture is contained in an open-ended tube, and a match or another ignition source is applied to one end of the tube. The gas mixture at this end is heated and eventually ignites. The intense heat generated by the combustion reaction raises the chemical species formed during the reaction to high energy states. When these species return to lower energy states, some of the energy they lose is given off in the form of light. The result is a visible **flame** accompanying the combustion.

Initially the flame is located at the end of the tube that was ignited. However, the heat of combustion quickly raises the adjacent unburned gas to its ignition point, causing the flame to "travel" toward the other end of the tube. At some point, the tube appears as follows.



The flame front moves in the direction of the unburned gases at a velocity called the **flame velocity**, which typically has a value of 0.3 to 1 m/s. The exact value of the flame velocity depends on a number of things, including the type of fuel, fuel-to-air ratio, initial temperature and pressure of the unburned gases, and the geometry of the combustion chamber.

Suppose now that instead of being stationary in the tube, the combustion mixture is fed continuously into the bottom (as in a Bunsen burner), and the top is ignited. If the velocity with which the gases leave the tube equals the velocity with which the flame would travel down in a stationary gas, a **stationary flame** is achieved at the top. The wall of the tube lowers the flame velocity, so that the flame burns at the end but does not penetrate into the tube.



If the gas flow rate is increased, the flame size and rate of heat generation both increase, since a larger quantity of gas is being burned. However, once the flow rate reaches a critical value, the flame can no longer travel back as fast as the combustion region is transported away from the burner. The gases in the combustion region become increasingly diluted with air, until the region finally falls outside the flammability limits and the fire is literally blown out.

On the other hand, if the gas flow rate to the burner tube is decreased, the gas velocity in the tube may become lower than the flame propagation velocity in the tube. The result is **flashback**—the flame travels back through the tube toward the fuel source. Flashback is extremely dangerous, and any flow system involving combustible gases must be designed to guarantee that the flow rate stays above the flame propagation velocity.

When combustion of a well-mixed fuel–air mixture occurs, the fuel rapidly reacts with oxygen to form a number of unstable intermediate species (such as oxygen and hydrogen atoms, and OH and H_2O radicals), which then proceed through a complicated chain mechanism to form CO_2 and H_2O. Some of these species undergo transitions that cause them to emit radiation whose wavelength falls within the blue region of the visible spectrum. The result is that the flame appears blue.

On the other hand, when the fuel and air are not well mixed (such as when a pure hydrocarbon gas is burned as it emerges from a stack and mixes with atmospheric air), the combustion proceeds relatively slowly, and some of the hydrocarbon fuel decomposes to form elementary carbon and hydrogen before oxidation takes place. The heat of reaction is sufficient to raise the temperature to a point where the carbon particles glow incandescently. A yellow flame is the result.

Finally, suppose ignition of a gas takes place in a confined or partially confined space. The large temperature rise in the combustion region causes a rapid buildup of pressure in this region. If the combustion is fast enough and the heat of reaction is high enough, a **detonation** may result, wherein a sharply defined high-pressure front, or **shock wave,** travels through the gas at a velocity well in excess of the flame propagation velocity in the gas. The shock wave rapidly compresses and ignites the gas as it passes through, giving the appearance of an instantaneous combustion.

Even after the combustion reaction that gave rise to the detonation has consumed all the available fuel, the shock wave can persist for large distances, carrying with it considerable energy. The energy of even a small shock wave is sufficient to vibrate the eardrums of anyone near the site of the detonation, producing the bang that always accompanies an explosion. The energy of a large shock wave may be sufficient to demolish a city.

TEST YOURSELF (Answers, p. 661)

You are the guest lecturer at a junior high school science fair. The following questions are put to you. How would you answer them in terms an intelligent 14-year-old might understand?

1. What is a flame?
2. What is a yellow flame? A blue flame?
3. What is detonation? What is the loud noise you hear when something explodes? What is it that knocks buildings over when dynamite is set off? How does a gun work?
4. (This one is from one of the science teachers who thought they should have asked *him* to give the lecture.) You say that hydrogen and oxygen react explosively to form water. Why is it that I can mix hydrogen and oxygen in a flask and nothing will happen? (*Hint:* Reread the beginning of Section 9.6c.)

9.7 SUMMARY

Large internal energy and enthalpy changes are often associated with chemical reactions, leading to substantial heat transfer (heating or cooling) requirements for chemical reactors. This chapter outlines methods of calculating $\Delta\dot{H}$ for open reactive systems and ΔU and ΔH for closed systems. Once the appropriate quantity has been determined, it may be substituted into the energy balance to determine the required heat transfer.

- The **heat of reaction** (or **enthalpy of reaction**), $\Delta\hat{H}_r(T, P)$, is the enthalpy change when stoichiometric quantities of reactants at temperature T and pressure P are consumed completely to form products at the same temperature and pressure. The **standard heat of reaction,** $\Delta\hat{H}_r^\circ$, is the heat of reaction at a specified reference temperature and pressure, in this text 25°C and 1 atm. At low to moderate pressures, the heat of reaction is nearly independent of P.

  For example, the standard heat of reaction for the complete combustion of methane is

  $$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l): \quad \Delta\hat{H}_r^\circ = -890.3 \text{ kJ/mol}$$

  which signifies that if 1 g-mole of gaseous methane and 2 g-moles of gaseous oxygen at 25°C and 1 atm react completely to form 1 g-mole of gaseous carbon dioxide and 2 g-moles of liquid water and the products are brought back to 25°C and 1 atm, the net enthalpy change would be $\Delta H = -890.3$ kJ. If the energy balance reduces to $Q = \Delta H$, 890.3 kJ of heat would have to be transferred away from the reactor to keep the products at 25°C.
- If $\Delta\hat{H}_r(T, P) < 0$, the reaction is **exothermic** at T and P: less energy is required to break the bonds holding the reactant molecules together than is released when the product bonds form, resulting in a net release of energy as the reaction proceeds. This energy may be transferred from the reactor as heat or it may serve to raise the temperature of the reaction mixture.
- Similarly, if $\Delta\hat{H}_r(T, P) > 0$, the reaction is **endothermic**: more energy is required to break the reactant bonds than is released when the product bonds form, leading to a net absorption of energy as the reaction proceeds. Unless this energy is supplied to the reactor as heat, the mixture temperature decreases.
- Provided that gaseous reactants and products behave ideally and the specific volumes of liquid and solid reactants and products are negligible compared with the specific volumes of the gases, the **internal energy of reaction** may be calculated from Equation 9.1-5. (This quantity is required for energy balances on constant-volume batch reactors.)
- According to **Hess's law,** if a stoichiometric equation for a reaction can be obtained as a linear combination of the equations for other reactions (i.e., by adding and subtracting those

equations), the heat of the first reaction can be calculated as the same linear combination of the heats of the other reactions.

- The **standard heat of formation** of a species, $\Delta\hat{H}_f^\circ$, is the heat of the reaction in which one mole of the species is formed from its constituent elemental species in their naturally occurring states at 25°C and 1 atm. Standard heats of formation of many species are listed in Table B.1.
- A consequence of Hess's law is that the standard heat of any reaction may be calculated as

  $$\Delta\hat{H}_r^\circ = \sum \nu_i \, \Delta\hat{H}_{fi}^\circ$$

  where ν_i is the stoichiometric coefficient of reactant or product species i (positive for products, negative for reactants), and $\Delta\hat{H}_{fi}^\circ$ is the standard heat of formation of that species.
- The **standard heat of combustion** of a species, $\Delta\hat{H}_c^\circ$, is the heat of the reaction in which one mole of the species undergoes complete combustion to form products in specified states. Standard heats of combustion of many species are listed in Table B.1, with the presumed combustion products being CO_2, $H_2O(l)$, SO_2 for species containing sulfur, and N_2 for species containing nitrogen. A consequence of Hess's law is that the standard heat of any reaction involving only oxygen and combustible species may be calculated as

  $$\Delta\hat{H}_r^\circ = -\sum \nu_i \, \Delta\hat{H}_{ci}^\circ$$

  As before, ν_i is the stoichiometric coefficient of species i.
- When performing energy balances on a reactive chemical process, two procedures may be followed in the calculation of $\Delta\dot{H}$ (or ΔH or ΔU) that differ in the choice of reference states for enthalpy or internal energy calculations. In the **heat of reaction method,** the references are the reactant and product species at 25°C and 1 atm in the phases (solid, liquid, or gas) for which the heat of reaction is known. In the **heat of formation method,** the references are the elemental species that constitute the reactant and product species [e.g., C(s), $O_2(g)$, $H_2(g)$, etc.] at 25°C and 1 atm. In both methods, reference states for nonreactive species may be chosen for convenience, as was done for the nonreactive processes of Chapters 7 and 8.
- The heat of reaction method may be slightly easier when only one reaction occurs and the heat of reaction is known. When this method is used, the specific enthalpy of each species in every feed or product stream is calculated by choosing a process path from the reference state to the process state, calculating $\Delta\hat{H}$ for each heating and cooling step and each phase change in the path, and summing the enthalpies for the steps. When specific enthalpies have been calculated for all species in all of their inlet and outlet states, $\Delta\dot{H}$ for a continuous process is calculated as

  $$\Delta\dot{H} = \dot{\xi}\,\Delta\hat{H}_r^\circ + \sum_{\text{out}} \dot{n}_i\hat{H}_i - \sum_{\text{in}} \dot{n}_i\hat{H}_i$$

  In this equation, $\dot{\xi}$ is the extent of reaction (determined from Equation 9.1-3); $\dot{n}_i$ and $\hat{H}_i$ are respectively the molar flow rate and specific enthalpy of a process species in an inlet or outlet stream; and the summations are taken over all species in all of their inlet and outlet states. Once calculated, $\Delta\dot{H}$ is substituted in the open-system energy balance, which is solved for $\dot{Q}$ or whichever other variable is unknown.[10]
- The heat of formation method is generally easier when there are multiple reactions. When this method is used, the specific enthalpy of a species in a feed or product stream is calculated by choosing a process path from the reference state (the elements at 25°C) to the process state, beginning with the formation of the species from the elements ($\Delta\hat{H} = \Delta\hat{H}_f^\circ$); evaluating $\Delta\hat{H}$ for each subsequent heating and cooling step and each phase change in the path; and summing the enthalpies for the steps (including the formation step). When specific enthalpies have been calculated for all species in all of their inlet and outlet states, $\Delta\dot{H}$ is calculated for

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[10] If the system in question is a closed system at constant pressure, the dots over variables would be deleted in the above formulas, and if the system is a closed system at constant volume, U would replace H.

an open system as

$$\Delta \dot{H} = \sum_{\text{out}} \dot{n}_i \hat{H}_i - \sum_{\text{in}} \dot{n}_i \hat{H}_i$$

As before, the summations are taken over all species in all of their inlet and outlet states. Once calculated, $\Delta \dot{H}$ is substituted in the open-system energy balance, which is solved for $\dot{Q}$ or whichever other variable is unknown (see footnote 10).

- Sometimes the feed conditions and heat input to a reactor are specified (as in an adiabatic reactor) and the outlet temperature, T_{out}, is to be determined. The procedure is to derive expressions for the specific enthalpies of the reactor outlet species in terms of T_{out}; substitute these expressions into the summation $\sum_{\text{out}} \dot{n}_i \hat{H}_i$ in the expression for $\Delta \dot{H}$; substitute in turn for $\Delta \dot{H}(T_{\text{out}})$ in the energy balance, and solve the resulting equation for T_{out}.
- The **standard heat of formation of a liquid solution** is the sum of the standard heat of formation of the solute and the standard heat of solution calculated using the methods of Section 8.5. The standard heat of a reaction involving solutions may be determined as the weighted sum of the heats of formation of the reactants and products (including the solutions), with the weighting factors being the stoichiometric coefficients (positive for products, negative for reactants). An energy balance for a reactor in which solutions react or form may be written by taking the feed and product solutions at 25°C and 1 atm as references and using the heat of reaction method.
- **Combustion** is a rapid high-temperature reaction between a fuel and oxygen. The **higher heating value** of a fuel is the negative of the standard heat of combustion of the fuel$(-\Delta \hat{H}_c^\circ)$ with $H_2O(l)$ as a combustion product, and the **lower heating value** is the negative of the standard heat of combustion based on $H_2O(v)$ as a product. The relationship between the two heating values is given by Equation 9.6-1.
- The **adiabatic flame temperature** of a fuel is the temperature that would be attained if the fuel were burned in an adiabatic combustion chamber and all of the energy released went into raising the temperature of the reaction products (as opposed to being absorbed by or transferred through the reactor wall).
- When the temperature of a combustible mixture exceeds a certain value, after a short time lag the rate of the reaction and the reaction temperature increase extremely rapidly. This phenomenon is called **ignition,** and the time interval after T_{ignition} is reached and before the temperature increases sharply is the **ignition lag.** The lowest temperature at which ignition may occur for a fuel is the **autoignition temperature** of the fuel.
- If the mole percentage of a fuel in a fuel-air mixture falls below a certain value (the **lower flammability limit**) or above another value (the **upper flammability limit**), the mixture will not ignite or explode, even if exposed to a flame or spark. The composition range between the flammability limits is called the **explosive range** of the mixture.

Interactive Tutorial #6
Questions with Immediate Feedback → *Note*: This would be a good time to work through Interactive Tutorial #6.

PROBLEMS

9.1. The standard heat of the reaction

$$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 6\ H_2O(g)$$

is

$$\Delta \hat{H}_r^\circ = -904.7\ \text{kJ/mol}$$

(a) Briefly explain what that means. Your explanation may take the form "When ______ (specify quantities of reactant species and their physical states) react to form ______ (quantities of product species and their physical state), the change in enthalpy is ______."

(b) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(c) What is $\Delta\hat{H}_r^\circ$ for

$$2\,NH_3(g) + \tfrac{5}{2}\,O_2 \longrightarrow 2\,NO(g) + 3\,H_2O(g)$$

(d) What is $\Delta\hat{H}_r^\circ$ for

$$NO(g) + \tfrac{3}{2}\,H_2O(g) \longrightarrow NH_3(g) + \tfrac{5}{4}\,O_2$$

(e) Estimate the enthalpy change associated with the consumption of 340 g NH_3/s if the reactants and products are all at 25°C. (See Example 9.1-1.) What have you assumed about the reactor pressure? (You don't have to assume that it equals 1 atm.)

(f) The values of $\Delta\hat{H}_r^\circ$ given in this problem apply to water vapor at 25°C and 1 atm, and yet the normal boiling point of water is 100°C. Can water exist as a vapor at 25°C and a total pressure of 1 atm? Explain your answer.

Student Workbook

9.2. The standard heat of reaction for the combustion of liquid *n*-nonane to form CO_2 and liquid water at 25°C and 1 atm is $\Delta\hat{H}_r^\circ = -6124$ kJ/mol.

(a) Briefly explain what that means. Your explanation may take the form "When ______ (specify quantities of reactant species and their physical states) react to form ______ (quantities of product species and their physical state), the change in enthalpy is ______."

(b) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(c) If 25.0 mol/s of liquid nonane is consumed and the reactants and products are all at 25°C, estimate the required rate of heat input or output (state which) in kilowatts, assuming that $\dot{Q} = \Delta\dot{H}$ for the process. What have you also assumed about the reactor pressure in your calculation? (You don't have to assume that it equals 1 atm.)

(d) The standard heat of combustion of *n*-nonane *vapor* is $\Delta\hat{H}_r^\circ = -6171$ kJ/mol. What is the physical significance of the 47 kJ/mol difference between this heat of combustion and the one given previously?

(e) The value of $\Delta\hat{H}_r^\circ$ given in part (d) applies to *n*-nonane vapor at 25°C and 1 atm, and yet the normal boiling point of *n*-nonane is 150.6°C. Can *n*-nonane exist as a vapor at 25°C and a total pressure of 1 atm? Explain your answer.

9.3. The standard heat of the combustion reaction of liquid *n*-hexane to form $CO_2(g)$ and $H_2O(l)$, with all reactants and products at 77°F and 1 atm, is $\Delta\hat{H}_r^\circ = -1.791 \times 10^6$ Btu/lb-mole. The heat of vaporization of hexane at 77°F is 13,550 Btu/lb-mole and that of water is 18,934 Btu/lb-mole.

(a) Is the reaction exothermic or endothermic at 77°F? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(b) Use the given data to calculate $\Delta\hat{H}_r^\circ$(Btu/lb-mole) for the combustion of *n*-hexane vapor to form $CO_2(g)$and $H_2O(g)$.

(c) If $\dot{Q} = \Delta\dot{H}$, at what rate in Btu/s is heat absorbed or released (state which) if 120 lb_m/s of O_2 is consumed in the combustion of hexane vapor, water vapor is the product, and the reactants and products are all at 77°F?

9.4. The standard heat of the reaction

$$CaC_2(s) + 5\,H_2O(l) \longrightarrow CaO(s) + 2\,CO_2(g) + 5\,H_2(g)$$

is $\Delta\hat{H}_r^\circ = +69.36$ kJ/mol.

(a) Is the reaction exothermic or endothermic at 25°C? Would you have to heat or cool the reactor to keep the temperature constant? What would the temperature do if the reactor ran adiabatically? What can you infer about the energy required to break the molecular bonds of the reactants and that released when the product bonds form?

(b) Calculate $\Delta\hat{U}_r^\circ$ for this reaction. (See Example 9.1-2.) Briefly explain the physical significance of your calculated value.

(c) Suppose you charge 150.0 g of CaC_2 and liquid water into a rigid container at 25°C, heat the container until the calcium carbide reacts completely, and cool the products back down to 25°C, condensing essentially all the unconsumed water. Write and simplify the energy balance equation for this closed constant-volume system and use it to determine the net amount of heat (kJ) that must be transferred to or from the reactor (state which).

9.5. Use Hess's law to calculate the standard heat of the water-gas shift reaction

$$CO(g) + H_2O(v) \longrightarrow CO_2(g) + H_2(g)$$

from each of the two sets of data given here.

(a) $CO(g) + H_2O(l) \longrightarrow CO_2(g) + H_2(g)$: $\Delta\hat{H}_r^\circ = +1226$ Btu/lb-mole
$H_2O(l) \longrightarrow H_2O(v)$: $\Delta\hat{H}_v = +18{,}935$ Btu/lb-mole

(b) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$: $\Delta\hat{H}_r^\circ = -121{,}740$ Btu/lb-mole
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(v)$: $\Delta\hat{H}_r^\circ = -104{,}040$ Btu/lb-mole

9.6. Formaldehyde may be produced in the reaction between methanol and oxygen:

$$2\,CH_3OH(l) + O_2(g) \longrightarrow 2\,HCHO(g) + 2\,H_2O(l): \quad \Delta\hat{H}_r^\circ = -326.2 \text{ kJ/mol}$$

The standard heat of combustion of hydrogen is

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l): \quad \Delta\hat{H}_r^\circ = -285.8 \text{ kJ/mol}$$

(a) Use these heats of reaction and Hess's law to determine the standard heat of the direct decomposition of methanol to form formaldehyde:

$$CH_3OH(l) \longrightarrow HCHO(g) + H_2(g)$$

(b) Explain why you would probably use the method of part (a) to determine the heat of the methanol decomposition reaction experimentally rather than carrying out the decomposition reaction and measuring $\Delta\hat{H}_r^\circ$ directly.

9.7. Use tabulated heats of formation (Table B.1) to determine the standard heats of the following reactions in kJ/mol, letting the stoichiometric coefficient of the first reactant in each reaction equal one.

(a) Nitrogen + oxygen react to form nitric oxide (NO).

(b) Gaseous *n*-pentane + oxygen react to form carbon monoxide + liquid water.

(c) Liquid *n*-hexane + oxygen react to form carbon dioxide + water vapor. After doing the calculation, write the stoichiometric equations for the formation of the reactant and product species, then use Hess's law to derive the formula you used to calculate $\Delta\hat{H}_r^\circ$.

(d) Liquid sodium sulfate + carbon monoxide react to form liquid sodium sulfide + carbon dioxide. (Note that Table B.1 only lists the heats of formation of the solid sodium salts. To estimate the required heat of reaction, you will also need to use tabulated heats of fusion.)

9.8. Trichloroethylene, a widely used degreasing solvent for machine parts, is produced in a two-step reaction sequence. Ethylene is first chlorinated to yield tetrachloroethane, which is dehydrochlorinated to form trichloroethylene.

$$C_2H_4(g) + 2\,Cl_2(g) \rightarrow C_2H_2Cl_4(l) + H_2(g): \quad \Delta\hat{H}_r^\circ = -385.76 \text{ kJ/mol}$$

$$C_2H_2Cl_4(l) \rightarrow C_2HCl_3(l) + HCl(g)$$

The standard heat of formation of liquid trichloroethylene is −276.2 kJ/mol.

(a) Use the given data and tabulated standard heats of formation of ethylene and hydrogen chloride to calculate the standard heat of formation of tetrachloroethane and the standard heat of the second reaction.

(b) Use Hess's law to calculate the standard heat of the reaction

$$C_2H_4(g) + 2\,Cl_2(g) \rightarrow C_2HCl_3(l) + H_2(g) + HCl(g)$$

(c) If 300 mol/h of $C_2HCl_3(l)$ is produced in the reaction of part (b) and the reactants and products are all at 25°C and 1 atm, how much heat is evolved or absorbed in the process? (Assume $\dot{Q} = \Delta\dot{H}$.)

9.9. The standard heat of combustion of gaseous acetylene is listed in Table B.1 as −1299.6 kJ/mol.

(a) In your own words, briefly explain what that means. (Your explanation should mention the reference states used to define the tabulated heats of combustion.)

(b) Use tabulated heats of formation to verify the given value of $\Delta\hat{H}_c^\circ$.

(c) Calculate the standard heat of the acetylene hydrogenation reaction

$$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$$

using (i) tabulated heats of formation and (ii) tabulated heats of combustion (Equation 9.4-1).

(d) Write the stoichiometric equations for the combustion reactions of acetylene, hydrogen, and ethane, and use Hess's law to derive the formula you used in part (c-ii).

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9.10. The standard heat of combustion ($\Delta\hat{H}_c^\circ$) of liquid 2,3,3-trimethylpentane [C_8H_{18}] is reported in a table of physical properties to be −4850 kJ/mol. A footnote indicates that the reference temperature for the reported value is 25°C and the presumed combustion products are $CO_2(g)$ and $H_2O(g)$.

(a) In your own words, briefly explain what all that means.

(b) There is some question about the accuracy of the reported value, and you have been asked to determine the heat of combustion experimentally. You burn 2.010 grams of the hydrocarbon with pure oxygen in a constant-volume calorimeter and find that the net heat released when the reactants and products [$CO_2(g)$ and $H_2O(g)$] are all at 25°C is sufficient to raise the temperature of 1.00 kg of liquid water by 21.34°C. Write an energy balance to show that the heat released in the calorimeter equals $n_{C_8H_{18}}\,\Delta\hat{U}_c^\circ$, and calculate $\Delta\hat{U}_c^\circ$ (kJ/mol). Then calculate $\Delta\hat{H}_c^\circ$.(See Example 9.1-2.) By what percentage of the measured value does the tabulated value differ from the measured one?

(c) Use the result of part (b) to estimate $\Delta\hat{H}_f^\circ$ for 2,3,3-trimethylpentane. Why would the heat of formation of 2,3,3-trimethylpentane probably be determined this way rather than directly from the formation reaction?

9.11. *n*-Butane is converted to isobutane in a continuous isomerization reactor that operates isothermally at 149°C. The feed to the reactor contains 93 mole% *n*-butane, 5% isobutane, and 2% HCl at 149°C, and a 40% conversion of *n*-butane is achieved.

(a) Taking a basis of 1 mol of feed gas, calculate the moles of each component of the feed and product mixtures and the extent of reaction, ξ(mol).

(b) Calculate the standard heat of the isomerization reaction (kJ/mol). Then, taking the feed and product species at 25°C as references, prepare an inlet–outlet enthalpy table and calculate and fill in the component amounts (mol) and specific enthalpies (kJ/mol). (See Example 9.5-1.)

(c) Calculate the required rate of heat transfer (kJ) to or from the reactor (state which it is). Then determine the required heat transfer rate (kW) for a reactor feed of 325 mol/h.

(d) Use your calculated results to determine the heat of the isomerization reaction at 149°C, $\Delta\hat{H}_r(149°C)$(kJ/mol).

Equipment Encyclopedia
reactors—CVD

9.12. In the production of many microelectronic devices, continuous **chemical vapor deposition** (CVD) processes are used to deposit thin and exceptionally uniform silicon dioxide films on silicon wafers. One CVD process involves the reaction between silane and oxygen at a very low pressure.

$$SiH_4(g) + O_2(g) \longrightarrow SiO_2(s) + 2\,H_2(g)$$

The feed gas, which contains oxygen and silane in a ratio 8.00 mol O_2/mol SiH_4, enters the reactor at 298 K and 3.00 torr absolute. The reaction products emerge at 1375 K and 3.00 torr absolute. Essentially all of the silane in the feed is consumed.

(a) Taking a basis of 1 m^3 of feed gas, calculate the moles of each component of the feed and product mixtures and the extent of reaction, ξ(mol).

(b) Calculate the standard heat of the silane oxidation reaction (kJ/mol). Then, taking the feed and product species at 298 K (25°C) as references, prepare an inlet–outlet enthalpy table and calculate and fill in the component amounts (mol) and specific enthalpies (kJ/mol). (See Example 9.5-1.)

Data

$$(\Delta\hat{H}_f^\circ)_{SiH_4(g)} = -61.9 \text{ kJ/mol}, \quad (\Delta\hat{H}_f^\circ)_{SiO_2(s)} = -851 \text{ kJ/mol}$$

$$(C_p)_{SiH_4(g)}[\text{kJ/(mol·K)}] = 0.01118 + 12.2 \times 10^{-5}T - 5.548 \times 10^{-8}T^2 + 6.84 \times 10^{-12}T^3$$

$$(C_p)_{SiO_2(s)}[\text{kJ/(mol·K)}] = 0.04548 + 3.646 \times 10^{-5}T - 1.009 \times 10^3/T^2$$

The temperatures in the formulas for C_p are in kelvin.

(c) Calculate the heat (kJ) that must be transferred to or from the reactor (state which it is). Then determine the required heat transfer rate (kW) required for a reactor feed of 27.5 m^3/h.

9.13. The production of most of the steel manufactured in the United States begins with the reduction of hematite ore (mostly ferric oxide) with coke (carbon) in a blast furnace to obtain pig iron. The basic reaction is

$$Fe_2O_3(s) + 3\ C(s) \longrightarrow 2\ Fe(s) + 3\ CO(g): \quad \Delta\hat{H}_r(77°F) = 2.111 \times 10^5\ \text{Btu/lb-mole}$$

Suppose that stoichiometric amounts of ferric oxide and carbon are fed at 77°F, the reaction is complete, the iron emerges as a liquid at 2800°F, and CO emerges at 570°F. Perform the following calculations for a basis of 1 ton of iron produced.

(a) Draw and label a flowchart and perform all the material balance calculations needed to determine the amounts (lb-mole) of each feed and product stream component.

(b) Taking the reactant and product species in their normal states at 77°F as references, prepare an inlet–outlet enthalpy table and calculate and fill in all unknown component specific enthalpies (Btu/lb-mole). Use the following physical property data for iron:

$$\begin{aligned} Fe(s)&: \quad C_p[\text{Btu/(lb-mole·°F)}] = 5.90 + 1.50 \times 10^{-3}\, T(°F) \\ T_m &= 2794°F, \quad \Delta\hat{H}_m(T_m) = 6496\ \text{Btu/lb-mole} \\ Fe(l)&: \quad C_p[\text{Btu/(lb-mole·°F)}] = 8.15 \end{aligned}$$

(c) Estimate the furnace heat requirement (Btu/ton Fe produced).

(d) List the assumptions that make the value calculated in part (b) only an approximate estimate of the furnace heat requirement. (One of the assumptions has something to do with the reactor pressure.)

9.14. Normal heptane is dehydrocyclicized to toluene and hydrogen in a continuous vapor-phase reaction:

$$C_7H_{16} \longrightarrow C_6H_5CH_3 + 4\ H_2$$

Pure heptane at 400°C is fed to the reactor. The reactor operates isothermally at 400°C and the reaction goes to completion. *Data:* The average heat capacity of n-heptane beween 25°C and 400°C is 0.2427 kJ/(mol · °C).

(a) Taking a basis of 1 mol of heptane fed, draw and label a flowchart.

(b) Taking elemental species [C(s), $H_2(g)$] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table. (See Example 9.5-2.)

(c) Calculate the required heat transfer to or from the reactor (state which it is) in kJ.

(d) What is the heat of the heptane dehydrocyclization reaction ($\Delta\hat{H}_r$) at 400°C and 1 atm?

9.15. The thermal decomposition of dimethyl ether

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

is to be carried out in an isothermal 2.00-liter laboratory reactor at 600°C. The reactor is charged with pure dimethyl ether at a pressure of 350 torr. After about two hours, the reactor pressure is 875 torr.

(a) Has the reaction proceeded to completion at the end of the two-hour period? If not, what percentage of the dimethyl ether has decomposed?

(b) Taking elemental species [C(s), $H_2(g)$, $O_2(g)$] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table. (See Example 9.5-2.) Use tabulated data for methane, hydrogen, and carbon monoxide, and the following data for dimethyl ether:

$$\begin{aligned} \Delta\hat{H}_f^\circ &= -180.16\ \text{kJ/mol} \\ C_p[\text{J/(mol·K)}] &= 26.86 + 0.1659T - 4.179 \times 10^{-5}T^2 \quad (T\ \text{in kelvin}) \end{aligned}$$

(c) Calculate $\Delta\hat{H}_r(600°C)$ and $\Delta\hat{U}_r(600°C)$ for the dimethyl ether decomposition reaction.

(d) How much heat (kJ) was transferred to or from the reactor (state which it is) during the two-hour period of the reaction?

Student Workbook

9.16. Sulfur dioxide is oxidized to sulfur trioxide in a small pilot-plant reactor. SO_2 and 100% excess air are fed to the reactor at 450°C. The reaction proceeds to a 65% SO_2 conversion, and the products emerge from the reactor at 550°C. The production rate of SO_3 is 1.00×10^2 kg/min. The reactor is surrounded by a water jacket into which water at 25°C is fed.

(a) Calculate the feed rates (standard cubic meters per second) of the SO_2 and air feed streams and the extent of reaction, $\dot{\xi}$(kmol/s).

(b) Calculate the standard heat of the SO_2 oxidation reaction, $\Delta\hat{H}_r^\circ$(kJ/mol). Then, taking molecular species at 25°C as references, prepare and fill in an inlet–outlet enthalpy table and write an energy balance to calculate the heat (kW) that must be transferred from the reactor to the cooling water.

(c) Calculate the minimum flow rate of the cooling water if its temperature rise is to be kept below 15°C.

(d) Briefly state what would have been different in your calculations and results if you had taken elemental species as references in part (b).

9.17. Carbon monoxide at 25°C and steam at 150°C are fed to a continuous water-gas shift reactor. The product gas, which contains 40.0 mole% H_2, 40.0% CO_2, and the balance $H_2O(v)$, emerges at 500°C at a rate of 2.50 SCMH (standard cubic meters per hour) and goes to a condenser. The gas and liquid streams leaving the condenser are in equilibrium at 15°C and 1 atm. The liquid may be taken to be pure water (no dissolved gases).

(a) Calculate the percent excess steam fed to the reactor and the rate of condensation of the water (kg/h).

(b) Calculate the rate (kW) at which heat must be transferred from the condenser.

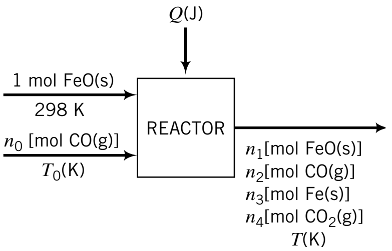
(c) Taking atomic species at 25°C as references, prepare and fill in an inlet–outlet enthalpy table and calculate the required rate of heat transfer (kW) to or from the reactor.

(d) It has been suggested that the carbon monoxide feed stream could pass through a heat exchanger prior to entering the reactor and the reactor product gas could pass through the same heat exchanger before entering the condenser. Sketch and label a flowchart of the heat exchanger and state economic benefits that might result from its use. (*Hint:* Heating and cooling operations are both expensive.)

***9.18.** Metallic iron is produced in the reaction between ferrous oxide and carbon monoxide:

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g), \qquad \Delta\hat{H}_r^\circ = -16.480 \text{ kJ/mol}$$

The flowchart shown below depicts this process for a basis of 1 mol FeO fed at 298 K.



(a) We wish to explore the effects of the variables n_0 (the molar feed ratio of CO to FeO), T_0 (the feed temperature of the carbon monoxide), X (the fractional conversion of FeO), and T (the product temperature) on Q (the heat duty on the reactor). *Without doing any calculations,* sketch the shapes of the curves you would expect to obtain for the following plots:

(i) Let $n_0 = 1$ mol CO fed/mol FeO fed, $T_0 = 400$ K, and $X = 1$. Vary T from 298 K to 1000 K, calculate Q for each T, and plot Q versus T.

(ii) Let $n_0 = 1$ mol CO fed/mol FeO fed, $T = 700$ K, and $X = 1$. Vary T_0 from 298 K to 1000 K, calculate Q for each T_0, and plot Q versus T_0.

(iii) Let $n_0 = 1$ mol CO fed/mol FeO fed, $T_0 = 400$ K, and $T = 500$ K. Vary X from 0 to 1, calculate Q for each X, and plot Q versus X.

(iv) Let $X = 0.5$, $T_0 = 400$ K, and $T = 400$ K. Vary n_0 from 0.5 to 2 mol CO fed/mol FeO fed, calculate Q for each n_0, and plot Q versus n_0.

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*Computer problem.

(b) Following is an inlet-outlet enthalpy table for the process:

References: **FeO(s), CO(g), Fe(s), CO_2(g) at 25°C**

Substance	n_{in} (mol)	$\hat{H}_{\text{in}}$ (kJ/mol)	n_{out} (mol)	$\hat{H}_{\text{out}}$ (kJ/mol)
FeO	1.00	0	n_1	$\hat{H}_1$
CO	n_0	$\hat{H}_0$	n_2	$\hat{H}_2$
Fe	—	—	n_3	$\hat{H}_3$
CO_2	—	—	n_4	$\hat{H}_4$

Write an expression for the heat duty on the reactor, Q(kJ), in terms of the n's and $\hat{H}$'s in the table, the standard heat of the given reaction, and the extent of reaction, ξ. Then derive expressions for the quantities ξ, n_1, n_2, n_3, and n_4 in terms of the variables n_0 and X. Finally, derive expressions for $\hat{H}_0$ as a function of T_0 and for $\hat{H}_1$, $\hat{H}_2$, $\hat{H}_3$, and $\hat{H}_4$ as functions of T. In the latter derivations, use the following formulas for C_p[kJ/(mol·K)] in terms of T(K) adapted from Table 2-194 of *Perry's Chemical Engineers' Handbook* (see footnote 1):

$$\text{FeO(s):} \quad C_p = 0.05280 + 6.243 \times 10^{-6}T - 3.188 \times 10^{2}\,T^{-2}$$

$$\text{Fe(s):} \quad C_p = 0.01728 + 2.67 \times 10^{-5}\,T$$

$$\text{CO(g):} \quad C_p = 0.02761 + 5.02 \times 10^{-6}\,T$$

$$\text{CO}_2\text{(g):} \quad C_p = 0.04326 + 1.146 \times 10^{-5}T - 8.180 \times 10^{2}T^{-2}$$

(c) Calculate the heat duty, Q(kJ), for $n_0 = 2.0$ mol CO, $T_0 = 350$ K, $T = 550$ K, and $X = 0.700$ mol FeO reacted/mol FeO fed.

(d) Prepare a spreadsheet that has the following format (a partial solution is given for one set of process variables):

Ferrous oxide reduction problem														
	FeO + CO → Fe + CO2								DHr=	−16.480	kJ/mol			
n0	T0	X	T	Xi	n1	n2	n3	n4	H0	H1	H2	H3	H4	Q
(mol)	(K)		(K)	(mol)	(mol)	(mol)	(mol)	(mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ/mol)	(kJ)
2	350	0.7	550	0.7	0.3	1.3	0.7	0.7	1.520	13.482	...	...	...	11.863

where DHr ($= \Delta\hat{H}_r^\circ$) denotes the standard heat of the FeO reduction reaction and Xi (ξ) is the extent of reaction. Use the spreadsheet to generate the four plots described in part (a). If the shapes of the plots do not match your predictions, explain why.

9.19. Ethyl alcohol (ethanol) can be produced by the **fermentation** of sugars derived from grains and other agricultural products. Some countries without large petroleum and natural gas reserves—such as Brazil—have found it profitable to convert a portion of their abundant grains to ethanol for blending with gasoline as an octane enhancer or for use as a feedstock in the synthesis of other chemicals.

In one such process, a portion of the starch in corn is converted to ethanol in two consecutive reactions. In a *saccharification* reaction, starch decomposes in the presence of certain enzymes (biological catalysts) to form an aqueous *mash* containing maltose ($C_{12}H_{22}O_{11}$, a sugar) and several other decomposition products. The mash is cooled and combined with additional water and a yeast culture in a batch fermentation tank (fermentor). In the fermentation reaction (actually a complex series of reactions), the yeast culture grows and in the process converts maltose to ethanol and carbon dioxide:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 4\,C_2H_5OH + 4\,CO_2$$

The fermentor is a 550,000 gallon tank filled to 90% of its capacity with a suspension of mash and yeast in water. The mass of the yeast is negligible compared to the total mass of the tank contents. Thermal energy is released by the exothermic conversion of maltose to ethanol. In an adiabatic operating stage, the temperature of the tank contents increases from an initial value of 85°F to 95°F, and in a second stage the temperature is kept at 95°F by a reactor cooling system. The final reaction mixture contains carbon dioxide dissolved in a slurry containing 7.1 wt% ethanol, 6.9 wt% soluble and suspended solids, and the balance water. The mixture is pumped to a flash evaporator in which CO_2 is vaporized, and the ethanol product is then separated from the remaining mixture components in a series of distillation and stripping operations.

Data

- One bushel (56 lb_m) of corn yields 25 gallons of mash fed to the fermentor, which in turn yields 2.6 gallons of ethanol. Roughly 101 bushels of corn is harvested from an acre of land.
- A batch fermentation cycle (charging the fermentation tank, running the reaction, discharging the tank, and preparing the tank to receive the next load) takes eight hours. The process operates 24 hours per day, 330 days per year.
- The specific gravity of the fermentation reaction mixture is approximately constant at 1.05. The average heat capacity of the mixture is 0.95 Btu/(lb_m·°F).
- The standard heat of combustion of maltose to form $CO_2(g)$ and $H_2O(l)$ is $\Delta\hat{H}_c^\circ = -5649.1$ kJ/mol.

(a) Calculate (i) the quantity of ethanol (lb_m) produced per batch, (ii) the quantity of water (gal) that must be added to the mash and yeast in the fermentation tank, and (iii) the acres of land that must be harvested per year to keep the process running.

(b) Calculate the standard heat of the maltose conversion reaction, $\Delta\hat{H}_r^\circ$(Btu/lb-mole).

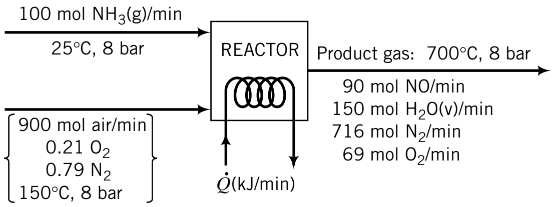
(c) Estimate the total amount of heat (Btu) that must be transferred from the fermentor during the reaction period. Take only the maltose conversion into account in this calculation (i.e., neglect the yeast growth reaction and any other reactions that may occur in the fermentor), assume that the heat of reaction is independent of temperature in the range from 77°F (= 25°C) to 95°F, and neglect the heat of solution of carbon dioxide in water.

(d) Although Brazil and Venezuela are neighboring countries, producing ethanol from grain for use as a fuel is an important process in Brazil and an almost nonexistent one in Venezuela. What difference between the two countries probably accounts for this observation?

9.20. Ammonia is oxidized with air to form nitric oxide in the first step of the production of nitric acid. Two principal reactions occur:

$$4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6\,H_2O$$
$$2\,NH_3 + \tfrac{3}{2}\,O_2 \longrightarrow N_2 + 3\,H_2O$$

A flowchart of the reactor follows.



(a) Taking elemental species [$N_2(g)$, $H_2(g)$, $O_2(g)$] at 25°C as references, prepare and fill in an inlet–outlet enthalpy table.

(b) Calculate the required rate of heat transfer to or from the reactor in kW.

(c) What would have been different in your calculations and results in parts (a) and (b) if you had taken molecular species as references in part (a)?

Student Workbook

9.21. Ethanol is produced commercially by the hydration of ethylene:

$$C_2H_4(g) + H_2O(v) \rightleftharpoons C_2H_5OH(v)$$

Some of the product is converted to diethyl ether in the undesired side reaction

$$2\ C_2H_5OH(v) \rightleftharpoons (C_2H_5)_2O(v) + H_2O(v)$$

The combined feed to the reactor contains 53.7 mole% C_2H_4, 36.7% H_2O and the balance nitrogen which enters the reactor at 310°C. The reactor operates isothermally at 310°C. An ethylene conversion of 5% is achieved, and the yield of ethanol (moles ethanol produced/mole ethylene consumed) is 0.900.

Data for Diethyl Ether

$$\begin{aligned} \Delta\hat{H}_f^\circ &= -272.8 \text{ kJ/mol } \textit{for the liquid} \\ \Delta\hat{H}_v &= 26.05 \text{ kJ/mol} \quad \text{(assume independent of } T) \\ C_p[\text{kJ/(mol·°C)}] &= 0.08945 + 40.33 \times 10^{-5}T(°\text{C}) - 2.244 \times 10^{-7}T^2 \end{aligned}$$

(a) Calculate the reactor heating or cooling requirement in kJ/mol feed.

(b) Why would the reactor be designed to yield such a low conversion of ethylene? What processing step (or steps) would probably follow the reactor in a commercial implementation of this process?

9.22. Benzaldehyde is produced from toluene in the catalytic reaction

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CHO + H_2O$$

Dry air and toluene vapor are mixed and fed to the reactor at 350°F and 1 atm. Air is supplied in 100% excess. Of the toluene fed to the reactor, 13% reacts to form benzaldehyde and 0.5% reacts with oxygen to form CO_2 and H_2O. The product gases leave the reactor at 379°F and 1 atm. Water is circulated through a jacket surrounding the reactor, entering at 80°F and leaving at 105°F. During a four-hour test period, 29.3 lb_m of water is condensed from the product gases. (Total condensation may be assumed.) The standard heat of formation of benzaldehyde vapor is −17,200 Btu/lb-mole; the heat capacities of both toluene and benzaldehyde vapors are approximately 31 Btu/(lb-mole·°F); and that of liquid benzaldehyde is 46 Btu/(lb-mole·°F).

(a) Calculate the volumetric flow rates (ft^3/h) of the combined feed stream to the reactor and the product gas.

(b) Calculate the required rate of heat transfer from the reactor (Btu/h) and the flow rate of the cooling water (gal/min).

9.23. Lime (calcium oxide) is widely used in the production of cement, steel, medicines, insecticides, plant and animal food, soap, rubber, and many other familiar materials. It is usually produced by heating and decomposing limestone ($CaCO_3$), a cheap and abundant mineral, in a *calcination* process:

$$CaCO_3(s) \xrightarrow{\text{heat}} CaO(s) + CO_2(g)$$

(a) Limestone at 25°C is fed to a continuous calcination reactor. The calcination is complete, and the products leave at 900°C. Taking 1 metric ton (1000 kg) of limestone as a basis and elemental species [Ca(s), C(s), $O_2(g)$] at 25°C as references for enthalpy calculations, prepare and fill in an inlet–outlet enthalpy table and prove that the required heat transfer to the reactor is 2.7×10^6 kJ.

(b) In a common variation of this process, hot combustion gases containing oxygen and carbon monoxide (among other components) are fed into the calcination reactor along with the limestone. The carbon monoxide is oxidized in the reaction

$$CO(g) + \frac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$$

Suppose

- the combustion gas fed to a calcination reactor contains 75 mole% N_2, 2.0% O_2, 9.0% CO, and 14% CO_2;
- the gas enters the reactor at 900°C in a feed ratio of 20 kmol gas/kmol limestone;
- the calcination is complete;
- all of the oxygen in the gas feed is consumed in the CO oxidation reaction;
- the reactor effluents are at 900°C.

Again taking a basis of 1 metric ton of limestone calcined, prepare and fill in an inlet–outlet enthalpy table for this process [don't recalculate enthalpies already calculated in part (a)] and calculate the required heat transfer to the reactor.

(c) You should have found that the heat that must be transferred to the reactor is significantly lower with the combustion gas in the feed than it is without the gas. By what percentage is the heat requirement reduced? Give two reasons for the reduction.

***9.24.** A pair of gas-phase reactions with the following stoichiometric equations take place in a continuous reactor:

$$A + B \longrightarrow C$$
$$2\,C \longrightarrow D + B$$

The reactions of ethylene and water to form ethanol and of ethanol to form diethyl ether and water constitute such a reaction system. (See Problem 9.21.)

(a) Suppose the reactor feed contains A, B, and inerts (I), with mole fractions x_{A0}, x_{B0}, and x_{I0}, respectively. Letting f_A denote the fractional conversion of A (mol A consumed/mol A fed) and Y_C the yield of C based on consumption of A (mol C generated/mol A consumed), prove that for a basis of 1 mol of feed, the number of moles of each species at the outlet are as follows:

$$\begin{aligned} n_A &= x_{A0}(1 - f_A) \\ n_C &= x_{A0} f_A Y_C \\ n_D &= \tfrac{1}{2}(x_{A0} f_A - n_C) \\ n_B &= x_{B0} - x_{A0} f_A + n_D \\ n_I &= x_{I0} \end{aligned}$$

(b) Write a spreadsheet to perform material and energy balance calculations for a basis of 1.00 mol feed. The program should take as inputs

(i) the standard heats of formation (kJ/mol) of A(g), B(g), C(g), and D(g);
(ii) the coefficients (a, b, c, d) of the formulas $C_p = a + bT + cT^2 + dT^3$ for gaseous A, B, C, D, and I, where C_p has units of kJ/(mol·°C);
(iii) the feed and product temperatures, T_f(°C) and T_p(°C);
(iv) x_{A0}, x_{B0}, f_A, and Y_C.

It should generate an inlet–outlet enthalpy table based on elemental species at 25°C as references and then calculate the required heat transfer to or from the reactor, Q(kJ). The spreadsheet should be tested using the species and reactions of Problem 9.21 and should appear as shown below. (Some of the input data and calculated results are shown.)

---

*Computer problem.

Chapter 9—Problem 9.24						
Species	Formula	DHf	a	b	c	d
A	C2H4(v)	52.28	0.04075	11.47e-5	−6.891e-8	17.66e-12
B	H2O(v)					
C	C2H5OH(v)					
D	(C4H10)O(v)	−246.8	0.08945	40.33e-5	−2.244e-7	
I	N2(g)					
Tf	Tp	xA0	xB0	xI0	fA	YC
310	310	0.537	0.367	0.096	0.05	0.90
	n(in)	H(in)	n(out)	H(out)		
Species	(mol)	(kJ/mol)	(mol)	(kJ/mol)		
A						
B						
C						
D						
I						
Q(kJ)=	−1.31					

where DHf $[= \Delta\hat{H}_f^\circ(\text{kJ/mol})]$ denotes the standard heat of formation.

(c) Use the program to calculate Q at the reactor conditions shown in the spreadsheet, then for a feed temperature of 125°C and all other input parameters the same. (The enthalpy table and the value of Q should automatically correct themselves as soon as you type in the new value of T_f.) Print out and turn in your program output for the second feed temperature.

(d) Run the program for several different values of T_p, f_A, and Y_C. Summarize the effects of each of these parameters on Q and briefly explain why your results make sense.

9.25. A gas mixture containing 85 mole% methane and the balance oxygen is to be charged into an evacuated well-insulated 10-liter reaction vessel at 25°C and 200 kPa. An electrical coil in the reactor, which delivers heat at a rate of 100 watts, will be turned on for 85 seconds and then turned off. Formaldehyde will be produced in the reaction

$$CH_4 + O_2 \longrightarrow HCHO + H_2O$$

The reaction products will be cooled and discharged from the reactor.

(a) Calculate the maximum pressure that the reactor is likely to have to withstand, assuming that there are no side reactions. If you were ordering the reactor, why would you specify an even greater pressure in your order? (Give several reasons.)

(b) Why would heat be added to the feed mixture rather than running the reactor adiabatically?

(c) Suppose the reaction is run as planned, the reaction products are analyzed chromatographically, and some CO_2 is found. Where did it come from? If you had taken it into account, would your calculated pressure in part (a) have been larger, smaller, or can't you tell without doing the detailed calculations?

9.26. Ethylene oxide is produced by the catalytic oxidation of ethylene:

$$C_2H_4(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_4O(g)$$

An undesired competing reaction is the combustion of ethylene to CO_2.

The feed to a reactor contains 2 mol C_2H_4/mol O_2. The conversion and yield in the reactor are respectively 25% and 0.70 mol C_2H_4O produced/mol C_2H_4 consumed. A multiple-unit process separates the reactor outlet stream components: C_2H_4 and O_2 are recycled to the reactor, C_2H_4O is sold, and CO_2 and H_2O are discarded. The reactor inlet and outlet streams are each at 450°C, and the fresh feed and all species leaving the separation process are at 25°C. The combined fresh feed-recycle stream is preheated to 450°C.

(a) Taking a basis of 2 mol of ethylene entering the reactor, draw and label a flowchart of the complete process (show the separation process as a single unit) and calculate the molar amounts and compositions of all process streams.

(b) Calculate the heat requirement (kJ) for the entire process and that for the reactor alone.

Data for C_2H_4O (g)

$$\Delta\hat{H}_f^\circ = -51.00 \text{ kJ/mol}$$

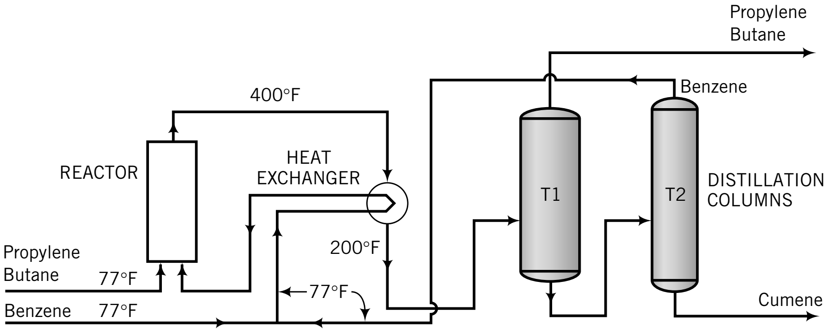
$$C_p[\text{J/(mol·K)}] = -4.69 + 0.2061T - 9.995 \times 10^{-5}T^2$$

where T is in kelvin.

(c) Calculate the flow rate (kg/h) and composition of the fresh feed and the overall and reactor heat requirements (kW) for a production rate of 1500 kg C_2H_4O/day.

9.27. Cumene ($C_6H_5C_3H_7$) is produced by reacting benzene with propylene [$\Delta\hat{H}_r^\circ(77°F) = -39{,}520$ Btu/lb-mole].

Equipment Encyclopedia
reactor, heat exchanger, distillation column



A liquid feed containing 75 mole% propylene and 25% *n*-butane and a second liquid stream containing essentially pure benzene are fed to the reactor. Fresh benzene and recycled benzene, both at 77°F, are mixed in a 1:3 ratio (1 mole fresh feed/3 moles recycle) and passed through a heat exchanger, where they are heated by the reactor effluent before being fed to the reactor. The reactor effluent enters the exchanger at 400°F and leaves at 200°F. The pressure in the reactor is sufficient to maintain the effluent stream as a liquid.

After being cooled in the heat exchanger, the reactor effluent is fed to a distillation column (T1). All of the butane and unreacted propylene are removed as overhead product from the column, and the cumene and unreacted benzene are removed as bottoms product and fed to a second distillation column (T2) where they are separated. The benzene leaving the top of the second column is the recycle that is mixed with the fresh benzene feed. Of the propylene fed to the process, 20% does not react and leaves in the overhead product from the first distillation column. The production rate of cumene is 1200 lb_m/h.

(a) Calculate the mass flow rates of the streams fed to the reactor, the molar flow rate and composition of the reactor effluent, and the molar flow rate and composition of the overhead product from the first distillation column, T1.

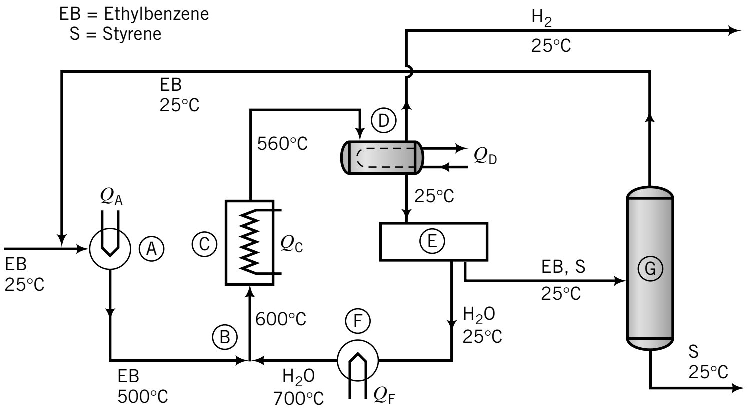
(b) Calculate the temperature of the benzene stream fed to the reactor and the required rate of heat addition to or removal from the reactor. Use the following approximate heat capacities in your calculations: C_p [Btu/(lb$_m$·°F)] = 0.57 for propylene, 0.55 for butane, 0.45 for benzene, and 0.40 for cumene.

Equipment Encyclopedia
reactor, settler, distillation column, heat exchanger

9.28. Ethylbenzene is converted to styrene in the catalytic dehydrogenation reaction

$$C_8H_{10}(g) \rightarrow C_8H_8(g) + H_2: \quad \Delta\hat{H}_r^\circ(600^\circ C) = +124.5 \text{ kJ/mol}$$

A flowchart of a simplified version of the commercial process is shown here.



Fresh and recycled liquid ethylbenzene combine and are heated from 25°C to 500°C Ⓐ, and the heated ethylbenzene is mixed adiabatically with steam at 700°C Ⓑ to produce the feed to the reactor at 600°C. (The steam suppresses undesired side reactions and removes carbon deposited on the catalyst surface.) A once-through conversion of 35% is achieved in the reactor Ⓒ, and the products emerge at 560°C. The product stream is cooled to 25°C Ⓓ, condensing essentially all of the water, ethylbenzene, and styrene and allowing hydrogen to pass out as a recoverable by-product of the process.

The water and hydrocarbon liquids are immiscible and are separated in a settling tank decanter Ⓔ. The water is vaporized and heated Ⓕ to produce the steam that mixes with the ethylbenzene feed to the reactor. The hydrocarbon stream leaving the decanter is fed to a distillation tower Ⓖ (actually, a series of towers), which separates the mixture into essentially pure styrene and ethylbenzene, each at 25°C after cooling and condensation steps have been carried out. The ethylbenzene is recycled to the reactor preheater, and the styrene is taken off as a product.

(a) Calculate on the basis of 100 kg/h styrene produced the required fresh ethylbenzene feed rate, the flow rate of recycled ethylbenzene, and the circulation rate of water, all in mol/h. (Assume $P = 1$ atm.)

(b) Calculate the required rates of heat input or withdrawal in kJ/h for the ethylbenzene preheater Ⓐ, steam generator Ⓕ, and reactor Ⓒ.

(c) Suggest possible ways to improve the energy economy of this process.

Physical Property Data

Ethylbenzene: $(C_p)_{\text{liquid}} = 182$ J/(mol·°C)
$(\Delta\hat{H}_v) = 36.0$ kJ/mol at 136°C
$(C_p)_{\text{vapor}}$[J/(mol·°C)] $= 118 + 0.30T$(°C)

Styrene: $(C_p)_{\text{liquid}} = 209$ J/(mol·°C)
$(\Delta\hat{H}_v) = 37.1$ kJ/mol at 145°C
$(C_p)_{\text{vapor}}$[J/(mol·°C)] $= 115 + 0.27T$(°C)

Equipment Encyclopedia
reactor, boiler

9.29. Formaldehyde is produced by decomposing methanol over a silver catalyst:

$$CH_3OH \rightarrow HCHO + H_2$$

To provide heat for this endothermic reaction, some oxygen is included in the feed to the reactor, leading to the partial combustion of the hydrogen produced in the methanol decomposition.

The feed to an adiabatic formaldehyde production reactor is obtained by bubbling a stream of air at 1 atm through liquid methanol. The air leaves the vaporizer saturated with methanol and contains 42% methanol by volume. The stream then passes through a heater in which its temperature is raised to 145°C. To avoid deactivating the catalyst, the maximum temperature attained in the reactor must be limited to 600°C. For this purpose, saturated steam at 145°C is metered into the air–methanol stream, and the combined stream enters the reactor. A fractional methanol conversion of 70.0% is achieved in the reactor, and the product gas contains 5.00 mole% hydrogen. The product gas is cooled to 145°C in a waste heat boiler in which saturated steam at 3.1 bar is generated from liquid water at 30°C. Several absorption and distillation units follow the waste heat boiler, and formaldehyde is ultimately recovered in an aqueous solution containing 37.0 wt% HCHO. The plant is designed to produce 36 metric kilotons of this solution per year, operating 350 days/yr.

(a) Draw the process flowchart and label it completely. Show the absorption/distillation train as a single unit with the reactor product gas and additional water entering and the formaldehyde solution and a gas stream containing methanol, oxygen, nitrogen, and hydrogen leaving.

(b) Calculate the operating temperature of the methanol vaporizer.

(c) Calculate the required feed rate of steam to the reactor (kg/h) and the molar flow rate and composition of the product gas.

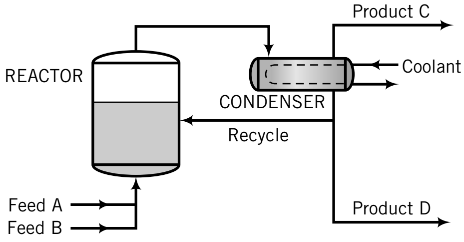
(d) Calculate the rate (kg/h) at which steam is generated in the waste heat boiler.

Equipment Encyclopedia
reactor, condenser

9.30. The synthesis of ethyl chloride is accomplished by reacting ethylene with hydrogen chloride in the presence of an aluminum chloride catalyst:

$$C_2H_4(g) + HCl(g) \xrightarrow{\text{catalyst}} C_2H_5Cl(g): \quad \Delta\hat{H}_r(0°C) = -64.5 \text{ kJ/mol}$$

Process data and a simplified schematic flowchart are given here.



Data

Reactor: adiabatic, outlet temperature = 50°C
Feed A: 100% HCl(g), 0°C
Feed B: 93 mole% C_2H_4, 7% C_2H_6, 0°C
Product C: Consists of 1.5% of the HCl, 1.5% of the C_2H_4, and all of the C_2H_6 that enter the reactor
Product D: 1600 kg $C_2H_5Cl(l)$/h, 0°C
Recycle to reactor: $C_2H_5Cl(l)$, 0°C
C_2H_5Cl: $\Delta\hat{H}_v = 24.7$ kJ/mol (assume independent of T)
$(C_p)_{C_2H_5Cl(v)}[\text{kJ/(mol·°C)}] = 0.052 + 8.7 \times 10^{-5}T(°C)$

The reaction is exothermic, and if the heat of reaction is not removed in some way the reactor temperature could increase to an undesirably high level. To avoid this occurrence, the reaction is carried out with the catalyst suspended in liquid ethyl chloride. As the reaction proceeds, most of the heat liberated goes to vaporize the liquid, making it possible to keep the reaction temperature at or below 50°C.

The stream leaving the reactor contains ethyl chloride formed by reaction and that vaporized in the reactor. This stream passes through a heat exchanger where it is cooled to 0°C, condensing essentially all of the ethyl chloride and leaving only unreacted C_2H_4, HCl, and C_2H_6 in the gas phase. A portion of the liquid condensate is recycled to the reactor at a rate equal to the rate at which ethyl chloride is vaporized, and the rest is taken off as product. At the process conditions, heats of mixing and the influence of pressure on enthalpy may be neglected.

(a) At what rates (kmol/h) do the two feed streams enter the process?

(b) Calculate the composition (component mole fractions) and molar flow rate of product stream C.

(c) Write an energy balance around the reactor and use it to determine the rate at which ethyl chloride must be recycled.

(d) A number of simplifying assumptions were made in the process description and the analysis of this process system, so the results obtained using a more realistic simulation would differ considerably from those you should have obtained in parts (a)–(c). List as many of these assumptions as you can think of.

9.31. Ammonia is oxidized in a well-insulated continuous reactor:

$$4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(v): \quad \Delta\hat{H}_r^\circ = -904.7 \text{ kJ/mol}$$

The feed stream enters at 200°C and the products leave at temperature T_{out}(°C). The inlet–outlet enthalpy table for the reactor appears as follows:

References: NH_3(g), O_2(g), NO(g), H_2O(v) at 25°C, 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
NH_3(g)	4.00	$\hat{H}_1$	—	—
O_2(g)	6.00	$\hat{H}_2$	$\dot{n}_3$	$\hat{H}_3$
NO(g)	—	—	$\dot{n}_4$	$\hat{H}_4$
H_2O(v)	—	—	$\dot{n}_5$	$\hat{H}_5$

(a) Draw and label a process flowchart and calculate the molar amounts of the product stream components and the extent of reaction, $\dot{\xi}$(mol/s). Fill in the values of $\dot{n}_3, \dot{n}_4$, and $\dot{n}_5$ on the enthalpy table.

(b) The energy balance for this reactor reduces to $\Delta\dot{H} \approx 0$. Summarize the assumptions that must be made to obtain this result.

(c) Calculate the values of $\hat{H}_1$ and $\hat{H}_2$ and write expressions for $\hat{H}_3$, $\hat{H}_4$, and $\hat{H}_5$ in terms of the outlet temperature, T_{out}. Then calculate T_{out} from the energy balance, using either a spreadsheet or a programmable calculator. (See Example 9.5-3.)

(d) A design engineer obtained a preliminary estimate of the reactor outlet temperature using only the first terms of the heat capacity formulas in Table B.2. [For example, $(C_p)_{NH_3} \approx 0.03515$ kJ/(mol·°C).] What value did she calculate? Taking the result of part (c) to be correct, determine the percentage error in T_{out} that results from using the one-term heat capacity formulas.

(e) The preliminary estimate of T_{out} was mistakenly used as the basis of the design and construction of the reactor. Was this a dangerous error from the standpoint of reactor safety or did it in fact lower the hazard potential? Explain.

9.32. Coke can be converted into CO—a fuel gas—in the reaction

$$CO_2(g) + C(s) \rightarrow 2\,CO(g)$$

A coke that contains 84% carbon by mass and the balance noncombustible ash is fed to a reactor with a stoichiometric amount of CO_2. The coke is fed at 77°F, and the CO_2 enters at 400°F. Heat is transferred to the reactor in the amount of 5859 Btu/lb_m coke fed. The gaseous products and the solid reactor effluent (the ash and unburned carbon) leave the reactor at 1830°F. The heat capacity of the solid is 0.24 Btu/(lb_m·°F).

(a) Calculate the percentage conversion of the carbon in the coke.

(b) The carbon monoxide produced in this manner can be used as a fuel for residential home heating, as can the coke. Speculate on the advantages and disadvantages of using the gas. (There are several of each.)

Student Workbook

9.33. The synthesis of methanol from carbon monoxide and hydrogen is carried out in a continuous vapor-phase reactor at 5.00 atm absolute. The feed contains CO and H_2 in stoichiometric proportion and enters the reactor at 25°C and 5.00 atm at a rate of 17.1 m^3/h. The product stream emerges from the reactor at 127°C. The rate of heat transfer from the reactor is 17.05 kW. Calculate the fractional conversion achieved and the volumetric flow rate (m^3/h)of the product stream. (See Example 9.5-4.)

Equipment Encyclopedia
reactor, heat exchanger

9.34. Carbon disulfide, a key component in the manufacture of rayon fibers, is produced in the reaction between methane and sulfur vapor over a metal oxide catalyst:

$$CH_4(g) + 4\,S(v) \rightarrow CS_2(g) + 2\,H_2S(g)$$
$$\Delta\hat{H}_r(700°C) = -274\ \text{kJ/mol}$$

Methane and molten sulfur, each at 150°C, are fed to a heat exchanger in stoichiometric proportion. Heat is exchanged between the reactor feed and product streams, and the sulfur in the feed is vaporized. The gaseous methane and sulfur leave the exchanger and pass through a second preheater in which they are heated to 700°C, the temperature at which they enter the reactor. Heat is transferred from the reactor at a rate of 41.0 kJ/mol of feed. The reaction products emerge from the reactor at 800°C, pass through the heat exchanger, and emerge at 200°C with sulfur as a liquid. Use the heat capacity data given below to perform the following calculations.

Heat capacities: C_p [J/(mol·°C)] ≈ 29.4 for S(l), 36.4 for S(v), 71.4 for CH_4(g), 31.8 for CS_2, and 44.8 for H_2S(g).

(a) Estimate the fractional conversion achieved in the reactor.

(b) Estimate the quantity of heat (kJ/mol feed) that must be transferred in the second preheater to bring the feed up to 700°C.

(c) Suggest a method to improve the energy economy of the process.

***9.35.** The equilibrium constant for the ethane dehydrogenation reaction,

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

is defined as

$$K_p(\text{atm}) = \frac{x_{C_2H_4} x_{H_2}}{x_{C_2H_6}} P$$

where P(atm) is the total pressure and x_i is the mole fraction of the ith substance in an equilibrium mixture. The equilibrium constant has been found experimentally to vary with temperature according to the formula

$$K_p(T) = 7.28 \times 10^6 \exp[-17{,}000/T(\text{K})] \qquad \textbf{(1)}$$

The heat of reaction at 1273K is +145.6 kJ/mol, and the heat capacities of the reactive species may be approximated by the formulas

$$\left.\begin{aligned} (C_p)_{C_2H_4} &= 9.419 + 0.1147T(\text{K}) \\ (C_p)_{H_2} &= 26.90 + 4.167 \times 10^{-3}T(\text{K}) \\ (C_p)_{C_2H_6} &= 11.35 + 0.1392T(\text{K}) \end{aligned}\right\} [\text{J/(mol·K)}]$$

Suppose pure ethane is fed to a continuous constant-pressure adiabatic reactor at 1273 K and pressure P(atm), the products emerge at T_f(K) and P(atm), and the residence time of the reaction mixture in the reactor is large enough for the outlet stream to be considered an equilibrium mixture of ethane, ethylene, and hydrogen.

(a) Prove that the fractional conversion of ethane in the reactor is

$$f = \left(\frac{K_p}{P + K_p}\right)^{1/2} \qquad \textbf{(2)}$$

(b) Write an energy balance on the reactor, and use it to prove that

$$f = \frac{1}{1 + \phi(T_f)} \qquad \textbf{(3)}$$

where

$$\phi(T_f) = \frac{\Delta\hat{H}_r(1273\text{ K}) - \displaystyle\int_{T_f}^{1273\text{K}} [(C_p)_{C_2H_4} + (C_p)_{H_2}]\,dT}{\displaystyle\int_{T_f}^{1273\text{K}} (C_p)_{C_2H_6}\,dT} \qquad \textbf{(4)}$$

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*Computer problem.

Finally, substitute for $\Delta\hat{H}_r$ and the heat capacities in Equation 4 to derive an explicit expression for $\phi(T_f)$.

(c) We now have two expressions for the fractional conversion f: Equation 2 and Equation 3. If these expressions are equated, K_p is replaced by the expression of Equation 1, and $\phi(T_f)$ is replaced by the expression derived in part (b), the result is one equation in one unknown, T_f. Derive this equation, and transpose the right side to obtain an expression of the form

$$\psi(T_f) = 0 \tag{5}$$

(d) Write a spreadsheet program to take P as input, solve Equation 5 for T_f (use goalseek), and determine the final fractional conversion, f. (*Suggestion:* Set up columns for P, T_f, f, K_p, ϕ, and ψ.) Run the program for $P(\text{atm}) = 0.01, 0.05, 0.10, 0.50, 1.0, 5.0$, and 10.0. Plot T_f versus P and f versus P, using a logarithmic coordinate scale for P.

(e) Use a symbolic mathematics program or write a program in Fortran or some other language to perform the calculations of part (d).

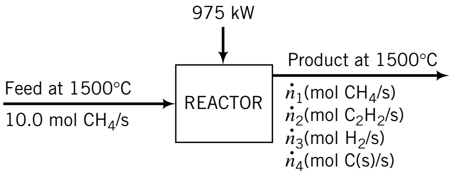
9.36. You are checking the performance of a reactor in which acetylene is produced from methane in the reaction

$$2\,CH_4(g) \rightarrow C_2H_2(g) + 3\,H_2(g)$$

An undesired side reaction is the decomposition of acetylene:

$$C_2H_2(g) \rightarrow 2\,C(s) + H_2(g)$$

Methane is fed to the reactor at 1500°C at a rate of 10.0 mol CH_4/s. Heat is transferred to the reactor at a rate of 975 kW. The product temperature is 1500°C and the fractional conversion of methane is 0.600. A flowchart of the process and an enthalpy table are shown below.



References: C(s), H_2(g), at 25°C, 1 atm

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
CH_4	10.0	41.65	$\dot{n}_1$	$\hat{H}_1$
C_2H_2	—	—	$\dot{n}_2$	$\hat{H}_2$
H_2	—	—	$\dot{n}_3$	$\hat{H}_3$
C	—	—	$\dot{n}_4$	$\hat{H}_4$

(a) Using the heat capacities given below for enthalpy calculations, write and solve material balances and an energy balance to determine the product component flow rates and the yield of acetylene (mol C_2H_2 produced/mol CH_4 consumed).

$$\begin{aligned} CH_4(g)&: \quad C_p \approx 0.079\ \text{kJ/(mol·°C)} \\ C_2H_2(g)&: \quad C_p \approx 0.052\ \text{kJ/(mol·°C)} \\ H_2(g)&: \quad C_p \approx 0.031\ \text{kJ/(mol·°C)} \\ C(s)&: \quad C_p \approx 0.022\ \text{kJ/(mol·°C)} \end{aligned}$$

For example, the specific enthalpy of methane at 1500°C relative to methane at 25°C is [0.079 kJ/(mol·°C)](1500°C −25°C) = 116.5 kJ/mol.

(b) The reactor efficiency may be defined as the ratio (actual acetylene yield/acetylene yield with no side reaction). What is the reactor efficiency for this process?

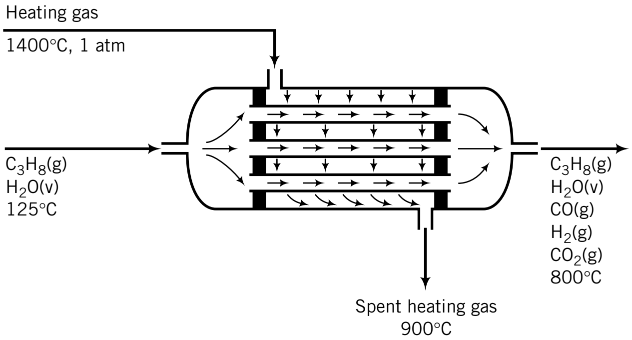
9.37. Hydrogen is produced in the steam reforming of propane:

$$C_3H_8(g) + 3\ H_2O(v) \rightarrow 3\ CO(g) + 7\ H_2(g)$$

The water–gas shift reaction also takes place in the reactor, leading to the formation of additional hydrogen:

$$CO(g) + H_2O(v) \rightarrow CO_2(g) + H_2(g)$$

The reaction is carried out over a nickel catalyst in the tubes of a shell-and-tube reactor. The feed to the reactor contains steam and propane in a 6:1 molar ratio at 125°C, and the products emerge at 800°C. The excess steam in the feed assures essentially complete consumption of the propane. Heat is added to the reaction mixture by passing a hot gas over the outside of the tubes that contain the catalyst. The gas is fed at 4.94 m^3/mol C_3H_8, entering the unit at 1400°C and 1 atm and leaving at 900°C. The unit may be considered adiabatic.



Calculate the molar composition of the product gas, assuming that the heat capacity of the heating gas is 0.040 kJ/(mol·°C).

9.38. In a **coal gasification** process, carbon (the primary constituent of coal) reacts with steam to produce carbon monoxide and hydrogen (*synthesis gas*). The gas may either be burned or subjected to further processing to produce any of a variety of chemicals.

A coal contains 10.5 wt% moisture (water) and 22.6 wt% noncombustible ash. The remaining fraction of the coal contains 81.2 wt% C, 13.4% O, and 5.4% H. A coal slurry containing 2.00 kg coal/kg water is fed at 25°C to an adiabatic gasification reactor along with a stream of pure oxygen at the same temperature. The following reactions take place in the reactor:

$$C(s) + H_2O(v) \longrightarrow CO(g) + H_2(g): \quad \Delta\hat{H}_r^\circ = +131.3\ \text{kJ/mol} \qquad \textbf{(1)}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g): \quad \Delta\hat{H}_r^\circ = -393.5\ \text{kJ/mol} \qquad \textbf{(2)}$$

$$2H(\text{in coal}) + \tfrac{1}{2}\ O_2(g) \longrightarrow H_2O(v): \quad \Delta\hat{H}_r^\circ \approx -242\ \text{kJ/mol} \qquad \textbf{(3)}$$

Gas and slag (molten ash) leave the reactor at 2500°C. The gas contains CO, H_2, CO_2, and H_2O.[11]

(a) Feeding oxygen to the reactor lowers the yield of synthesis gas, but no gasifier ever operates without supplementary oxygen. Why does the oxygen lower the yield? Why it is nevertheless always supplied. (*Hint:* All the necessary information is contained in the first two stoichiometric equations and associated heats of reaction shown above.)

(b) Suppose the oxygen gas fed to the reactor and the oxygen in the coal combine with all the hydrogen in the coal (Reaction 3) and with some of the carbon (Reaction 2), and the remainder of the carbon is consumed in Reaction 1. Taking a basis of 1.00 kg coal fed to the reactor and letting n_0 equal the moles of O_2 fed, draw and label a flowchart. Then derive expressions for the molar flow rates of the four outlet gas species in terms of n_0. (Partial solution: $n_{H_2} = 51.5 - n_0$.)

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[11] In a real coal gasification reactor, sulfur in the coal would form hydrogen sulfide in the product gas, nitrogen in the coal would form N_2, some of the carbon monoxide formed in the first reaction would react with steam to form carbon dioxide and more hydrogen, and some of the carbon in the coal would react with hydrogen to form methane. For simplicity, we are ignoring these reactions.

(c) The standard heat of combustion of the coal has been determined to be −21,400 kJ/kg, taking $CO_2(g)$ and $H_2O(l)$ to be the combustion products. Use this value and the given elemental composition of the coal to prove that the standard heat of formation of the coal is –1510 kJ/kg. Then use an energy balance to calculate n_0, using the following approximate heat capacities in your calculation:

Species	O_2	CO	H_2	CO_2	$H_2O(v)$	Slag(l)
C_p[kJ/(mol·°C)]	0.0336	0.0332	0.0300	0.0508	0.0395	—
C_p[kJ/(kg·°C)]	—	—	—	—	—	1.4

Take the heat of fusion of ash (the heat required to convert ash to slag) to be 710 kJ/kg.

9.39. Three cubic meters of a 1.00-molar aqueous sulfuric acid solution (SG = 1.064) is stored at 25°C. Use data in Tables B.1 and B.11 to calculate the standard heat of formation of the solution in kJ/mol H_2SO_4 relative to the solute elements and water, and the total enthalpy of the solution relative to the same reference conditions.

9.40. Calculate the standard heat (kJ/mol) of the neutralization reaction between dilute hydrochloric acid and dilute sodium hydroxide solutions, taking the heat of solution of NaCl to be +4.87 kJ/mol. Then calculate the standard heat of the reaction between hydrogen chloride gas and solid sodium hydroxide to form solid sodium chloride and liquid water. What is the physical significance of the difference between the two calculated values?

9.41. A 10.0 mole% aqueous sulfuric acid solution (SG = 1.27) is to be titrated to neutrality at 25°C with a 3.00-molar caustic soda (sodium hydroxide) solution (SG = 1.13):

$$H_2SO_4(aq) + 2\,NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2\,H_2O(l)$$

(a) Calculate the required volume ratio (cm^3 caustic solution/cm^3 acid solution).

(b) Calculate the standard heats of formation (kJ/mol solute) of each of the three solutions involved in this process, and the heat released (kJ/cm^3 acid solution neutralized) if the reactants and products are all at 25°C. The heat of solution of sodium sulfate is −1.17 kJ/mol. Assume that $Q = \Delta H$ for the process. (See Example 9.5-5.)

9.42. Most of the world's chlorine and sodium hydroxide are obtained through the electrolysis of brine:

$$NaCl(aq) + H_2O(l) \rightarrow \tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,Cl_2(g) + NaOH(aq)$$

(a) Determine the standard heats of formation of NaCl(aq) and NaOH(aq) and then the standard heat of the brine electrolysis reaction. The standard heat of solution of NaCl is $\Delta\hat{H}_s(r = \infty) = +4.87$ kJ/mol NaCl.

(b) Several years ago, the annual production of chlorine in the United States was roughly 8500 metric kilotons. Calculate the energy requirement in MW·h/yr corresponding to this production rate, assuming that all of the chlorine is produced by electrolysis at 25°C and the required energy input equals ΔH for the process.

9.43. You have been given the task of determining the standard heat of the reaction in which calcium chloride hexahydrate is formed from anhydrous calcium chloride:

$$CaCl_2(s) + 6\,H_2O(l) \longrightarrow CaCl_2 \cdot 6H_2O(s): \quad \Delta\hat{H}_r^\circ\ (\text{kJ/mol}) = ?$$

By definition, the desired quantity is the *heat of hydration* of calcium chloride hexahydrate. You cannot carry out the hydration reaction directly, so you resort to an indirect method. You first dissolve 1.00 mol of anhydrous $CaCl_2$ in 10.0 mol of water in a calorimeter and determine that 64.85 kJ of heat must be transferred away from the calorimeter to keep the solution temperature at 25°C. You next dissolve 1.00 mol of the hexahydrate salt in 4.00 mol of water and find that 32.1 kJ of heat must be transferred *to* the calorimeter to keep the temperature at 25°C.

(a) Use these results to calculate the desired heat of hydration. (*Suggestion:* Begin by writing out the stoichiometric equations for the two dissolution processes.)

(b) Calculate the standard heat of formation of $CaCl_2(aq, r = 10)$ in kJ/mol $CaCl_2$ relative to Ca(s), $Cl_2(g)$, and $H_2O(l)$ at 25°C.

9.44. A dilute aqueous solution of sulfuric acid at 25°C is used to absorb ammonia in a continuous reactor, thereby producing ammonium sulfate, a fertilizer:

$$2\,NH_3(g) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

(a) If the ammonia enters the absorber at 75°C, the sulfuric acid enters at 25°C, and the product solution emerges at 25°C, how much heat must be withdrawn from the unit per mol of $(NH_4)_SO_4$ produced? (All needed physical property data may be found in Appendix B.)

(b) Estimate the final temperature if the reactor of part (a) is adiabatic and the product of the solution contains 1.00 mole % ammonium sulfate. Take the heat capacity of the solution to be that of pure liquid water [4.184 kJ/(kg·°C)].

(c) In a real (imperfectly insulated) reactor, would the final solution temperature be less than, equal to, or greater than the value calculated in part (b), or is there no way to tell without more information? Briefly explain your answer.

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9.45. A 2.00 mole% sulfuric acid solution is neutralized with a 5.00 mole% sodium hydroxide solution in a continuous reactor. All reactants enter at 25°C. The standard heat of solution of sodium sulfate is –1.17 kJ/mol Na_2SO_4, and the heat capacities of all solutions may be taken to be that of pure liquid water [4.184 kJ/(kg·°C)].

(a) How much heat (kJ/kg acid solution fed) must be transferred to or from the reactor contents (state which it is) if the product solution emerges at 40°C?

(b) Estimate the product solution temperature if the reactor is adiabatic, neglecting heat transferred between the reactor contents and the reactor wall.

Equipment Encyclopedia
scrubber

9.46. A 12.0-molar solution of sodium hydroxide (SG = 1.37) is neutralized with 75.0 mL of a 4.0 molar solution of sulfuric acid (SG = 1.23) in a well-insulated container.

(a) Estimate the volume of the sodium hydroxide solution and the final solution temperature if both feed solutions are at 25°C. The heat capacity of the product solution may be taken to be that of pure liquid water, the standard heat of solution of sodium sulfate is –1.17 kJ/mol, and the energy balance reduces to $Q = \Delta H$ for this constant-pressure batch process.

(b) List several additional assumptions you made to arrive at your estimated volume and temperature.

9.47. Ammonia scrubbing is one of many processes for removing sulfur dioxide from flue gases. The gases are bubbled through an aqueous solution of ammonium sulfite, and the SO_2 reacts to form ammonium bisulfite:

$$(NH_4)_2SO_3(aq) + SO_2(g) + H_2O(l) \rightarrow 2NH_4HSO_3(aq)$$

Subsequent process steps yield concentrated SO_2 and regenerate ammonium sulfite, which is recycled to the scrubber. The sulfur dioxide is either oxidized and absorbed in water to form sulfuric acid or reduced to elemental sulfur.

Flue gas from a power plant boiler containing 0.30% SO_2 by volume enters a scrubber at a rate of 50,000 mol/h at 50°C. The gas is bubbled through an aqueous solution containing 10.0 mole% ammonium sulfite that enters the scrubber at 25°C. The gas and liquid effluents from the scrubber both emerge at 35°C. The scrubber removes 90% of the SO_2 entering with the flue gas. The effluent liquid is analyzed and is found to contain 1.5 moles $(NH_4)_2SO_3$ per mole of NH_4HSO_3. The heat of formation of $(NH_4)_2SO_3(aq)$ at 25°C is −890.0 kJ/mol, and that of $NH_4HSO_3(aq)$ is −760 kJ/mol. The heat capacities of all liquid solutions may be taken to be 4.0 J/(g·°C) and that of the flue gas may be taken to be that of nitrogen. Evaporation of water may be neglected. Calculate the required rate of heat transfer to or from the scrubber (kW).

9.48. A natural gas is analyzed and found to consist of 87.5% v/v (volume percent) methane, 7.0% ethane, 2.0% propane, and 3.5% N_2 (noncombustible).

(a) Calculate the higher heating value and the lower heating value of this fuel in kJ/mol, using the heats of combustion in Table B.1.

(b) Calculate the lower heating value of the fuel in kJ/kg.

(c) State in your own words the meaning of the quantity calculated in part (b).

9.49. An **ultimate analysis** of a coal is a series of operations that yields the percentages by mass of carbon, hydrogen, nitrogen, oxygen, and sulfur in the coal. The heating value of a coal is best determined in a calorimeter, but it may be estimated with reasonable accuracy from the ultimate analysis using the **Dulong formula:**

$$HHV(\text{kJ/kg}) = 33{,}801(\text{C}) + 144{,}158[(\text{H}) - 0.125(\text{O})] + 9413(\text{S})$$

where (C), (H), (O), and (S) are the mass fractions of the corresponding elements. The 0.125(O) term accounts for the hydrogen bound in the water contained in the coal.

(a) Derive an expression for the higher heating value (*HHV*) of a coal in terms of C, H, O, and S, and compare your result with the Dulong formula. Suggest a reason for the difference.

(b) A coal with an ultimate analysis of 75.8 wt% C, 5.1% H, 8.2% O, 1.5% N, 1.6% S, and 7.8% ash (noncombustible) is burned in a power plant boiler furnace. All of the sulfur in the coal forms SO_2. The gas leaving the furnace is fed through a tall stack and discharged to the atmosphere. The ratio ϕ(kg SO_2 in the stack gas/kJ heating value of the fuel) must be below a specified value for the power plant to be in compliance with Environmental Protection Agency regulations regarding sulfur emissions. Estimate ϕ, using the Dulong formula for the heating value of the coal.

(c) An earlier version of the EPA regulation specified that the mole fraction of SO_2 in the stack gas must be less than a specified amount to avoid a costly fine and the required installation of an expensive stack gas scrubbing unit. When this regulation was in force, a few unethical plant operators blew clear air into the base of the stack while the furnace was operating. Briefly explain why they did so and why they stopped this practice when the new regulation was introduced.

9.50. A fuel gas is known to contain methane, ethane, and carbon monoxide. A sample of the gas is charged into an initially evacuated 2.000-liter vessel at 25°C and 2323 mm Hg absolute. The vessel is weighed before and after being charged, and the mass difference is found to be 4.929 g. Next, the higher heating value of the gas is determined in a calorimeter to be 841.9 kJ/mol. Calculate the molar composition of the gas.

9.51. A fuel gas containing 85.0 mole% methane and the balance ethane is burned completely with pure oxygen at 25°C, and the products are brought back down to 25°C.

(a) Suppose the reactor is continuous. Take a basis of calculation of 1 mol/s of the fuel gas, assume some value for the percent excess oxygen fed to the reactor (the value you choose will not affect the results), and calculate $-\dot{Q}$(kW), the rate at which heat must be transferred from the reactor.

(b) Now suppose the combustion takes place in a constant-volume batch reactor. Take a basis of calculation of 1 mol of the fuel gas charged into the reactor, assume any percent excess oxygen, and calculate $-Q$(kJ). (*Hint:* Recall Equation 9.1-5.)

(c) Briefly explain why the results in parts (a) and (b) do not depend on the percent excess O_2 and why they would not change if air rather than pure oxygen were fed to the reactor.

9.52. A mixture of air and a fine spray of gasoline at ambient (outside air) temperature is fed to a set of piston-fitted cylinders in an automobile engine. Sparks ignite the combustible mixtures in one cylinder after another, and the consequent rapid increase in temperature in the cylinders causes the combustion products to expand and drive the pistons. The back-and-forth motion of the pistons is converted to rotary motion of a crank shaft, motion that in turn is transmitted through a system of shafts and gears to propel the car.

Consider a car driving on a day when the ambient temperature is 298 K and suppose that the rate of heat loss from the engine to the outside air is given by the formula

$$-\dot{Q}_1\left(\frac{\text{kJ}}{\text{h}}\right) \approx \frac{15 \times 10^6}{T_a(\text{K})}$$

where T_a is the ambient temperature.

(a) Take gasoline to be a liquid with a specific gravity of 0.70 and a higher heating value of 49.0 kJ/g, assume complete combustion and that the combustion products leaving the engine are at 298 K, and calculate the minimum feed rate of gasoline (gal/h) required to produce 100 hp of shaft work.

(b) If the exhaust gases are well above 298 K (which they are), is the work delivered by the pistons more or less than the value determined in part (a)? Explain.

(c) If the ambient temperature is much lower than 298 K, the work delivered by the pistons would decrease. Give two reasons.

9.53. The heating value of a fuel oil is to be measured in a constant-volume bomb calorimeter. The bomb is charged with oxygen and 0.00215 lb_m of the fuel and is then sealed and immersed in an insulated container of water. The initial temperature of the system is 77.00°F. The fuel–oxygen mixture is ignited, and the fuel is completely consumed. The combustion products are $CO_2(g)$ and $H_2O(v)$. The final calorimeter temperature is 87.06°F. The mass of the calorimeter, including the bomb and its contents, is 4.62 lb_m, and the average heat capacity of the system (C_v) is 0.900 Btu/(lb_m·°F).

(a) Calculate $\Delta\hat{U}_c^\circ$ (Btu/lb_m oil) for the combustion of the fuel oil at 77°F. Briefly explain your calculation.

(b) What more would you need to know to determine the higher heating value of the oil?

9.54. Methanol vapor is burned with excess air in a catalytic combustion chamber. Liquid methanol initially at 25°C is vaporized at 1.1 atm and heated to 100°C; the vapor is mixed with air that has been preheated to 100°C, and the combined stream is fed to the reactor at 100°C and 1 atm. The reactor effluent emerges at 300°C and 1 atm. Analysis of the product gas yields a dry-basis composition of 4.8% CO_2, 14.3% O_2, and 80.9% N_2.

(a) Calculate the percentage excess air supplied and the dew point of the product gas.

(b) Taking a basis of 1 g-mole of methanol burned, calculate the heat (kJ) needed to vaporize and heat the methanol feed, and the heat (kJ) that must be transferred from the reactor.

Student Workbook

Equipment Encyclopedia
boiler

9.55. Methane at 25°C is burned in a boiler furnace with 10.0% excess air preheated to 100°C. Ninety percent of the methane fed is consumed, the product gas contains 10.0 mol CO_2/mol CO, and the combustion products leave the furnace at 400°C.

(a) Calculate the heat transferred from the furnace, $-\dot{Q}$(kW), for a basis of 1000 mol CH_4 fed/s. (The greater the value of $-\dot{Q}$, the more steam is produced in the boiler.)

(b) Would the following changes increase or decrease the rate of steam production? (Assume the fuel feed rate and fractional conversion of methane remain constant.) Briefly explain your answers. (i) Increasing the temperature of the inlet air; (ii) increasing the percent excess air for a given stack gas temperature; (iii) increasing the selectivity of CO_2 to CO formation in the furnace; and (iv) increasing the stack gas temperature.

9.56. A gaseous fuel containing methane and ethane is burned with excess air. The fuel enters the furnace at 25°C and 1 atm, and the air enters at 200°C and 1 atm. The stack gas leaves the furnace at 800°C and 1 atm and contains 5.32 mole% CO_2, 1.60% CO, 7.32% O_2, 12.24% H_2O, and the balance N_2.

(a) Calculate the molar percentages of methane and ethane in the fuel gas and the percentage excess air fed to the reactor.

(b) Calculate the heat (kJ) transferred from the reactor per cubic meter of fuel gas fed.

Equipment Encyclopedia
boiler

9.57. A coal contains 73.0 wt% C, 4.7% H (not including the hydrogen in the coal moisture), 3.7% S, 6.8% H_2O, and 11.8% ash. The coal is burned at a rate of 50,000 lb_m/h in a power plant boiler with air 50% in excess of that needed to oxidize all the carbon in the coal to CO_2. The air and coal are both fed at 77°F and 1 atm. The solid residue from the furnace is analyzed and is found to contain 28.7 wt% C, 1.6% S, and the balance ash. The coal sulfur oxidized in the furnace is converted to $SO_2(g)$. Of the ash in the coal, 30% emerges in the solid residue and the balance is emitted with the stack gases as fly ash. The stack gas and solid residue emerge from the furnace at 600°F. The higher heating value of the coal is 18,000 Btu/lb_m.

(a) Calculate the mass flow rates of all components in the stack gas and the volumetric flow rate of this gas. (Ignore the contribution of the fly ash in the latter calculation, and assume that the stack gas contains a negligible amount of CO.)

(b) Assume that the heat capacity of the solid furnace residue is 0.22 Btu/(lb_m·°F), that of the stack gas is the heat capacity per unit mass of nitrogen, and 35% of the heat generated in the furnace is used to produce electricity. At what rate in MW is electricity produced?

(c) Calculate the ratio (heat transferred from the furnace)/(heating value of the fuel). Why is this ratio less than one?

(d) Suppose the air fed to the furnace were preheated rather than being fed at ambient temperature, but that everything else (feed rates, outlet temperatures, and fractional coal conversion) were the same. What effect would this change have on the ratio calculated in part (c)? Explain. Suggest an economical way in which this preheating might be accomplished.

Equipment Encyclopedia
boiler

9.58. A mixture of methane, ethane, and argon at 25°C is burned with excess air in a power plant boiler. The hydrocarbons in the fuel are completely consumed. The following variable definitions will be used throughout this problem:

x_m = mole fraction of methane in the fuel
x_a = mole fraction of argon in the fuel
$P_{xs}(\%)$ = percent excess air fed to the furnace
$T_a(°C)$ = temperature of the entering air
$T_s(°C)$ = stack gas temperature
r = ratio of CO_2 to CO in the stack gas (mol CO_2/mol CO)
$\dot{Q}$(kW) = rate of heat transfer from the furnace to the boiler tubes

(a) Without doing any calculations, sketch the shapes of the plots you would expect to obtain for plots of $\dot{Q}$ versus (i) x_m, (ii) x_a, (iii) P_{xs}, (iv) T_a, (v) T_s, and (vi) r, assuming in each case that the other variables are held constant. Briefly state your reasoning for each plot.

(b) Take a basis of 1.00 mol/s of fuel gas, draw and label a flowchart, and derive expressions for the molar flow rates of the stack gas components in terms of x_m, x_a, P_{xs}, and r. Then take as references the elements at 25°C, prepare and fill in an inlet–outlet enthalpy table for the furnace, and derive expressions for the specific molar enthalpies of the feed and stack gas components in terms of T_a and T_s.

(c) Calculate $\dot{Q}$(kW) for $x_m = 0.85$ mol CH_4/mol, $x_a = 0.05$ mol Ar/mol, $P_{xs} = 5\%$, $r = 10.0$ mol CO_2/mol CO, $T_a = 150°C$, and $T_s = 700°C$. (*Solution:* $\dot{Q} = -655$ kW.)

***(d)** Prepare a spreadsheet that has columns for x_m, x_a, P_{xs}, T_a, r, T_s, and $\dot{Q}$, plus columns for any other variables you might need for the calculation of $\dot{Q}$ from given values of the preceding six variables (e.g., component molar flow rates and specific enthalpies). Use the spreadsheet to generate plots of $\dot{Q}$ versus each of the following variables over the specified ranges:

x_m = 0.00–0.85 mol CH_4/mol
x_a = 0.01–0.05 mol Ar/mol
P_{xs} = 0%–100%
T_a = 25°C–250°C
r = 1–100 mol CO_2/mol CO (make the r axis logarithmic)
T_s = 500°C–1000°C

When generating each plot, use the variable values given in part (c) as base values. (For example, generate a plot of $\dot{Q}$ versus x_m for $x_a = 0.05$, $P_{xs} = 5\%$, and so on, with x_m varying from 0.00 to 0.85 on the horizontal axis.) If possible, include the plots on the same spreadsheet as the data.

Equipment Encyclopedia
condenser, boiler

9.59. A gas stream consisting of *n*-hexane in methane is fed to a condenser at 60°C and 1.2 atm. The dew point of the gas (considering hexane as the only condensable component) is 55°C. The gas is cooled to 5°C in the condenser, recovering pure hexane as a liquid. The effluent gas leaves the condenser saturated with hexane at 5°C and 1.1 atm and is fed to a boiler furnace at a rate of 207.4 L/s, where it is burned with 100% excess air that enters the furnace at 200°C. The stack gas emerges at 400°C and 1 atm and contains no carbon monoxide or unburned hydrocarbons. The heat transferred from the furnace is used to generate saturated steam at 10 bar from liquid water at 25°C.

(a) Calculate the mole fractions of hexane in the condenser feed and product gas streams and the rate of hexane condensation (liters condensate/s).

(b) Calculate the rate at which heat must be transferred from the condenser (kW) and the rate of generation of steam in the boiler (kg/s).

Equipment Encyclopedia
boiler, heat exchanger

9.60. In the preliminary design of a furnace for industrial boiler, methane at 25°C is burned completely with 20% excess air, also at 25°C. The feed rate of methane is 450 kmol/h. The hot combustion gases leave the furnace at 300°C and are discharged to the atmosphere. The heat transferred from the furnace ($\dot{Q}$) is used to convert boiler feedwater at 25°C into superheated steam at 17 bar and 250°C.

Use the following approximate heat capacities [kJ/(mol·°C)] in your solution of this problem: $CH_4(g) = 0.0431$, $CO_2(g) = 0.0423$, $H_2O(g) = 0.0343$, $O_2(g) = 0.0312$, $N_2(g) = 0.0297$.

(a) Draw and label a flowchart of this process [the chart should look like the one shown in part (b) without the preheater] and calculate the composition of the gas leaving the furnace. Then, using the given constant heat capacities, calculate the average molar heat capacity of the gas. (See Equation 8.3-13.) Finally, calculate $\dot{Q}$(kJ/h) and the rate of steam production in the boiler (kg/h).

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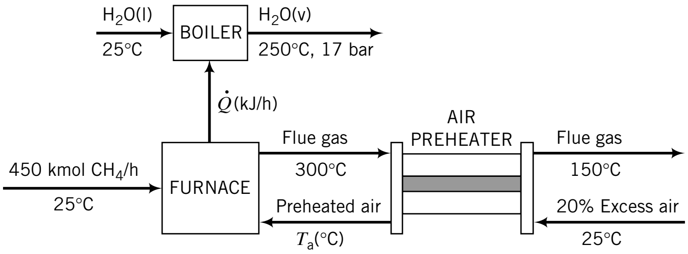
*Computer problem.

(b) In the actual boiler design, the air feed at 25°C and the combustion gas leaving the furnace at 300°C pass through a heat exchanger (the *air preheater*). The combustion (flue) gas is cooled to 150°C in the preheater and is then discharged to the atmosphere, and the heated air is fed to the furnace.

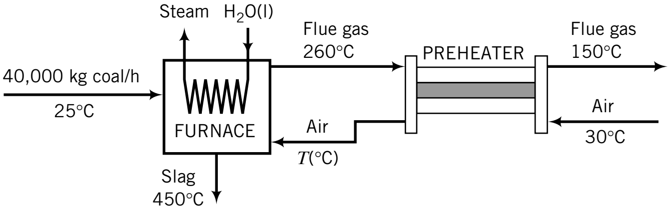


Calculate the temperature of the air entering the furnace (a trial-and-error solution is required) and the rate of steam production (kg/h).

(c) Explain why preheating the air increases the rate of steam production. (*Suggestion:* Use the energy balance on the furnace in your explanation.) Why does it make sense economically to use the combustion gas as the heating medium?

Equipment Encyclopedia
heat exchanger

9.61. A bituminous coal is burned with air in a boiler furnace. The coal is fed at a rate of 40,000 kg/h and has an ultimate analysis of 76 wt% C, 5% H, 8% O, negligible amounts of N and S, and 11% noncombustible ash (see Problem 9.49), and a higher heating value of 25,700 kJ/kg. Air enters a preheater at 30°C and 1 atm with a relative humidity of 30%, exchanges heat with the hot flue gas leaving the furnace, and enters the furnace at temperature T_a(°C). The flue gas contains 7.71 mole% CO_2 and 1.29 mole% CO *on a dry basis,* and the balance a mixture of O_2, N_2, and H_2O. It emerges from the furnace at 260°C and is cooled to 150°C in the preheater. Noncombustible residue (*slag*) leaves the furnace at 450°C and has a heat capacity of 0.97 kJ/(kg·°C).



(a) Prove that the air-to-fuel ratio is 16.1 standard cubic meters/kg coal and that the flue gas contains 4.6% H_2O by volume.

(b) Calculate the rate of cooling required to cool the flue gas from 260°C to 150°C and the temperature to which the air is preheated. (*Note:* A trial-and-error calculation is required.)

(c) If 60% of the heat transferred from the furnace ($-\dot{Q}$) goes into producing saturated steam at 30 bar from liquid boiler feedwater at 50°C, at what rate (kg/h) is steam generated?

9.62. Carbon monoxide is burned with excess air at 1 atm in an adiabatic reactor. The reactants are fed at 25°C and the final temperature (i.e., the adiabatic flame temperature) is 1400°C.

(a) Calculate the percentage excess air fed to the reactor.

(b) If the percentage excess air were increased, how would the adiabatic flame temperature change and why would it change in this manner?

Equipment Encyclopedia
boiler

9.63. A natural gas containing 82.0 mole% CH_4 and the balance C_2H_6 is burned with 20% excess air in a boiler furnace. The fuel gas enters the furnace at 298 K, and the air is preheated to 423 K. The heat capacities of the stack gas components may be assumed to have the following constant values:

$$CO_2: \quad C_p = 50.0\ \text{J/(mol·K)}$$
$$H_2O(v): \quad C_p = 38.5\ \text{J/(mol·K)}$$
$$O_2: \quad C_p = 33.1\ \text{J/(mol·K)}$$
$$N_2: \quad C_p = 31.3\ \text{J/(mol·K)}$$

(a) Assuming complete combustion of the fuel, calculate the adiabatic flame temperature.

(b) How would the flame temperature change if the percent excess air were increased? How would it change if the percentage of methane in the fuel increased? Briefly explain both of your answers.

9.64. In a surface coating operation, a polymer (plastic) dissolved in liquid acetone is sprayed on a solid surface and a stream of hot air is then blown over the surface, vaporizing the acetone and leaving a residual polymer film of uniform thickness. Because environmental standards do not allow discharging acetone into the atmosphere, a proposal to incinerate the stream is to be evaluated.

The proposed process uses two parallel columns containing beds of solid particles. The air–acetone stream, which contains acetone and oxygen in stoichiometric proportion, enters one of the beds at 1500 mm Hg absolute at a rate of 1410 standard cubic meters per minute. The particles in the bed have been preheated and transfer heat to the gas. The mixture ignites when its temperature reaches 562°C, and combustion takes place rapidly and adiabatically. The combustion products then pass through and heat the particles in the second bed, cooling down to 350°C in the process. Periodically the flow is switched so that the heated outlet bed becomes the feed gas preheater/combustion reactor and vice versa.

Use the following average values for C_p[kJ/(mol·°C)] in solving the problems to be given: 0.126 for C_3H_6O, 0.033 for O_2, 0.032 for N_2, 0.052 for CO_2, and 0.040 for $H_2O(v)$.

(a) If the relative saturation of acetone in the feed stream is 12.2%, what is the stream temperature?

(b) Determine the composition of the gas after combustion, assuming that all of the acetone is converted to CO_2 and H_2O, and estimate the temperature of this stream.

(c) Estimate the rates (kW) at which heat is transferred from the inlet bed particles to the feed gas prior to combustion and from the combustion gases to the outlet bed particles. Suggest an alternative to the two-bed feed switching arrangement that would achieve the same purpose.

9.65. Liquid *n*-pentane at 25°C is burned with 30% excess oxygen (not air) fed at 75°C. The adiabatic flame temperature is T_{ad}(°C).

(a) Take as a basis of calculation 1.00 mol $C_5H_{12}(l)$ burned and use an energy balance on the adiabatic reactor to derive an equation of the form $f(T_{\text{ad}}) = 0$, where $f(T_{\text{ad}})$ is a fourth-order polynomial $[f(T_{\text{ad}}) = c_0 + c_1T_{\text{ad}} + c_2T_{\text{ad}}^2 + c_3T_{\text{ad}}^3 + c_4T_{\text{ad}}^4]$. If your derivation is correct, the ratio c_0/c_4 should equal -6.892×10^{14}. Then solve the equation to determine T_{ad}. (This solution is easily obtained using the goalseek tool on a spreadsheet.)

(b) Repeat the calculation of part (a) using successively the first two terms, the first three terms, and the first four terms of the fourth-order polynomial equation. If the solution of part (a) is taken to be exact, what percentage errors are associated with the linear (two-term), quadratic (three-term), and cubic (four-term) approximations?

(c) Determine the fourth-order solution using Newton's method (Appendix A.2), taking the linear approximation as the first guess and stopping when $|f(T_{\text{ad}})| < 0.01$.

(d) Why is the fourth-order solution at best an approximation and quite possibly a poor one? (*Hint:* Examine the conditions of applicability of the heat capacity formulas you looked up in Table B.2.)

9.66. Methane is burned with 25% excess air in a continuous adiabatic reactor. The methane enters the reactor at 25°C and 1.10 atm at a rate of 5.50 L/s, and the entering air is at 150°C and 1.1 atm. Combustion in the reactor is complete, and the reactor effluent gas emerges at 1.05 atm. Calculate (a) the temperature and (b) the degrees of superheat of the reactor effluent. (Consider water to be the only condensable species in the effluent.)

[12]**9.67.** Methane and 30% excess air are to be fed to a combustion reactor. An inexperienced technician mistakes his instructions and charges the gases together in the required proportion into an evacuated closed tank. (The gases were supposed to be fed directly into the reactor.) The contents of the charged tank are at 25°C and 4.00 atm absolute.

(a) Calculate the standard internal energy of combustion of the methane combustion reaction, $\Delta\hat{U}_c^\circ$(kJ/mol), taking $CO_2(g)$ and $H_2O(v)$ as the presumed products. Then prove that if the constant-pressure heat capacity of an ideal gas species is independent of temperature, the specific internal energy of that species at temperature T(°C) relative to the same species at 25°C is

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[12] Modified version of a problem in D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry,* AIChE Center for Chemical Process Safety, New York, 1993.

given by the expression

$$\hat{U} = (C_p - R_g)(T - 25°\text{C})$$

where R_g is the gas constant. Use this formula in the next part of the problem.

(b) You wish to calculate the maximum temperature, $T_{\max}$(°C), and corresponding pressure, $P_{\max}$(atm), that the tank would have to withstand if the mixture it contains were to be accidentally ignited. Taking molecular species at 25°C as references and treating all species as ideal gases, prepare an inlet–outlet internal energy table for the closed system combustion process. In deriving expressions for each $\hat{U}_i$ at the final reactor condition ($T_{\max}$, $P_{\max}$), use the following approximate values for C_{pi}[kJ/(mol·°C)]: 0.033 for O_2, 0.032 for N_2, 0.052 for CO_2, and 0.040 for H_2O(v). Then use an energy balance and the ideal gas equation of state to perform the required calculations.

(c) Why would the actual temperature and pressure attained in a real tank be less than the values calculated in part (a)? (State several reasons.)

(d) Think of ways that the tank contents might be accidentally ignited. The list should suggest why accepted plant safety regulations prohibit the storage of combustible vapor mixtures.

***9.68.** Natural gas that contains methane, ethane, and propane is to be burned with humid air. The adiabatic flame temperature is to be calculated from specified values of the following quantities:

$y_{CH_4}, y_{C_2H_6}, y_{C_3H_8}$ = mole fractions of fuel components

T_f, T_a = inlet temperatures of fuel and air, °C

P_{xs} = percent excess air

y_{W0} = mole fraction of water in the inlet air

(a) Without doing any calculations, predict the direction of change (increase, decrease, no change) in the adiabatic flame temperature you would expect for an increase in (i) y_{CH_4} with $y_{C_3H_8}$ held constant, (ii) T_f, (iii) T_a, (iv) P_{xs}, and (v) y_{W0}. Briefly state your reasoning for each variable.

(b) For a basis of 1 g-mole of natural gas, calculate the gram-moles of each molecular species in the feed and product streams, assuming complete combustion and negligible CO formation. The answer should be expressed in terms of the variables given above.

(c) Given here are expressions for the specific enthalpies of the feed and product components, relative to their elements at 25°C.

$$\hat{H}_i(\text{kJ/mol}) = a_i + b_iT + c_iT^2 + d_iT^3 + e_iT^4, \quad T \text{ in °C}$$

Substance (i)	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^8$	$e \times 10^{12}$
(1) CH_4	−75.72	3.431	2.734	0.122	−2.75
(2) C_2H_6	−85.95	4.937	6.96	−1.939	1.82
(3) C_3H_8	−105.6	6.803	11.30	−4.37	7.928
(4) N_2	−0.7276	2.900	0.110	0.191	−0.7178
(5) O_2	−0.7311	2.910	0.579	−0.2025	0.3278
(6) H_2O(v)	−242.7	3.346	0.344	0.2535	−0.8982
(7) CO_2	−394.4	3.611	2.117	−0.9623	1.866

Derive the given expression for the specific enthalpy of methane from the heat capacity data in Table B.2. Then show that ΔH for the reactor is given by an expression of the form

$$\Delta H = \alpha_0 + \alpha_1T + \alpha_2T^2 + \alpha_3T^3 + \alpha_4T^4$$

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*Computer problem.

where T is the product temperature, and

$$\alpha_0 = \sum_{i=4}^{7}(n_i)_{\text{out}}a_i - \sum_{i=1}^{3}(n_i)_{\text{in}}\hat{H}_i(T_{\text{f}}) - \sum_{i=4}(n_i)_{\text{in}}\hat{H}_i(T_{\text{a}})$$

$$\alpha_1 = \sum_{i=4}^{7}(n_i)_{\text{out}}b_i \qquad \alpha_3 = \sum_{i=4}^{7}(n_i)_{\text{out}}d_i$$

$$\alpha_2 = \sum_{i=4}^{7}(n_i)_{\text{out}}c_i \qquad \alpha_4 = \sum_{i=4}^{7}(n_i)_{\text{out}}e_i$$

(d) Write a spreadsheet program to take as input values of y_{CH_4}, $y_{\text{C}_3\text{H}_8}$, T_{f}, T_{a}, P_{xs}, and y_{W0}, and to solve the energy balance equation $[\Delta H(T) = 0]$ to determine the adiabatic flame temperature. Run the program for the following sets of input variable values:

Variable	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
y_{CH_4}	0.75	0.86	0.75	0.75	0.75	0.75
$y_{\text{C}_3\text{H}_8}$	0.04	0.04	0.04	0.04	0.04	0.04
T_{f}(°C)	40	40	150	40	40	40
T_{a}(°C)	150	150	150	250	150	150
P_{xs}	25%	25%	25%	25%	100%	25%
y_{W0}	0.0306	0.0306	0.0306	0.0306	0.0306	0.10

Suggestion: Near the top of the spreadsheet, enter the values of a, b, c, d, and e for each species. Starting several rows below the last of these entries, list in Column A labels for the input variables and all calculated variables (component molar flow rates, specific enthalpies, $T_{\text{ad}}, \alpha_0, \alpha_1, \ldots, \alpha_4, \Delta H$), and enter in adjacent columns the corresponding values or formulas for these variables in successive runs. (*Solution for Run 1:* T_{ad} = 1743.1°C.)

(e) Write a computer program to carry out the above calculations using Newton's rule (Appendix A.2), with an initial guess of 1000°C for each run. Build in a limit on the number of iterations in case the program fails to converge.

Equipment Encyclopedia
reactor,
absorption
column,
stripper

9.69. Acetylene is produced by pyrolyzing—decomposing at high temperature—natural gas (predominantly methane):

$$2\,\text{CH}_4(\text{g}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + 3\,\text{H}_2$$

The heat required to sustain this endothermic reaction is provided by feeding oxygen to the reactor and burning a portion of the methane to form primarily CO and some CO_2.

A simplified version of the process is as follows. A stream of natural gas, which for the purposes of this problem may be considered pure methane, and a stream containing 96.0 mole% oxygen and the balance nitrogen are each preheated from 25°C to 650°C. The streams are combined and fed into an adiabatic converter, in which most of the methane and all of the oxygen are consumed, and the product gas is rapidly quenched to 38°C as soon as it emerges from the converter. The residence time in the converter is less than 0.01 s, low enough to prevent most but not all of the methane from decomposing to form hydrogen and solid carbon particles (soot). Of the carbon in the feed, 5.67% emerges as soot.

The cooled effluent passes through a carbon filter in which the soot is removed. The clean gas is then compressed and fed to an absorption column, where it is contacted with a recycled liquid solvent, dimethylformamide, or DMF (MW = 73.09). The off-gas leaving the absorber contains all of the hydrogen and nitrogen, 98.8% of the CO, and 95% of the methane in the gas fed to the column. The "lean" solvent fed to the absorber is essentially pure DMF; the "rich" solvent leaving the column contains all of the water and CO_2 and 99.4% of the acetylene in the gas feed. This solvent is analyzed and found to contain 1.55 mole% C_2H_2, 0.68% CO_2, 0.055% CO, 0.055% CH_4, 5.96% H_2O, and 91.7% DMF.

The rich solvent goes to a multiple-unit separation process from which three streams emerge. One—the *product gas*—contains 99.1 mole% C_2H_2, 0.059% H_2O, and the balance CO_2; the second—the *stripper off-gas*—contains methane, carbon monoxide, carbon dioxide, and water; and the third—the *regenerated solvent*—is the liquid DMF fed to the absorber.

A plant is designed to produce 5 metric tons/day of product gas. Calculate the following quantities.

(a) The required flow rates (SCMH) of the methane and oxygen feed streams.

(b) The molar flow rates (kmol/h) and compositions of the gas feed to the absorber, the absorber off-gas, and the stripper off-gas.

(c) The DMF circulation rate (kmol/h).

(d) The overall product yield (mol C_2H_2 in product gas/mol CH_4 in the feed to the reactor), and the fraction that this quantity represents of its theoretical maximum value.

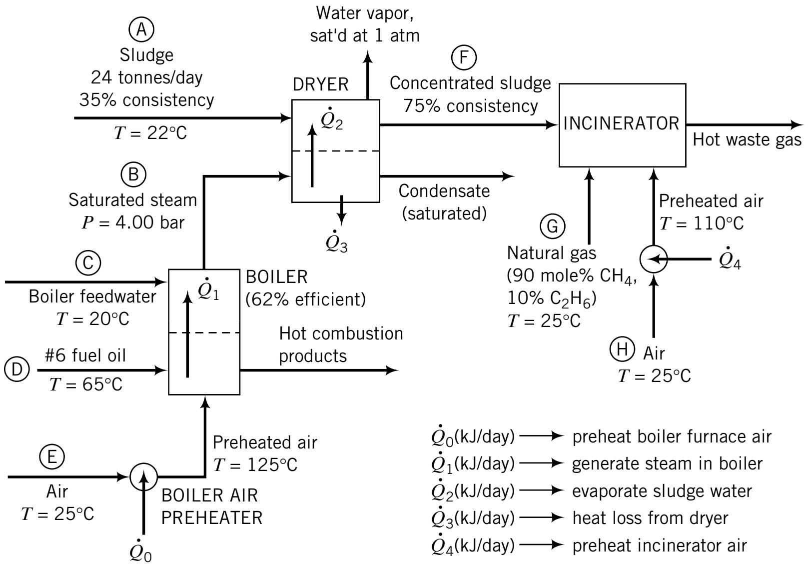
(e) The total heating requirements (kW) for the methane and oxygen feed preheaters.

(f) The temperature attained in the converter.

Equipment Encyclopedia
boiler, dryer

[13]**9.70.** The wastewater treatment plant at the Ossabaw Paper Company paper mill generates about 24 tonnes of sludge per day (1 tonne = 1 metric ton = 1000 kg). The *consistency* of the sludge is 35%, meaning that the sludge contains 35 wt% solids and the balance liquids. The mill currently spends \$40/tonne to dispose of the sludge in a landfill. The plant environmental engineer has determined that if the sludge consistency could be increased to 75%, the sludge could be incinerated (burned) to generate useful energy and to eliminate the environmental problems associated with landfill disposal.

A flowchart for a preliminary design of the proposed sludge treatment process follows. For simplicity, we will assume that the liquid in the sludge is just water.



Process description: The sludge from the wastewater treatment plant (Stream Ⓐ) passes through a dryer where a portion of the water in the sludge is vaporized. The heat required for the vaporization comes from condensing saturated steam at 4.00 bar (Stream Ⓑ). The steam fed to the dryer is produced in the plant's oil-fired boiler from feedwater at 20°C (Stream Ⓒ). The heat required to produce the steam is transferred from the boiler furnace, where fuel oil (Stream Ⓓ) is burned with 25% excess air (Stream Ⓔ). The concentrated sludge coming from the dryer (Stream Ⓕ), which has a consistency of 75%, is fed to an incinerator. The heating value of the sludge is insufficient to keep the incinerator temperature high enough for complete combustion, so natural gas (Stream Ⓖ) is used as a supplementary fuel. A stream of outside air at 25°C (Stream Ⓗ) is heated to 110°C and fed to the incinerator along with the concentrated sludge and natural gas. The waste gas from the incinerator is discharged to the atmosphere.

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[13] Problem based on material contributed by Joseph Lemanski of the Kimberly-Clark Corporation and Morton Barlaz of North Carolina State University.

Fuel oil: The oil is a low-sulfur No. 6 fuel oil. Its ultimate (elemental) analysis on a weight basis is 87% C, 10% H, 0.84% S, and the balance oxygen, nitrogen, and nonvolatile ash. The higher heating value of the oil is 3.75×10^4 kJ/kg and the heat capacity is $C_p = 1.8$ kJ/(kg·°C).

Boiler: The boiler has an efficiency of 62%, meaning that 62% of the heating value of the fuel oil burned is used to produce saturated steam at 4.00 bar from boiler feedwater at 20°C. Fuel oil at 65°C and dry air at 125°C are fed to the boiler furnace. The air feed rate is 25% in excess of the amount theoretically required for complete consumption of the fuel.

Sludge: The sludge from the wastewater treatment plant contains 35% w/w solids (S) and the balance liquids (which for the purposes of this problem may be treated as only water) and enters the dryer at 22°C. The sludge includes a number of volatile organic species, some of which may be toxic, and has a terrible odor. The heat capacity of the solids is approximately constant at 2.5 kJ/(kg·°C).

Dryer: The dryer has an efficiency of 55%, meaning that the heat transferred to the sludge, $\dot{Q}_2$, is 55% of the total heat lost by the condensing steam, and the remainder, $\dot{Q}_3$, is lost to the surroundings. The dryer operates at 1 atm, and the water vapor and concentrated sludge emerge at the corresponding saturation temperature. The steam condensate leaves the dryer as a liquid saturated at 4.00 bar.

Incinerator: The concentrated sludge has a heating value of 19,000 kJ/kg dry solids. For a feed sludge of 75% consistency, the incinerator requires 195 SCM natural gas/tonne wet sludge [1 SCM = 1 m^3(STP)]. The theoretical air requirement for the sludge is 2.5 SCM air/10,000 kJ of heating value. Air is fed in 100% excess of the amount theoretically required to burn the sludge and the natural gas.

(a) Use material and energy balances to calculate the mass flow rates (tonnes/day) of Streams Ⓑ, Ⓒ, Ⓓ, Ⓔ, Ⓕ, Ⓖ, and Ⓗ, and heat flows $\dot{Q}_0, \dot{Q}_1, \ldots, \dot{Q}_4$(kJ/day). Take the molecular weight of air to be 29.0. (*Caution:* Before you start doing lengthy and unnecessary energy balance calculations on the boiler furnace, remember the given furnace efficiency.)

(b) The money saved by implementing this process will be the current cost of disposing of the wastewater plant sludge in a landfill. Two major costs of implementing the process are the installed costs of the new dryer and incinerator. What other costs must be taken into account when determining the economic feasibility of the process? Why might management decide to go ahead with the project even if it proves to be unprofitable?

(c) What opportunities exist for improving the energy economy of the process? (*Hint:* Think about the need to preheat the fuel oil and the boiler and incinerator air streams and consider heat exchange possibilities.)

(d) The driving force for the introduction of this process is to eliminate the environmental cost of sludge disposal. What is that cost—that is, what environmental penalties and risks are associated with using landfills for hazardous waste disposal? What environmental problems might incineration introduce?

Chapter 10

Computer-Aided Balance Calculations

If you have worked your way through the preceding nine chapters, you are aware—maybe painfully so—that solving material and energy balance problems manually for even relatively simple systems can be a cumbersome and time-consuming task. Imagine what it must be like to do it for, say, an entire petroleum refinery! An alternative approach is to devise an *algorithm* (a systematic procedure) to perform the calculations and then to program a computer to implement it. This now common technique, referred to as *flowsheeting,* is the principal topic of this chapter.

10.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to do the following:

- Clearly define, in your own words, the terms: *design variables* and *state variables, sequential modular flowsheet simulation, equation-based flowsheet simulation, tear stream, convergence block,* and *design specification.*
- Given a description of a single-unit chemical process, determine the number of degrees of freedom and identify a set of design variables that leads to an efficient calculation procedure (one that minimizes the number of equations that must be solved simultaneously).
- Given a description of a multiple-unit process, determine the number of degrees of freedom, identify a set of feasible design variables, and if there are cycles in the flowchart, identify reasonable tear stream variables and outline the solution procedure. Draw a sequential modular block diagram for the process, inserting necessary convergence blocks.
- Set up a spreadsheet to perform material and energy balance calculations for single-unit and multiple-unit processes.

10.1 DEGREE-OF-FREEDOM ANALYSIS REVISITED

As defined in Section 4.3d, the *degrees of freedom* of a system, n_{df}, is the number of system variables whose values must be specified before the remaining variables can be calculated. *If a system is described by n_{e} independent equations in n_{v} variables, then $n_{\mathrm{df}} = n_{\mathrm{v}} - n_{\mathrm{e}}$.*

- If $n_{\mathrm{df}} = 0$ (e.g., if there are three independent equations in three unknowns), then the unknown system variables can, in principle, be calculated.
- If $n_{\mathrm{df}} > 0$—for example, three equations in five unknowns, so that $n_{\mathrm{df}} = 2$—then n_{df} variable values must be specified as part of the system definition, and the remaining unknown

variables may then be calculated from the system equations. Variables that are externally specified are called **design variables,** and those that are then calculated from the system equations are called **state variables.**

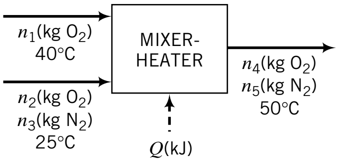
- If $n_{\mathrm{df}} < 0$, there are more equations than variables, and the process is *overdefined:* either you have written more equations than you are entitled to write (e.g., three material balances on a two-component system), or you have miscounted the variables, probably by not fully labeling the flowchart.

The remainder of this section illustrates degree-of-freedom analyses for increasingly complex systems: first a single nonreactive process unit, then a single reactive unit, and finally a system of several interconnected units.

10.1a Single Process Unit

The number of unknown variables for a single unit is the sum of the unknown component amounts or flow rates for all inlet and outlet streams, plus all unknown stream temperatures and pressures, plus the rates of energy transfer as heat and work. The equations available to determine these unknowns include material balances for each independent species, an energy balance, phase and chemical equilibrium relations, and additional specified relationships among the process variables.

Let us first consider a heated mixer in which a stream of oxygen and nitrogen at 25°C is blended with a stream of pure oxygen at 40°C, and the combined stream is heated to 50°C.



A degree-of-freedom analysis on this simple process would proceed as follows:

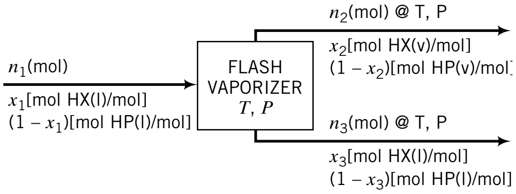
$$\begin{array}{l} 6 \text{ variables } (n_1, \ldots, n_5, \text{ and } Q) \\ \underline{-3 \text{ relations (2 material balances and 1 energy balance)}} \\ = 3 \text{ degrees of freedom} \end{array}$$

Thus, three specifications would have to be provided in the problem statement, following which the system equations could be solved for all remaining unknowns. Specifying values of three of the variables would suffice, as would giving values for two of the variables and a relationship between the masses of the two feed streams. (Convince yourself—choose values for any three variables and mentally go through the calculation of the remaining three from the system equations.)

The following example illustrates a degree-of-freedom analysis for a process that involves vapor–liquid equilibria between effluent process streams.

EXAMPLE 10.1-1 *Degree-of-Freedom Analysis of a Flash Vaporizer*

A liquid mixture of *n*-hexane (HX) and *n*-heptane (HP) at a high pressure is abruptly exposed to a lower pressure. A portion of the mixture evaporates, yielding a vapor mixture relatively rich in hexane (the more volatile of the two feed components) and a residual liquid mixture relatively rich in heptane. The two product streams are in equilibrium at temperature T and pressure P; their compositions are related by Raoult's law (Section 6.4b).



The relations among the system variables are as follows:

$$n_1 = n_2 + n_3 \qquad \text{(total mole balance)} \qquad \textbf{(1)}$$

$$n_1 x_1 = n_2 x_2 + n_3 x_3 \qquad \text{(hexane balance)} \qquad \textbf{(2)}$$

$$\left.\begin{aligned} x_2 P &= x_3 p^*_{\text{HX}}(T) \qquad \textbf{(3)} \\ (1 - x_2)P &= (1 - x_3)p^*_{\text{HP}}(T) \qquad \textbf{(4)} \end{aligned}\right\} \text{(Raoult's law)}$$

$$\left.\begin{aligned} \log[p^*_{\text{HX}}(T)] &= A_{\text{HX}} - B_{\text{HX}}/(T + C_{\text{HX}}) \qquad \textbf{(5)} \\ \log[p^*_{\text{HP}}(T)] &= A_{\text{HP}} - B_{\text{HP}}/(T + C_{\text{HP}}) \qquad \textbf{(6)} \end{aligned}\right\} \text{(Antoine equation)}$$

Perform a degree-of-freedom analysis on this system, and outline a solution procedure for the following sets of design variables:

1. n_1, x_1, T, and x_3.
2. n_2, x_2, n_3, and x_3.
3. n_1, n_2, n_3, and T.

SOLUTION

Ten variables—$n_1, n_2, n_3, x_1, x_2, x_3, T, P, p^*_{\text{HX}}$, and p^*_{HP}—appear in these six equations. The system consequently has $10 - 6 = 4$ degrees of freedom. Four of these variables must be specified in a problem statement, following which the remaining six variables can be calculated from the given six equations. Notice how the difficulty of the calculation depends dramatically on which four variables are specified (i.e., which ones are the design variables).

1. ***Design variables n_1, x_1, T, and x_3.*** If values of these four variables are specified, the following relatively straightforward solution procedure could be used to solve for the remaining (state) variables.

$$\boxed{\text{Specify values for } n_1, x_1, T, x_3}$$

$$\Downarrow$$

$$\boxed{\begin{aligned} p^*_{\text{HX}} &= \cdots \text{ (from Equation 5)} \\ p^*_{\text{HP}} &= \cdots \text{ (from Equation 6)} \end{aligned}}$$

$$\Downarrow$$

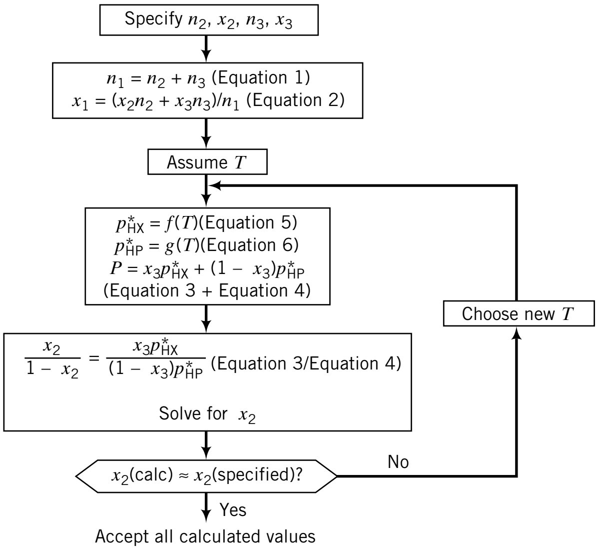
$$\boxed{\begin{aligned} P &= x_3 p^*_{\text{HX}} + (1 - x_3)p^*_{\text{HP}} \quad &\text{(Equations 3 + 4)} \\ x_2 &= x_3 p^*_{\text{HX}}/P &\text{(Equation 3)} \end{aligned}}$$

$$\Downarrow$$

$$\left.\boxed{\begin{aligned} n_2 + n_3 &= n_1 \quad &\text{(Equation 1)} \\ n_2 x_2 + n_3 x_3 &= n_1 x_1 &\text{(Equation 2)} \end{aligned}}\right\} \text{Solve for } n_2, n_3$$

The first four equations each contain one unknown and can be solved directly; the final two equations in two unknowns are linear, so they also can be solved without difficulty.

2. ***Design variables n_2, x_2, n_3, and x_3.*** For this choice of design variables, a relatively lengthy trial-and-error procedure is required to solve for the remaining variables. One possible procedure is shown here.



Several methods can be used for the trial-and-error calculation, such as defining $F(T) = x_2(\text{calc}) - x_2(\text{specified})$ and using the goalseek tool on a spreadsheet to find the value of T for which $F(T) \approx 0$.

3. ***Design variables n_1, n_2, n_3, and T.*** Some choices of design variables lead to contradictions of the system equations and so are not allowed. For example, choosing n_1, n_2, and n_3 as design variables is forbidden: once any two of these variables are specified, the third may not be assigned a value independently, but must be calculated from Equation 1.

TEST YOURSELF (Answers, p. 662)

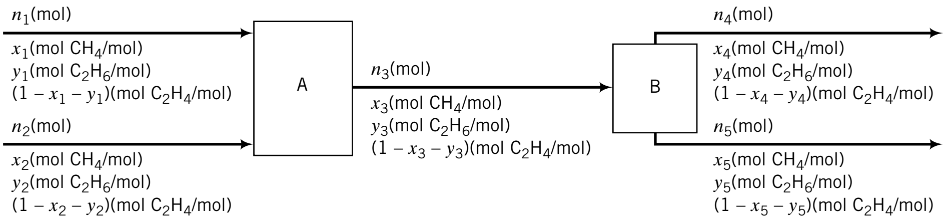
1. Consider the following set of equations:

$$x_1 + 2x_2 - x_3^2 = 0$$
$$5x_1 - x_2^3 + 4 = 0$$

   (a) How many degrees of freedom does this system possess?
   (b) Which choice of a design variable would lead to an easier procedure to solve for the state variables, x_1 or x_3?
2. A liquid stream containing species A, B, C, and D enters a vaporizer (flow rates $n_1, \ldots, n_4$ kg/s). Essentially all of the A, 25% of the B, and none of the D is vaporized. The C is distributed between the liquid and vapor products according to a known equilibrium relationship. How many degrees of freedom does this process possess?
3. Consider the equations (i) $5x - 3y = 7$, (ii) $10x - 3y - 6z = 14$, and (iii) $y = 2z$.
   (a) Try to solve this system of equations for x, y, and z, and explain why you can't do it.
   (b) Prove that the set of equations has one degree of freedom, choose a design variable, specify a value for it, and determine the corresponding state variable values.

10.1b Multiple-Unit Processes

A process that contains two or more interconnected units has fewer degrees of freedom than the sum of the degrees of freedom of the individual unconnected units. Suppose, for example, that an output stream from the first of two units is the feed stream to the second unit and that no reactions occur in either unit.



Let us first perform a degree-of-freedom analysis for unit A. We count nine variables (three for each stream entering or leaving the unit) and three equations (mass balances on methane, ethane, and ethylene) to obtain six degrees of freedom. The same result is obtained for unit B. Individually, then, there are 12 *local* degrees of freedom—local signifying that we are considering each unit as isolated, unconnected to the others.

In fact, the units *are* linked so that in the preceding analysis we have overcounted variables: specifically, the three variables associated with the product stream from unit A (n_3, x_3, and y_3) are identical to the three associated with the feed to unit B. The analysis proceeds as follows:

$$\begin{aligned} \text{system variables} &= 18 \text{ local} - 3 \text{ overcounted} = 15 \\ \underline{\text{system equations}} &\underline{= 3 \text{ balances for each unit} = 6} \\ \text{degrees of freedom} &= 9 \end{aligned}$$

Thus, nine process stream variable values must be specified for the given system, at which point balances can be used to determine the remaining six variables.

In general, the number of degrees of freedom of a system of linked units equals the number of degrees of freedom of the individual units—that is, the total local degrees of freedom—minus the number of **ties** (variables common to two or more units, and hence overcounted), minus the number of any additional relations that were not counted in the individual unit analyses.

The procedure for performing a degree-of-freedom analysis on a multi-unit process may be summarized as follows:

1. ***Draw and completely label the flowchart.***
2. ***Determine the local degrees of freedom for each process unit, mixing point, and stream-splitting point in the process.*** The local degrees of freedom equal the number of unknown variables involved in the unit equations minus the number of independent relations among these variables. The relations may include material balances, an energy balance, equilibrium relations, and specifications of conversions, yields, selectivities, and mass or mole ratios. If a relation involves any variables belonging to units other than the one in question, however, count it in step 3 rather than here.
3. ***Determine the degrees of freedom of the total process.*** This quantity equals the sum of the local degrees of freedom, minus the number of independent relations among process variables that were not counted in step 2 (such as overall reactant conversions or percentage recoveries), minus the number of ties (overcounted variables) between units.

If the number of degrees of freedom determined in this manner equals zero, all unknown variables can, in principle, be determined. If n_{df} is greater than zero, then n_{df} variable values must be specified as design variables, and the remaining state variables may then be calculated.

The following example illustrates this procedure.

EXAMPLE 10.1-2 *Degree-of-Freedom Analysis of a Multiple-Unit Process*

Equipment Encyclopedia
heat exchanger,
reactor, condenser

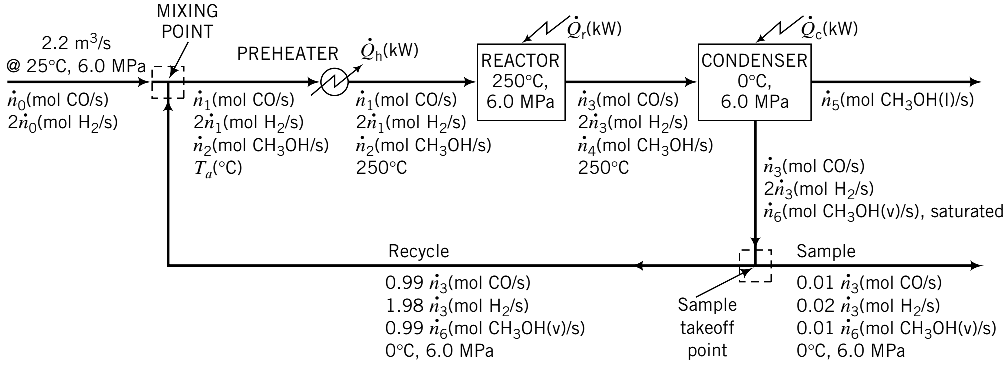
Methanol may be produced from carbon monoxide and hydrogen in the reaction

$$CO + 2H_2 \rightarrow CH_3OH$$

The fresh feed, which contains CO and H_2 in stoichiometric proportion, enters the process at a rate of 2.2 m^3/s at 25°C and 6.0 MPa and combines adiabatically with a recycle stream. The combined stream is heated to 250°C and fed to the reactor. The reactor effluent emerges at the same temperature and is cooled to 0°C at $P = 6.0$ MPa, partially condensing the methanol product. The gas leaving the condenser is saturated with methanol: 1% is taken off for process monitoring purposes and the remainder is recycled. An overall CO conversion of 98% is achieved. The ratio of H_2 to CO is 2 mol $H_2/1$ mol CO everywhere in the process system. Ideal gas behavior may be assumed.

Carry out a degree-of-freedom analysis for this process and show that the given information is sufficient to allow the calculation of the component flow rates for all streams, the required heat duties for all process units, and the temperature of the combined feed stream to the reactor preheater.

SOLUTION



In labeling the flowchart, we have taken advantage of the fact that CO and H_2 remain in stoichiometric proportion throughout the process, which cuts down on the number of unknown variables that must be defined: if the flow rate of CO is $\dot{n}_i$, the flow rate of H_2 must be $2\dot{n}_i$. However, this also means that we cannot write independent balances on these two species. We must therefore allow for no more than *two* independent material balances on each process unit when we do the degree-of-freedom analysis, rather than the three that would normally be allowed when three species are involved in a process.

Mixing Point 6 variables $(\dot{n}_0, \dot{n}_1, \dot{n}_2, \dot{n}_3, \dot{n}_6, T_a)$
$-$ 4 relations (2 material balances, 1 energy balance, and the ideal gas equation of state for the fresh feed)
$=$ 2 local degrees of freedom

Preheater 4 variables $(\dot{n}_1, \dot{n}_2, T_a, \dot{Q}_h)$
$-$ 1 relation (The energy balance. We cannot count material balances, since in labeling the outlet flow rates the same as the inlet flow rates, we have implicitly used up the two allowed material balances.)
$=$ 3 local degrees of freedom

Reactor 5 variables $(\dot{n}_1, \dot{n}_2, \dot{n}_3, \dot{n}_4, \dot{Q}_r)$
$-$ 3 relations (2 molecular species balances, 1 energy balance)
$+$ 1 chemical reaction
$=$ 3 local degrees of freedom

Condenser 5 variables $(\dot{n}_3, \dot{n}_4, \dot{n}_5, \dot{n}_6, \dot{Q}_c)$
$-$ 3 relations [1 material balance (Can you see why?), 1 energy balance, saturation condition at outlet]
$=$ 2 local degrees of freedom

Purge Point 2 variables ($\dot{n}_3, \dot{n}_6$)
$-$ 0 relations (In labeling the chart, we have built in all allowed balances. If this is not clear to you, try writing a balance on, say, hydrogen, and observe the result.)
$=$ 2 local degrees of freedom

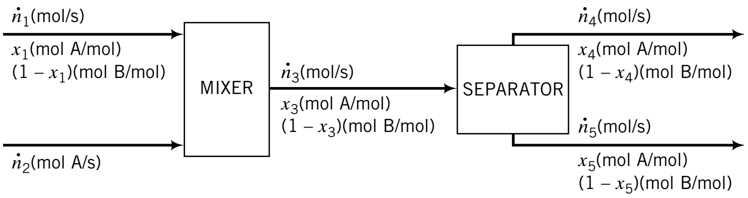
Process 12 local degrees of freedom (2 + 3 + 3 + 2 + 2)
$-$ 11 ties ($\dot{n}_1$, $\dot{n}_2$, and $\dot{n}_6$ were each counted three times, $\dot{n}_3$ was counted four times, and $\dot{n}_4$ and T_a were each counted twice)
$-$ 1 additional relation (98% overall conversion)
$=$ 0 degrees of freedom

The process is therefore completely specified.

The solution of the system equations for all unknown variables is straightforward. The ideal gas equation of state applied to the fresh feed stream yields $\dot{n}_0$. The specified overall CO conversion yields $\dot{n}_3$ from the equation $0.01\dot{n}_3 = (1 - 0.98)\dot{n}_0$. Raoult's law at the condenser outlet combined with the calculated value of $\dot{n}_3$ yields $\dot{n}_6$, and an overall carbon balance yields $\dot{n}_5$. Balances on CO and CH_3OH at the mixing point yield $\dot{n}_1$ and $\dot{n}_2$, and an energy balance for the same subsystem yields T_a. An energy balance on the preheater then yields $\dot{Q}_h$. A methanol balance on the condenser yields $\dot{n}_4$, and then energy balances on the reactor and the condenser yield $\dot{Q}_r$ and $\dot{Q}_c$, respectively.

TEST YOURSELF (Answers, p. 662)

Consider the flowchart shown here for a nonreactive mixing–separation process.



1. How many local degrees of freedom does each unit possess?
2. How many total degrees of freedom does the entire process system possess?

10.1c Solving Algebraic Equations

Once you have specified values for your design variables, you are faced with the task of solving the system equations for the state variables. For relatively simple processes, the manual techniques presented in previous chapters are applicable and should be used.

Unfortunately, chemical processes are seldom relatively simple. For example, most problems you have encountered in this text could eventually be reduced to the solution of linear algebraic equations.

$$0.21n_{\text{air}} = 2015 \qquad \text{Solve for } n_{\text{air}}$$

$$\left.\begin{aligned} n_1 + n_2 &= 100 \\ 0.96n_1 + 0.05n_2 &= 50 \end{aligned}\right\} \qquad \text{Solve for } n_1 \text{ and } n_2$$

However, some could not. You encountered nonlinear equations, for example, when learning about equations of state:

$$\frac{P\hat{V}}{RT} = 1 + \frac{B}{\hat{V}} + \frac{C}{\hat{V}^2} + \frac{D}{\hat{V}^4} + \frac{E}{\hat{V}^5} \qquad \text{Given } P \text{ and } T, \text{ solve for } \hat{V}$$

and when studying vapor–liquid equilibrium

$$\log_{10} p^* = A + B\big/(C + T) \qquad \text{Given } T, \text{ solve for } p^*$$

and when applying the first law of thermodynamics

$$\Delta\dot{H} = a(T - 25) + b(T^2 - 25^2) + c(T^3 - 25^3) \qquad \text{Given } \Delta\dot{H}, \text{ solve for } T$$

Solving sets of linear equations is tedious but straightforward. Solving nonlinear equations, on the other hand, may or may not be straightforward. Doing so in all but the simplest cases involves trial-and-error, and there is usually no guarantee that you will be able to find a solution, or that a solution you find is the only possible solution, or even that a solution exists.

We suggest the following guidelines for solving n algebraic equations in n unknowns.

- For linear equations with $n \leq 3$ or a single simple nonlinear equation, (e.g., $y^2 - 2y - 3 = 0$, $e^{-x} = 0.2$, or $\sin\theta = 0.5$), solve manually using high school algebra methods.
- For a single complex nonlinear equation of the form $f(x) = 0$, use a spreadsheet or an equation-solving program. If you use a spreadsheet, put an estimated value of x in one cell and the formula for $f(x)$ in a second cell, then use the goalseek tool to set the value in the second cell equal to zero by varying the value in the first cell. The final value in the first cell is the desired solution.
- For linear equations with $n > 3$ or nonlinear equations with $n \geq 2$, use an equation-solving program.

10.2 SEQUENTIAL MODULAR SIMULATION

As we noted at the beginning of this chapter, there are two broad approaches to the automated solution of the balance equations for a process system: the **sequential modular approach** and the **equation-based approach.** This section outlines the first of these methods. The balance equations (and any other equations that may arise from physical considerations or process specifications) for each unit are written and solved. If there are no recycle streams, the calculation moves from one unit to another, until all units have been covered. If there is a **cycle** (the conventional term for a recycle loop in a process flowchart), a trial-and-error procedure is required: values of one or more stream variables in the cycle are assumed; the balance equations for units in the cycle are solved, one unit at a time, until the values of the assumed variables are recalculated; new variable values are assumed; and the procedure is repeated until the assumed and calculated values agree.

The object of the presentation that follows is not to enable you to go out and simulate complex processes—the treatment is too brief and general for that—but simply to give you a sense of the structure of process simulation programs and calculations and to provide an idea of what such programs can do.

10.2a Elements of a Modular Simulation

The first step in setting up a process for the sequential modular approach is to reconstruct the process flowchart in terms of **blocks** or **modules** (process units or operations) and streams connecting them. Several types of blocks and names that might be given to them are as follows:

`MIX`	Mix several inlet streams adiabatically to form one product stream.
`SPLIT`	Split a single inlet stream into two or more product streams with the same composition and temperature.
`COMPRESS`	Raise the pressure of a gas by a specified amount.
`PUMP`	Raise the pressure of a liquid by a specified amount.
`FLASH`	Convert a liquid stream at one pressure to liquid and vapor streams in equilibrium at a lower pressure.

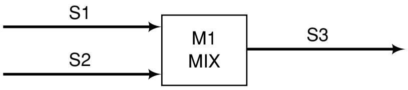
`DISTILL`
`EXTRACT`
`CRYSTAL`
`ABSORB`
	Simulate the separation processes of distillation, extraction, crystallization, and absorption.

`REACT`	Simulate a chemical reactor.

An additional block type—the convergence block—has a function to be described later.

The simulation program contains a built-in subprogram corresponding to each block type. To simulate a process, you would use the simulation program to build a flowchart and then enter known block and stream variable values in forms provided by the program. When you subsequently run the simulation, a series of calls to the block subroutines would lead to the solution of the process material and energy balance equations.

For example, suppose two streams labeled `S1` and `S2` are mixed adiabatically to form a third stream `S3`. A `MIX` block might be used to simulate this operation. (What the subprogram for this block might look like is the subject of the next example.)



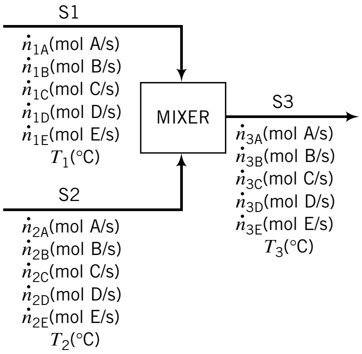
The step in the program that would perform the material and energy balances for this unit would be initiated by a statement equivalent to the program statement.

```
CALL MIX(M1,S1,S2,S3)
```

`M1` is a label, identifying the unit that has streams `S1` and `S2` as inputs and stream `S3` as an output. In the subprogram, `S1`, `S2`, and `S3` would each be arrays, the elements of which contain enough information to specify the flow rate, composition, and temperature of each stream. Prior to this statement in the program, the values of the elements of arrays `S1` and `S2` would have been either specified or determined as the outputs of other blocks. The subprogram would calculate the component flow rates of stream `S3` by solving material balance equations and (if required) the temperature of the stream by solving the energy balance equation ($\Delta\dot{H} = 0$).

EXAMPLE 10.2-1 *Structure of a Mixing Block Routine*

Two streams are mixed adiabatically. Each stream may contain any of five components (A, B, C, D, and E). No phase changes take place. The heat capacities of all components may be approximated as constants, and the heat of mixing may be neglected. A computer program is to be written to calculate the component molar flow rates and temperature of the product stream from specified values of these quantities for the feed streams.



1. Write equations for the product stream component flow rates and temperature.
2. Create a spreadsheet that would determine the product stream variables from given values of the feed stream variables.
3. Write a Fortran subroutine that would perform the same calculations.

SOLUTION

1. A degree-of-freedom analysis of this unit reveals 18 variables (six for each stream) and six equations (five material balances and an energy balance) for a net 12 degrees of freedom. The design variables are the 12 feed stream variables, leaving the product stream component flow rates and temperature as the state variables.

The material balance equations are trivial:

$$\dot{n}_{3\text{A}} = \dot{n}_{1\text{A}} + \dot{n}_{2\text{A}} \quad \textbf{(1)}$$

$$\dot{n}_{3\text{B}} = \dot{n}_{1\text{B}} + \dot{n}_{2\text{B}} \quad \textbf{(2)}$$

$$\dot{n}_{3\text{C}} = \dot{n}_{1\text{C}} + \dot{n}_{2\text{C}} \quad \textbf{(3)}$$

$$\dot{n}_{3\text{D}} = \dot{n}_{1\text{D}} + \dot{n}_{2\text{D}} \quad \textbf{(4)}$$

$$\dot{n}_{3\text{E}} = \dot{n}_{1\text{E}} + \dot{n}_{2\text{E}} \quad \textbf{(5)}$$

Let us choose as the reference state for each component the system phase (liquid or gas), temperature (T_1), and pressure (1 atm). The specific enthalpy of, say, component A in the product stream would be $\hat{H}_{3\text{A}} = C_{p\text{A}}(T_3 - T_1)$. (Remember that there are no phase changes and we are assuming constant heat capacities.) The energy balance for this open adiabatic system is $\Delta\dot{H} = 0$, or

$$\begin{aligned}\Delta\dot{H} &= \sum \dot{n}_{\text{out}}\hat{H}_{\text{out}} - \sum \dot{n}_{\text{in}}\hat{H}_{\text{in}} \\ &= [\dot{n}_{\text{A}3}C_{p\text{A}} + \dot{n}_{\text{B}3}C_{p\text{B}} + \cdots + \dot{n}_{\text{E}3}C_{p\text{E}}](T_3 - T_1) \\ &\quad - [\dot{n}_{\text{A}2}C_{p\text{A}} + \dot{n}_{\text{B}2}C_{p\text{B}} + \cdots + \dot{n}_{\text{E}2}C_{p\text{E}}](T_2 - T_1) = 0\end{aligned}$$

(All of the enthalpies of the stream 1 components are zero). Solving this equation for T_3 yields

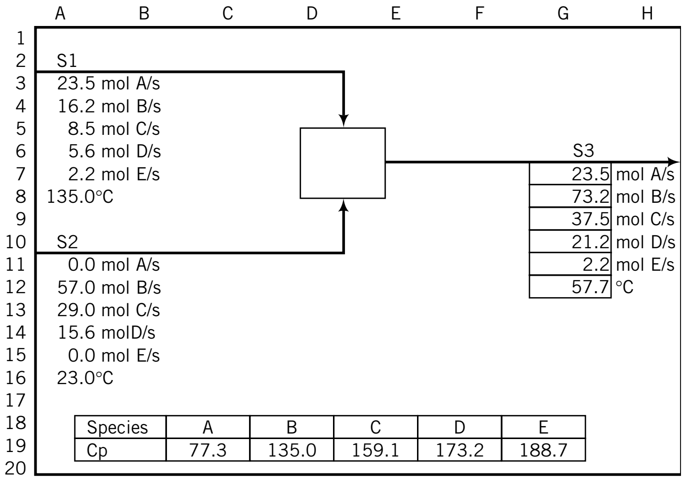
$$T_3 = T_1 + \frac{\dot{n}_{\text{A}2}C_{p\text{A}} + \dot{n}_{\text{B}2}C_{p\text{B}} + \dot{n}_{\text{C}2}C_{p\text{C}} + \dot{n}_{\text{D}2}C_{p\text{D}} + \dot{n}_{\text{E}2}C_{p\text{E}}}{\dot{n}_{\text{A}3}C_{p\text{A}} + \dot{n}_{\text{B}3}C_{p\text{B}} + \dot{n}_{\text{C}3}C_{p\text{C}} + \dot{n}_{\text{D}3}C_{p\text{D}} + \dot{n}_{\text{E}3}C_{p\text{E}}}(T_2 - T_1) \quad \textbf{(6)}$$

Equations 1 to 6 may be solved sequentially for the product stream variables.

2. A spreadsheet program that solves the six system equations is easy to construct. With a little more effort, a flowchart can be imbedded into the spreadsheet in such a way that the product stream variables are automatically updated if any of the input stream variables are changed. In the example that follows, the following heat capacities are used:

Species	A	B	C	D	E
C_p[J/(mol·°C)]	77.3	135.0	159.1	173.2	188.7

The spreadsheet might appear as follows.[1]



S1
23.5 mol A/s
16.2 mol B/s
8.5 mol C/s
5.6 mol D/s
2.2 mol E/s
135.0°C

S2
0.0 mol A/s
57.0 mol B/s
29.0 mol C/s
15.6 molD/s
0.0 mol E/s
23.0°C

S3
23.5 mol A/s
73.2 mol B/s
37.5 mol C/s
21.2 mol D/s
2.2 mol E/s
57.7 °C

Species	A	B	C	D	E
Cp	77.3	135.0	159.1	173.2	188.7

The flowchart shows a set of specified input variables for streams `S1` and `S2` and the calculated product stream variables determined from Equations 1 to 6. The formula of Equation 1 for $\dot{n}_{\text{A}3}(= \dot{n}_{\text{A}1} + \dot{n}_{\text{A}2})$ would be entered in Cell G7 as

```
= A3 + A11
```

---

[1] The spreadsheet was created with Microsoft Excel®. The values and formulas were first entered, and then the line and rectangle drawing tools were used to create the flowchart. For clarity, most grid lines are not shown.

indicating that the value in Cell G7 would be obtained as the sum of the values in Cells A3 and A11. If the value in either of these cells is changed on the spreadsheet, the value in G7 would change accordingly. Similarly, the formula of Equation 6 for T_3 would be entered in Cell G12 as

```
= A8 + (A11*C19 + A12*D19 + A13*E19 + A14*F19 + A15*G19)*(A16-A8)/
  (G7*C19 + G8*D19 + G9*E19 + G10*F19 + G11*G19)
```

(*Verify.*) Changing either T_1 (in Cell A8) or T_2 (in Cell A16) on the spreadsheet would cause the new value of T_3 to appear in Cell G12.

3. A Fortran subroutine that performs the same calculations follows.

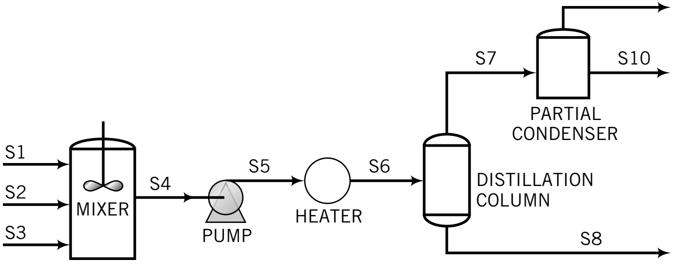
```
      SUBROUTINE MIX(M,S1,S2,S3)
C**** M IS A UNIT LABEL
C**** ARRAYS S1 AND S2 ARE INPUT, AND S3 IS OUTPUT
      DIMENSION S1(6),S2(6),S3(6)
      COMMON CP(5)
C**** SOLVE MATERIAL BALANCES
      DO 100J = 1,5
  100 S3(J) = S1(J) + S2(J)
C**** IF T1 = T2, SET T3 = T1 AND RETURN
      T1 = S1(6)
      T2 = S2(6)
      IF (T1.EQ.T2) GO TO 200
C**** EVALUATE SUMS FOR ENERGY BALANCES
      SUM2 = 0.0
      SUM3 = 0.0
      DO 150J = 1,5
      SUM2 = SUM2 + S2(J)*CP(J)
  150 SUM3 = SUM3 + S3(J)*CP(J)
C**** SOLVE ENERGY BALANCE FOR T3
      T3 = T1 + SUM2*(T2-T1)/SUM3
      S3(6) = T3
      RETURN
  200 S3(6) = T1
      RETURN
      END
```

The next example illustrates the structuring of a sequential modular process simulation using blocks of the types just described.

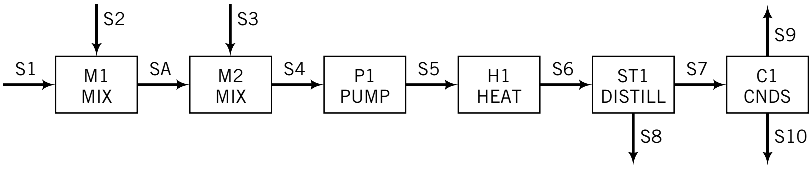
EXAMPLE 10.2-2 *Simulation of an Acyclic Process*

Equipment Encyclopedia
pump, heat exchanger, distillation column, condenser

The flowchart shown here depicts a multi-unit separation process. Three liquid streams are mixed adiabatically; the product stream is pumped through a heater to a distillation column, and the overhead product from the column is partially condensed to yield liquid and vapor products. Using the blocks `MIX` (mix two streams to form a third), `PUMP`, `HEAT`, `DISTILL`, and `CNDS`, construct a block diagram for the simulation of this process.



SOLUTION Since three streams are mixed in the process but the `MIX` routine can only handle two feed streams, we need to use this block twice. In other respects, the block diagram looks like the process flowchart.



In the main simulation program, a series of statements resembling the following would be included (the first argument of each calling statement is the unit identifier):

```
CALL MIX(M1,S1,S2,SA)
CALL MIX(M2,S3,SA,S4)
CALL PUMP(P1,S4,S5,parameters)
CALL HEAT(H1,S5,S6,parameters)
CALL DISTILL(ST1,S6,S7,S8,parameters)
CALL CNDS(C1,S7,S9,S10,parameters)
```

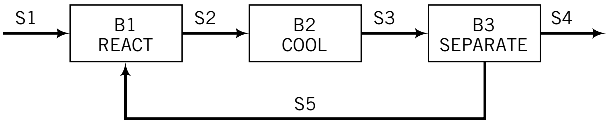
The `PUMP` calculation would cause the pressure of the liquid stream to be raised by a specified amount; the routine might also calculate the required shaft work for this operation and could go as far as to specify the type and size of pump needed for the job. The `HEAT` routine would calculate the heat input required to achieve the required temperature change and might also perform heat exchanger design calculations.

The `DISTILL` subroutine would solve material and energy balance equations to determine the flow rates and compositions of both product streams and the heat requirement for the distillation column. Depending on the level of sophistication of the simulation program, the subroutine might then go on to determine details of the column design for the given separation.

The `CNDS` subroutine would proceed in a similar manner for the condenser calculations—first solving material and energy balances to determine unknown flow rates and the heat duty, and then possibly performing design calculations.

10.2b Cyclic Systems and the Convergence Block

Suppose the block diagram of a process has the following appearance:



Further suppose that you know the values of the variables associated with stream `S1` and you wish to calculate the remaining stream variables.

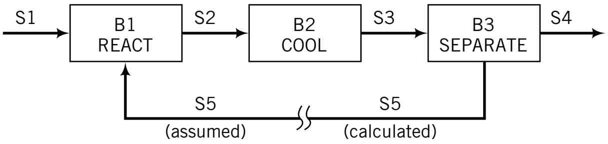
The procedure outlined in the previous section will not work, since there is no way to get the calculation started. To solve the equations for block `B1` you must know the variable values for both `S1` and `S5`, but you cannot know `S5` until you solve `B3`, for which you need `S3` and hence the solution of `B2`, which in turn requires a knowledge of `S2` and hence the solution of `B1`, and you are back where you began.

If the calculations were to be done by hand, overall system and subsystem balances would eventually yield n equations in n unknowns, and the equations could then in principle be solved for all the desired process variables. It would be difficult to write a sequential modular program to implement this method for an arbitrary process, however. Instead, the following iterative approach is used.

1. Assume variable values for a stream within the cycle (this is known as *tearing the cycle*).
2. Solve the system balance equations, working around the cycle from unit to unit until the tear stream variables are recalculated.

3. If the assumed and calculated tear stream variables agree within a specified tolerance, the solution is complete; if they do not, use the new values or some combination of the new and old values to initiate another swing around the cycle. Iterate in this manner until convergence is achieved.

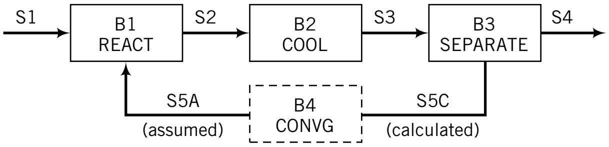
Suppose, for example, that in the process described above we choose `S5` as the tear stream. The flowchart might then appear as shown here:



The calculation would begin with an assumption of values of the variables associated with stream `S5`. The equations for blocks `B1`, `B2`, and `B3` could then be solved sequentially. The solution for `B3` would yield calculated variable values for stream `S5`. New assumed variable variables would be determined by one of several methods to be outlined, and the procedure would be repeated until the assumed and calculated values of the `S5` variables agree to within a specified tolerance.

The application of this procedure to a single tear stream variable is tantamount to solving an equation of the form $x = f(x)$, where $f(x)$ is the "function" that generates a new value of the tear stream variable x by working around the cycle. Techniques described in Appendix A.2—successive substitution and Wegstein's algorithm—can be used to perform this calculation.

Most simulation programs have a block, called a **convergence block,** that performs such calculations using the Wegstein algorithm. The output stream from this block contains the assumed set of tear stream variables, and the input stream contains the values calculated by working around the cycle. The block diagram for the simulated process would appear as follows:



It is conventional to show the convergence block using dashed lines, since it does not correspond to a physical operation in the process.

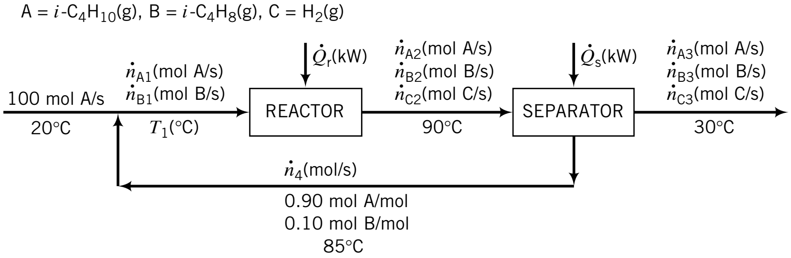
EXAMPLE 10.2-3 *Simulation of a Cyclic Process*

The gas-phase dehydrogenation of isobutane to isobutene

$$C_4H_{10} \rightarrow C_4H_8 + H_2$$

is carried out in a continuous reactor. A stream of pure isobutane (the fresh feed to the process) is mixed adiabatically with a recycle stream containing 90 mole% isobutane and the balance isobutene, and the combined stream goes to a catalytic reactor. The effluent from this process goes through a multistage separation process: one product stream containing all of the hydrogen and 1% of the isobutane leaving the reactor as well as some isobutene is sent to another part of the plant for additional processing, and the other product stream is the recycle to the reactor. The single-pass isobutane conversion in the reactor is 35%.

The process flowchart for a fresh feed of 100 mol isobutane is shown below. For simplicity, the symbol A will be used to denote isobutane, B denotes isobutene, and C denotes hydrogen.



All streams shown are gases. On the flowchart, $\dot{Q}_r$ is the required rate of heat transfer to the reactor and $\dot{Q}_s$ is the net rate of heat transfer to the separation process (which involves several heat addition and removal steps).

1. Perform a degree-of-freedom analysis on the process.
2. Choose a tear stream variable and convert the flowchart into a block diagram for a sequential modular simulation, using blocks `MIX`, `REACT`, `SEP`, and a convergence block `CONVG`.
3. Write a spreadsheet program to determine the labeled process variables on the chart.

SOLUTION

1. Three "units" comprise this process: the reactor, the separation process, and the mixing point, which in the process may be a stirred tank or simply a tee in the feed line. Let us first calculate the local degrees of freedom associated with each unit, and then the net degrees of freedom for the process.

Mixing Point 4 unknowns ($\dot{n}_{A1}, \dot{n}_{B1}, \dot{n}_4, T_1$)
− 3 balances (2 material balances, 1 energy balance)

1 local degree of freedom

Reactor (Count material balances on molecular species.)

7 unknowns ($\dot{n}_{A1}, \dot{n}_{B1}, \dot{n}_{A2}, \dot{n}_{B2}, \dot{n}_{C2}, T_1, \dot{Q}_r$)
− 4 balances (3 molecular species balances, 1 energy balance)
− 1 additional relation (35% single-pass conversion)
+ 1 chemical reaction

3 local degrees of freedom

Separator 8 unknowns ($\dot{n}_{A2}, \dot{n}_{B2}, \dot{n}_{C2}, \dot{n}_{A3}, \dot{n}_{B3}, \dot{n}_{C3}, \dot{n}_4, \dot{Q}_s$)
− 4 balances (3 material balances, 1 energy balance)
− 1 additional relation (isobutane split)

3 local degrees of freedom

(We used the information that the recycle contains no hydrogen when we did not label a variable n_{C4} on the flowchart, so we should not count this fact as a second additional relation.)

Overall Process 7 local degrees of freedom (1 + 3 + 3)
− 7 ties ($\dot{n}_{A1}, \dot{n}_{B1}, \dot{n}_{A2}, \dot{n}_{B2}, \dot{n}_{C2}, \dot{n}_4,$ and T_1 were each counted twice)

0 net degrees of freedom

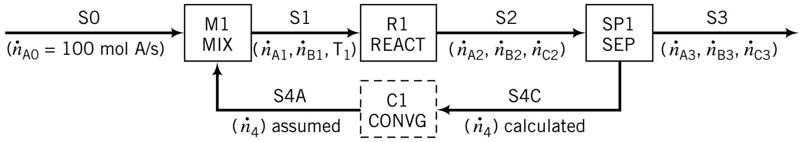
The problem can in principle be solved for all labeled variables.

2. Before planning the solution strategy, let us observe the flowchart and confirm that we cannot proceed in a unit-to-unit manner without trial and error.

   The mixing unit has one local degree of freedom and three unknowns. We cannot solve for $\dot{n}_{A1}$ and $\dot{n}_{B1}$ until we know $\dot{n}_4$. To determine this variable, we must solve the separation process balance equations, but we cannot do so unless we know $\dot{n}_{A2}, \dot{n}_{B2}$, and $\dot{n}_{C2}$. To calculate *these* variables, we must solve the reactor equations. Unfortunately, we cannot solve them either, since we must first know $\dot{n}_{A1}$ and $\dot{n}_{A2}$, for which we must solve the mixer equations, and we are back where we started.

The solution is to tear the cycle. We can tear it in any of three places: between the mixing point and the reactor, between the reactor and the separation process, or between the separation process and the mixing point. The first choice involves the trial-and-error determination of two variables, the second one involves three variables, and the third involves only one ($\dot{n}_4$). The fewer variables you have to determine by trial and error, the more likely you are to succeed. Let us therefore choose the recycle stream as the tear stream.

The block diagram for the simulation now appears as follows:

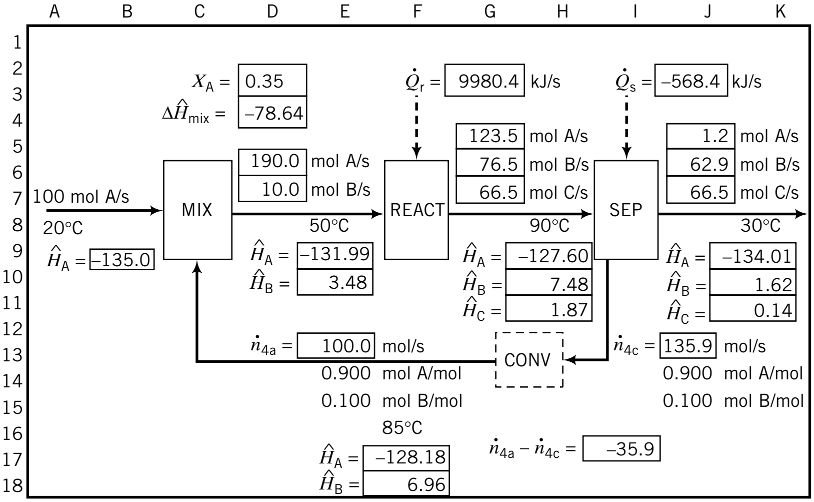


The program would take as input a guessed value for the tear stream variable $\dot{n}_4$ (stream S4A) and might contain the following sequence of statements:

```
CALL MIX(M1,S0,S4A,S1)
CALL REACT(R1,S1,S2,QR)
CALL SEP(SP1,S2,S3,S4R,QS)
CALL CONVG(C1,S4R,S4A)
```

(The first unit called is always the one following the tear stream.) The call of `SEP` would result in the recalculation of $\dot{n}_4$ from the separation process balances (stream `S4R`). `CONVG` would compare this value with the one initially assumed. If the two values agree to within a specified tolerance, the calculation would be terminated; otherwise, the new value would be used to begin another journey around the cycle. The nature of the iterative procedure performed by `CONVG` is discussed in greater detail in Appendix A.2.

3. Equations could be derived and solved for all of the unknown process variables, making trial-and-error solution unnecessary. However, for illustrative purposes we will set up the spreadsheet to parallel the sequential modular solution procedure of part 2.



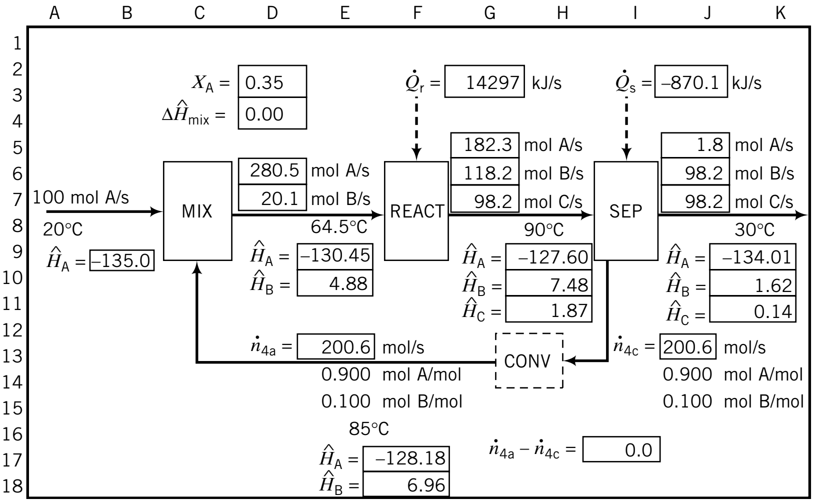
All $\hat{H}$s in kJ/mol

The spreadsheet shows an initially assumed value of the recycle flow rate ($\dot{n}_{4a}$) of 100.0 mol/s (Cell E13) and an assumed value of the mixing point outlet temperature of 50°C (Cell D8). The value of $\dot{n}_{4a}$ will be varied until the calculated recycle flow rate ($\dot{n}_{4c}$) in Cell J13 equals the assumed value, which it now does not. (The actual calculation will be done by finding the value of $\dot{n}_{4a}$ that drives the value of $\dot{n}_{4a} - \dot{n}_{4c}$ in Cell I17 to zero.) Once the flow rates are correct, the mixing point temperature will be varied to determine the value that drives $\Delta\dot{H} = \sum \dot{n}_{out}\hat{H}_{out} - \sum \dot{n}_{in}\hat{H}_{in}$ (in Cell D4) to zero for the adiabatic mixer.

The entries in selected spreadsheet cells are shown below, in the order in which they might be entered. The specific enthalpies are for the gaseous species at the stream temperatures relative to the elements at 25°C, with heats of formation taken from Table B.1 and heat capacity formulas taken from Table B.2. Their numerical values are in kJ/mol. The other cells contain labels to provide clarity (such as [$\hat{H}_A$ =] in Cell A9). A spreadsheet drawing tool is used to draw the lines (denoting streams) and boxes (denoting process steps).

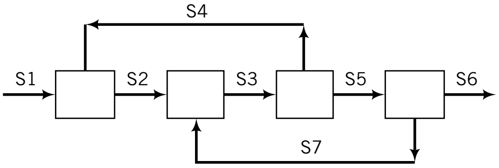
`D3 = 0.35` (given fractional conversion of A)
`A7 = 100` (basis of calculation)
`A8 = 20` (given fresh feed temperature)
`G8 = 90` (given reactor effluent temperature)
`J8 = 30` (given product stream temperature)
`E13 = 100` (initial guess for recycle stream flow rate)
`E14 = 0.900, J14 = 0.900` (given mole fraction of A in recycle stream)
`E15 = 0.100, J15 = 0.100` (calculated mole fraction of B in recycle stream)
`E16 = 85` (given temperature of recycle stream)
`D6 = A7 + E13*E14` (A balance on mixing point)
`D7 = E13*E15` (B balance on mixing point)
`D8 = 50` (initial guess for combined stream temperature. Later vary to make $\Delta\dot{H}_{\text{mixer}}$ `= 0.`)
`G5 = D6*(1-D3)` (unreacted A)
`G6 = D7 + D6*D3` (B balance on reactor: output = input + generation)
`G7 = D6*D3` (C balance on reactor: output = generation)
`J5 = 0.01*G5` (1% of A in reactor effluent)
`J13 = (G5-J5)/J14` (from A balance on separator)
`J6 = G6 - H13*H15` (B balance on separator)
`J7 = G7` (C balance on separator)
`B9 = -134.5 + 0.08946*(A8-25) + 30.13e-5*(A8^2-25^2)/2-18.91e-8*(A8^3-25^3)/3 + 49.87e-12*(A8^4 - 25^4)/4` [$= (\Delta\hat{H}_f^\circ)_A + \int C_{pA}dT$, specific enthalpy of A at 20°C relative to elements at 25°C.]
`F17, F18, E9, E10, H9, H10, H11, K9, K10, K11 =` specific enthalpies of A, B, and C at process temperatures (see formula for B9)
`D4 = D6*E9 + D7*E10 - A7*B9 - E13*E14*F17 - E13*E15*F18` ($\Delta\dot{H}_{\text{mixing point}}$)
`G3 = G5*H9 + G6*H10 + G7*H11 - D6*E9 - D7*E10` ($\Delta\dot{H}_{\text{reactor}}$)
`J3 = J5*K9 + J6*K10 + J7*K11 + J13*J14*F17 + J13*J15*F18 - G5*H9 - G6*H10 - G7*H11` ($\Delta\dot{H}_{\text{separator}}$)
`I17 = E13 - J13` (assumed recycle rate - recalculated recycle rate)

As noted previously, once the given spreadsheet has been set up, the value in Cell E13 ($= \dot{n}_{4a}$) is varied until the value in Cell I17 ($= \dot{n}_{4a} - \dot{n}_{4c}$) equals zero. This calculation is easily done using the goalseek tool in most spreadsheets. Then, the value in Cell D8 (the combined stream temperature) is varied until the value in Cell D4 ($\Delta\dot{H}_{\text{mixing point}}$) equals zero, reflecting the energy balance on the adiabatic mixing point. The resulting spreadsheet is the correct flowchart for the process, and appears as follows:

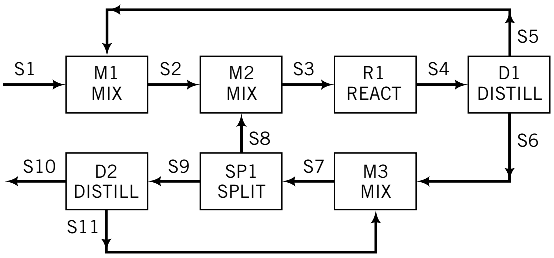


The recycle rate is 200.6 mol/s, and the adiabatic mixing temperature is 64.5°C. Any of the input variable values could now be changed and the flowchart easily recalculated.

Networks of recycle loops are commonly encountered in large processes, and a suitable choice of a tear stream may minimize the number of iterations required to solve the balance equations of such systems. For example, consider the block diagram shown below. There are two cycles in this process: `S2-S3-S4` and `S3-S5-S7`. To solve the system equations you could, for example, tear both `S4` and `S7`, which would require the inclusion of two convergence blocks and hence the simultaneous solution of two iterative loops; however, you can instead tear one stream common to both cycles (`S3`), probably decreasing the computation time required to achieve the solution.

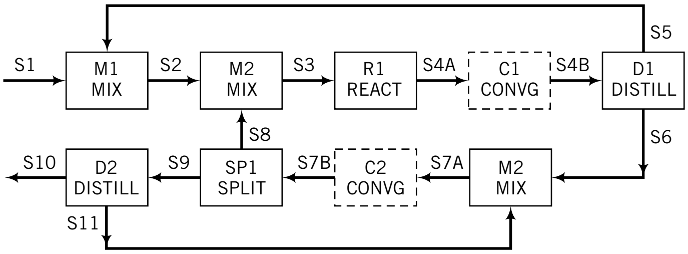


On the other hand, you will commonly encounter systems where you have no choice but to tear two or more streams, as in the next process.



There are three cycles: `S2-S3-S4-S5`, `S7-S9-S11`, and `S3-S4-S6-S7-S8`, and no single stream that if torn would permit the solution of all the system equations. For instance, if you tear `S3` you could work your way around the first cycle to unit `M2` but you would be stuck there for lack of knowledge of `S8`, and you would be similarly stuck at unit `M3` in the third cycle since you would not know `S11`.

One of many possible ways to analyze this system is to tear `S4` and `S7` (so that at least one stream in each cycle is torn). You must call the block programs in an order for which they can be solved. Remember that `S1`, `S4B`, and `S7B` are presumably known, and convince yourself that the program following the block diagram would in principle work.



```
CALL DISTILL (D1,S4B,S5,S6)     (Calculates S5,S6)
CALL MIX (M1,S1,S5,S2)          (Calculates S2)
CALL SPLIT (SP1,S7B,S8,S9)      (Calculates S8,S9)
CALL MIX (M2,S2,S8,S3)          (Calculates S3)
CALL REACT (R1,S3,S4A)          (Calculates S4A)
CALL CONVG (C1,S4A,D1,S4B)      (Forces convergence of S4)
CALL DISTILL (D2,S9,S10,S11)    (Calculates S10,S11)
CALL MIX (M3,S6,S11,S7A)        (Calculates S7A)
CALL CONVG (C2,S7A,D1,S7B)      (Forces convergence of S7)
```

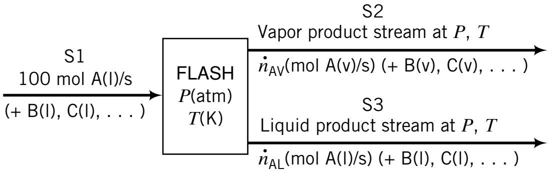
Other choices of tear streams could be made, and some simulation programs would permit you to use a single convergence block to force convergence of both tear streams simultaneously.

Techniques exist to determine systematically how many streams must be torn when multiple cycles occur and the order in which to carry out the subsequent calculations. We will not discuss these matters here.

10.2c Design Specifications

In the process simulations we have discussed so far, the direction of flow of information corresponded to the direction of flow of the process streams—from feeds to products and around cycles. This mode of information flow is appropriate if the object is to calculate the output of a process for a given input and set of process parameters (temperatures, pressures, etc.); however, it often happens that a desired output is specified and input or process unit parameters required to achieve this output are to be calculated. A feature of process simulation programs called a *design specification* is used for calculations of this type.

Consider, for example, a single adiabatic flash evaporator for which the flow rate, composition, temperature, and pressure of the feed stream are known.

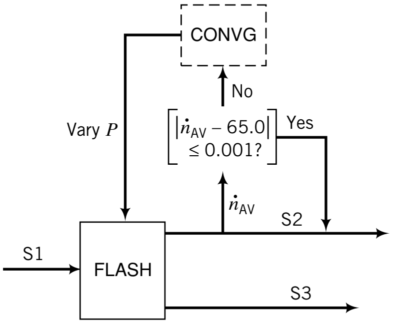


If the pressure in the evaporator is specified, a single call to the `FLASH` subprogram (which contains applicable vapor–liquid equilibrium correlations) yields the component flow rates in both product streams as well as the evaporator temperature. Suppose, however, that one of the component flow rates in one of the product streams is specified (e.g., $\dot{n}_{AV} = 65.0$ mol/s) and you wish to determine the value of P required to achieve the desired separation. The `FLASH` program by itself is incapable of performing this determination: it is set up to perform the forward calculation only. The approach is to set up an artificial cycle, varying the value of P (the *manipulated variable*) until the calculated output variable (the *sampled variable*) is within a specified tolerance of the desired value. For example, you might specify

$$|\dot{n}_{AV} - 65.0 \text{ mol A/s}| \leq 0.001 \text{ mol A/s (i.e., } 64.999 \text{ mol A/s} \leq \dot{n}_{AV} \leq 65.001 \text{ mol A/s)}$$

This inequality is called the *design specification* for the process.

A block diagram for the simulation with this design specification incorporated would be as follows:



A value of the manipulated variable (P) is initially guessed and the flash block equations are solved to generate the variables associated with streams `S2` (including $\dot{n}_{AV}$) and `S3`. The value of the sampled variable ($\dot{n}_{AV}$) is substituted into the design specification ($|\dot{n}_{AV} - 65.0 \text{ mol A/s}| \le 0.001$). If the specification is not satisfied, the convergence block generates a new value of P and the calculations are repeated. When the sampled variable value satisfies the design specification, the value of the manipulated variable is accepted and the simulation proceeds to downstream blocks. The sampled variables in a design specification (there may be several of them) may be associated with the product streams of the unit for which the manipulated variable is being adjusted (as in this example), or they may be associated with streams far removed from this unit.

Any number of design specifications may be built into a simulation, providing considerable flexibility for process design. You should remember, however (and if you do much simulation you will certainly be reminded), that whenever convergence blocks are part of a simulation there is no guarantee that convergence will be achieved, and the more convergence blocks you have the less likely you are to achieve it. In general, the better your initial guesses of the manipulated variable values, the more likely you are to achieve convergence and to achieve it rapidly.

An example of a sequential modular simulation of a relatively large process is given in Example 10.3-3, following a discussion of the second broad approach to process simulation.

10.3 EQUATION-BASED SIMULATION

The sequential modular approach to process simulation solves system equations in blocks corresponding to the unit operations that make up the process. The block diagram for the process looks very much like the traditional process flowchart. Since engineers are accustomed to viewing chemical processes as sequences of unit operations, they tend to feel comfortable with this approach.

In the **equation-based approach,** the equations for all units are collected and solved simultaneously. The natural decomposition of the system into its constituent unit operations is therefore lost. Moreover, the simultaneous solution of large numbers of equations, some of which may be nonlinear, can be a cumbersome and time-consuming problem, even for a powerful computer. For all these reasons, most commercial simulation programs were still based on the sequential modular approach when this text was written.

However, there are disadvantages associated with the sequential modular method. The block subroutines for simulating specific unit processes are designed to operate in a forward calculation mode only: that is, they calculate product stream variables from given values of feed stream variables and process conditions. Frequently, the problems the process engineer wants to solve fall into either of two other categories: (a) given process conditions and product stream variables, calculate feed stream variables; (b) given feed and product stream variables, calculate process conditions. In both cases, iterative calculations using design specifications and convergence blocks are required to solve the problems using a sequential modular program.

These difficulties vanish if the system equations are simply collected and solved for all unknown variables. Several powerful equation-solving algorithms are available in commercial programs like Maple®, Mathematica®, Matlab®, Mathcad®, and E-Z Solve® that make the equation-based approach competitive with the sequential modular approach. Many researchers in the field believe that as this trend continues, the former approach will replace the latter one as the standard method for flowsheet simulation. (Engineers are also working on "simultaneous modular" methods, which combine features of both sequential modular and equation-based approaches. We will not deal with these refinements here, however.)

The following example illustrates the equation-based approach.

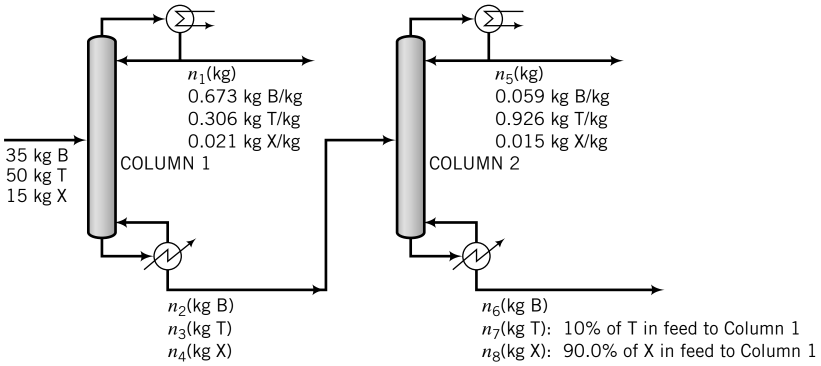
EXAMPLE 10.3-1 *Simulation and Design of a Two-Column Separation Process*

Equipment Encyclopedia
distillation column

A stream containing 35.0 wt% benzene (B), 50.0% toluene (T), and the balance xylene (X) is fed to a distillation column. The overhead product from the column contains 67.3 wt% benzene and 30.6% toluene. The bottoms product is fed to a second column. The overhead product from the second column contains 5.9 wt% benzene and 92.6% toluene. Of the toluene fed to the process, 10.0% is recovered in the bottoms product from the second column, and 90.0% of the xylene fed to the process is recovered in the same stream.

1. Perform a degree-of-freedom analysis on the process and outline a manual calculation procedure to determine the compositions of all streams.
2. Construct a set of n equations in the n unknown stream variables identified in part 1.

SOLUTION ***Basis: 100 kg Feed***



Column 1
4 variables ($n_1, \ldots, n_4$)
− 3 material balances
= 1 local degree of freedom

Column 2
7 variables ($n_2, \ldots, n_8$)
− 3 material balances
= 4 local degrees of freedom

Process
5 local degrees of freedom (1 + 4)
− 3 ties (n_2, n_3, n_4)
− 2 additional relations (fractional recoveries of toluene and xylene in column 2 bottoms)
= 0 net degrees of freedom

The process is therefore properly defined and all unknowns can in principle be determined.

A manual solution is easily outlined. The specified recoveries of toluene and xylene in the bottoms from the second column allow the immediate determination of n_7 and n_8, leaving three unknowns—

n_1, n_5, and n_6—in the overall process system. Overall toluene and xylene balances provide two equations in two unknowns—n_1 and n_5—and an overall mass balance then yields n_6. Finally, benzene, toluene, and xylene balances on either Column 1 or Column 2 yield solutions for n_2, n_3, and n_4.

The system equations are given below. We first write the allowed balances for column 1, then those for column 2, and finally the additional process specifications.

Column 1 Balances

B: $35.0 = 0.673n_1 + n_2$ **(1)**

T: $50.0 = 0.306n_1 + n_3$ **(2)**

X: $15.0 = 0.021n_1 + n_4$ **(3)**

Column 2 Balances

B: $n_2 = 0.059n_5 + n_6$ **(4)**

T: $n_3 = 0.926n_5 + n_7$ **(5)**

X: $n_4 = 0.015n_5 + n_8$ **(6)**

10% T recovery: $n_7 = 0.100(50.0) = 5.00$ **(7)**

93.3% X recovery: $n_8 = 0.933(15.0) = 14.0$ **(8)**

We thus have eight equations in eight unknowns. The equations may easily be entered into an equation-solving program and solved to obtain $n_1 = 48.1$, $n_2 = 2.65$, $n_3 = 35.3$, $n_4 = 14.0$, $n_5 = 32.7$, $n_6 = 0.72$, $n_7 = 5.0$, and $n_8 = 14.0$.

Although a computer is not needed to solve this particular set of equations, the same method can be used to derive sets of equations for much more complex processes—processes that do not easily yield to manual solution techniques.

The next example illustrates the equation-based approach for a system that involves nonlinear relations and recycle.

EXAMPLE 10.3-2 Simulation of an Equilibrium Reaction/Separation Process

Ethane is dehydrogenated to ethylene and acetylene in the following pair of catalytic reactions:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2 \qquad [A \rightleftharpoons B + D]$$

$$C_2H_6 \rightleftharpoons C_2H_2 + 2H_2 \qquad [A \rightleftharpoons C + 2D]$$

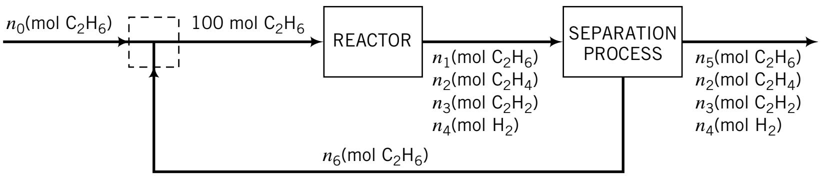
The reactions take place at 977°C and 1 atm and proceed to a point such that the product gas composition satisfies the following equilibrium conditions:

$$\frac{y_B y_D}{y_A} = 3.75 \qquad \frac{y_C y_D^2}{y_A} = 0.135$$

where y denotes mole fraction. The product gas goes to a complex separation process that separates 95% of the unreacted ethane from the ethlyene, acetylene, and hydrogen and recycles the separated ethane to the reactor.

Perform a degree-of-freedom analysis on this process, set up the equations for all unknown stream variables, and outline a method of solution.

SOLUTION ***Basis: 100 mol Ethane Fed to the Reactor***



The degree-of-freedom analysis proceeds in the customary manner.

Mixing Point 2 variables (n_0, n_6)
$-$ 1 balance (ethane)
$=$ 1 local degree of freedom

Reactor (Count balances on molecular species)

4 variables $(n_1, \ldots, n_4)$
$-$ 4 molecular species balances
$-$ 2 equilibrium relations
$+$ 2 chemical reactions
$=$ 0 local degrees of freedom

Separation Process 6 variables $(n_1, \ldots, n_6)$
$-$ 1 balance (Ethane. We implicitly used up the balances on ethylene, acetylene, and hydrogen when we labeled the outlet flow rates of these species n_2, n_3, and n_4.)
$-$ 1 additional relation (95% of the ethane fed to the separator leaves with the product.)
$=$ 4 local degrees of freedom

Process 5 local degrees of freedom (1 + 0 + 4)
$-$ 5 ties $(n_1, \ldots, n_4, n_6)$
$=$ 0 net degrees of freedom

The system equations are as follows.

Mixing Point

$$n_0 + n_6 = 100 \tag{1}$$

Reactor

We will use the extent of reaction method for the reactor analysis (see Section 4.7e). From the two given stoichiometric equations,

$$n_1 = 100 \text{ mol} - \xi_1 - \xi_2 \tag{2}$$

$$n_2 = \xi_1 \tag{3}$$

$$n_3 = \xi_2 \tag{4}$$

$$n_4 = \xi_1 + 2\xi_2 \tag{5}$$

$$n_{\text{tot}} = n_1 + n_2 + n_3 + n_4 = 100 \text{ mol} + \xi_1 + 2\xi_2 \tag{6}$$

The mole fraction of the ith component in the reactor effluent is n_i/n_{tot}. The mole fractions of all four species can be expressed in terms of ξ_1 and ξ_2 using Equations 2 through 6, and the resulting expressions can be substituted into the given equilibrium relations to yield the following equations:

$$\frac{\xi_1(\xi_1 + 2\xi_2)}{(100 - \xi_1 - \xi_2)(100 \text{ mol} + \xi_1 + 2\xi_2)} = 3.75 \tag{7}$$

$$\frac{\xi_2(\xi_1 + 2\xi_2)^2}{(100 - \xi_1 - \xi_2)(100 \text{ mol} + \xi_1 + 2\xi_2)^2} = 0.135 \tag{8}$$

Separation Process

Ethane split: $$n_5 = 0.05n_1 \tag{9}$$

Ethane balance: $$n_1 = n_5 + n_6 \tag{10}$$

We now have 10 equations in 10 unknowns $(n_0, \ldots, n_6, n_{\text{tot}}, \xi_1, \text{and } \xi_2)$. Once the equations are solved, any desired quantities may be determined, such as the component mole fractions in the reactor effluent, the overall and single-pass conversions, yields and selectivities, and (if stream phases and temperatures are specified) required heat duties on the reactor and separation process.

Examining the 10 equations, we see that two are nonlinear (Equations 7 and 8) and the remainder are linear. The full set of 10 simultaneous equations could be entered into an equation-solving program, or the following procedure involving no more than two simultaneous equations could be used:

Solve equations 7 and 8 simultaneously for ξ_1 and ξ_2 (trial and error—see below)

↓

$$
\begin{aligned}
n_1 &= 100 - \xi_1 - \xi_2 && \textbf{(2)}\\
n_2 &= \xi_1 && \textbf{(3)}\\
n_3 &= \xi_2 && \textbf{(4)}\\
n_4 &= \xi_1 + 2\xi_2 && \textbf{(5)}\\
n_{tot} &= n_1 + n_2 + n_3 + n_4 && \textbf{(6)}
\end{aligned}
$$

↓

$$
\begin{aligned}
n_5 &= 0.05 n_1 && \textbf{(9)}\\
n_6 &= n_1 - n_5 && \textbf{(10)}
\end{aligned}
$$

↓

$$n_0 = 100 - n_6 \qquad \textbf{(1)}$$

The only problem that remains is the simultaneous solution of Equations 7 and 8. We first rewrite each of the two equations in the form $f(\xi_1, \xi_2) = 0$ by multiplying through by the denominators of the left sides and bringing all terms to the left of the equal sign. Equation 7 becomes

$$f_1(\xi_1, \xi_2) = \xi_1(\xi_1 + 2\xi_2) - 3.75(100 - \xi_1 - \xi_2)(100 + \xi_1 + 2\xi_2) = 0$$

and from Equation 8

$$f_2(\xi_1, \xi_2) = \xi_2(\xi_1 + 2\xi_2)^2 - 0.135(100 - \xi_1 - \xi_2)(100 + \xi_1 + 2\xi_2)^2 = 0$$

These two equations may be solved simultaneously using an equation-solving program or a numerical procedure like the Newton–Raphson algorithm (Section A.2h). The solution is $\xi_1 = 83.06$ mol, $\xi_2 = 6.127$ mol. Equations 2–5, 9–10, and 1 then yield $n_1 = 10.81$ mol, $n_2 = 83.06$ mol, $n_3 = 6.127$ mol, $n_4 = 95.32$ mol, $n_5 = 0.5405$ mol, $n_6 = 10.27$ mol, $n_0 = 89.73$ mol.

The final example illustrates the analysis of a multiple-unit process with several internal cycles, using both the sequential modular and equation-based approaches.

EXAMPLE 10.3-3 Simulation of an Ammonium Nitrate Plant[2]

Equipment Encyclopedia
reactor, tank, heat exchanger, cyclone, condenser, screener

Ammonium nitrate, a constituent of many fertilizers, is manufactured in the reaction of ammonia and aqueous nitric acid:

$$NH_3(g) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$

A labeled flowchart is shown in Figure 10.3-1. The principal features of the process are summarized in the paragraphs that follow.

The nitric acid fed to the process is a 59.5 wt% solution that enters a charge tank at a rate of 10,970 kg/h. Also fed to the tank are two recycle streams coming from different parts of the process. Both of these streams contain ammonium nitrate, and one also contains dissolved ammonia.

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[2] This example is based on a process description in L. B. Andersen and L. A. Wenzel, *Introduction to Chemical Engineering,* McGraw-Hill, New York, 1961.

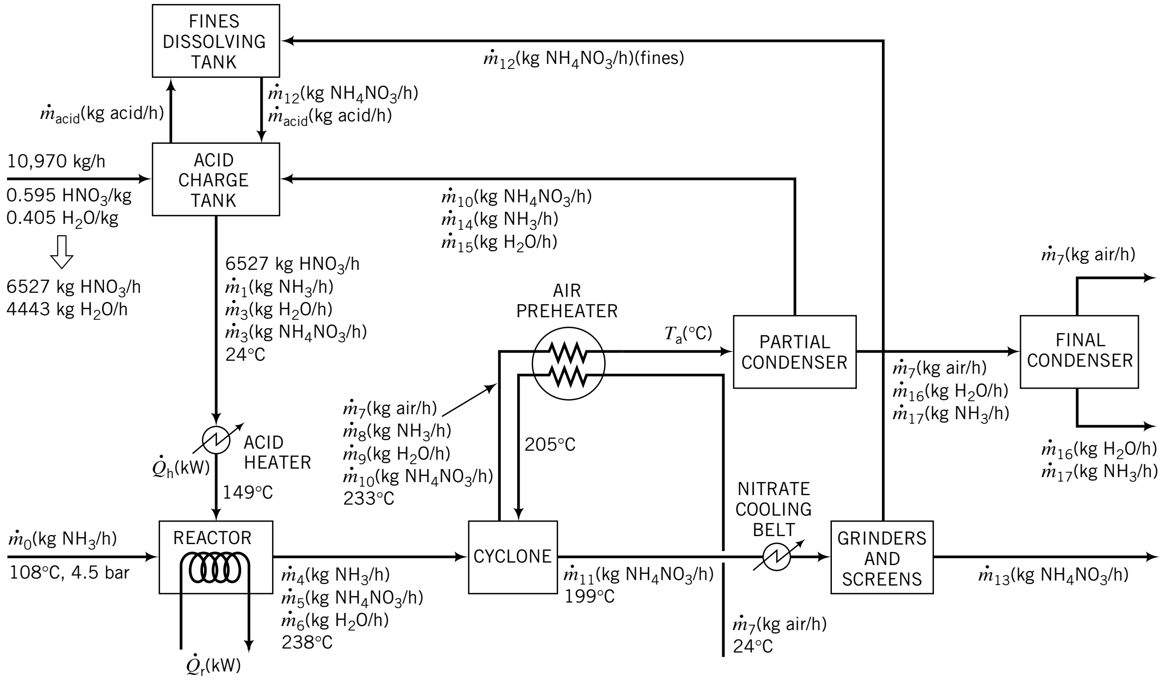


Figure 10.3-1 Flowchart of an ammonium nitrate production process.

A liquid stream from the charge tank is heated from 24°C to 149°C and fed to the reactor, along with a stream of ammonia vapor at 108°C and 4.5 bar. The total ammonia fed to the reactor is 5% in excess of the amount needed to react completely with the nitric acid in the feed. At the reactor operating conditions, the ammonium nitrate is formed as liquid droplets and most of the water in the acid is vaporized. The reaction goes to completion.

The reactor effluent—a gas–liquid mixture—leaves the reactor at a temperature of 238°C and flows into a cyclone separator. The tangential flow of the mixture generates a centrifugal force on the liquid droplets that impels them to the wall. The droplets adhere to and flow down the wall to the base of the unit where they are contacted with hot air, which vaporizes essentially all of the water and a small amount of the ammonium nitrate, leaving the remaining ammonium nitrate in a molten condition. The mass ratio of air to reactor effluent entering the cyclone is 0.045:1. Before entering the cyclone, the air is heated from 24°C to 205°C by exchange of heat with the gases leaving the cyclone.

The molten ammonium nitrate stream leaves the separator at 199°C and is air-cooled on a slowly moving belt to a temperature at which it all solidifies. The solid ammonium nitrate is then ground and screened. All but the smallest particles (the "fines") go through a coating process and then to bagging and shipping. The fines, which account for 16.4% of the nitrate fed to the grinding mill, are recycled to a tank where they are redissolved in acid and recycled to the charge tank.

The gas stream leaving the cyclone contains hot air, the excess ammonia, water evaporated from the nitric acid solution in the reactor and from the collected liquid in the cyclone, and 3% of the ammonium nitrate in the reactor effluent. The stream leaves the separator at 233°C, passes through the air preheater, and enters a partial condenser where some of the water and ammonia and essentially all of the nitrate are condensed. The equilibrium relationship between the compositions of the vapor and liquid streams leaving this unit may be expressed in the form

$$\begin{aligned} y_{H_2O} &= f_1(x_{H_2O}, x_{NH_3}) \\ y_{NH_3} &= f_2(x_{H_2O}, x_{NH_3}) \end{aligned}$$

where y and x denote mass fractions in the gas and liquid phases, respectively. The gas stream leaving the partial condenser passes to a second condenser, which removes the remaining water and ammonia, leaving essentially pure air to be discharged to the atmosphere.

It is desired to calculate the mass flow rates $\dot{m}_0, \ldots, \dot{m}_{17}$ (see Figure 10.3-1), the temperature of the gas entering the partial condenser (T_a), and the heat duties on the acid heater ($\dot{Q}_h$) and the reactor ($\dot{Q}_r$).

1. Carry out a degree-of-freedom analysis on the process.
2. Set up a sequential modular simulation of the process, using the following blocks:

`MIX`	Mix two or more streams of known composition adiabatically to form a single outlet stream. Calculate the component flow rates and temperature of the outlet stream.
`REACT`	Take as input a stream of reactants at a specified temperature and carry the reaction to completion at a specified outlet temperature.
`SEPR`	Separate a feed stream with specified component flow rates into two outlet streams. The fractions of each component that go into the first outlet stream are specified.
`CONDNS`	Carry out a partial condensation on a multicomponent feed stream.
`EXCH`	Exchange heat between two streams. The flow rates of both streams are specified, as are the inlet and outlet temperatures of one stream and the inlet temperature of the second.
`HEAT`	Raise or lower the temperature of a stream by a specified amount.
`CONVG`	Perform a Wegstein search to determine the value of one or more tear stream variables.
`CALC`	Perform a simple calculation of a specified stream variable from input stream variable values (a user-written subroutine).

3. Write a set of equations for all unknown variables; that is, set up the problem in a form suitable for solution using an equation-solving algorithm.

SOLUTION

1. ***Degree-of-freedom analysis.*** We will present the analysis with a minimum of comment. Try to justify to yourself the given number of relations for each process unit.

Reactor (Count balances on molecular species.)

8 variables ($\dot{m}_0, \ldots, \dot{m}_6, \dot{Q}_r$)
− 4 balances (ammonia, water, nitrate, energy) (We do not include a nitric acid balance, since we did not label an outlet flow rate for this species.)
− 2 additional relations (% excess ammonia, complete conversion)
+ 1 chemical reaction

= 3 local degrees of freedom

Cyclone

8 variables ($\dot{m}_4, \ldots, \dot{m}_{11}$)
− 3 balances (ammonia, water, ammonium nitrate)(Why not air?)
− 2 additional relations (air/reactor effluent mass ratio, ammonium nitrate split)

= 3 local degrees of freedom

Grinders

3 variables ($\dot{m}_{11}, \ldots, \dot{m}_{13}$)
− 1 balance (ammonium nitrate)
− 1 additional relation(% fines)

= 1 local degree of freedom

Preheater

5 variables ($\dot{m}_7, \ldots, \dot{m}_{10}, T_a$)
− 1 balance (energy—Why no material balances?)

= 4 local degrees of freedom

Partial Condenser

9 variables $(\dot{m}_7, \ldots, \dot{m}_{10}, \dot{m}_{14}, \ldots, \dot{m}_{17}, T_a)$
$-$ 2 balances (ammonia, water)
$-$ 2 additional relations (equilibrium relations for ammonia and water)
$=$ 5 local degrees of freedom

Final Condenser

3 variables $(\dot{m}_7, \dot{m}_{16}, \dot{m}_{17})$
$-$ 0 balances (Why?)
$=$ 3 local degrees of freedom

Fines Dissolving Tank

1 variable $(\dot{m}_{12})$ (We are ignoring $\dot{m}_{\text{acid}}$,
for reasons to be discussed below)
$-$ 0 balances
$=$ 1 local degree of freedom

Acid Charge Tank

7 variables $(\dot{m}_1, \dot{m}_2, \dot{m}_3, \dot{m}_{10}, \dot{m}_{12}, \dot{m}_{14}, \dot{m}_{15})$
$-$ 3 balances (ammonia, water, ammonium nitrate)
$=$ 4 local degrees of freedom

Acid Heater

4 variables $(\dot{m}_1, \dot{m}_2, \dot{m}_3, \dot{Q}_h)$
$-$ 1 balance (energy)
$=$ 3 local degrees of freedom

Process

27 local degrees of freedom
$-$ 27 ties (Referring to Figure 10.3-1, count them.)
$=$ 0 net degrees of freedom

The process is therefore well defined.

In our analysis of the fines dissolving tank, we paid no attention to $\dot{m}_{\text{acid}}$. The reason is that from the standpoint of the requested process analysis, the value of this flow rate is both indeterminate and immaterial. Whatever the quantity of acid that flows to the fines dissolving tank from the acid charge tank, the same quantity flows back. Since the value of $\dot{m}_{\text{acid}}$ has no bearing on any of the other material flows and we have no way of calculating this value from the given information about the process, we may as well ignore it when setting up the simulation.

2. ***Sequential modular simulation.*** Examination of the flowchart of Figure 10.3-1 shows that there are two cycles in the process. The first includes the reactor, cyclone, preheater, partial condenser, acid charge tank, and acid heater, and the second includes the reactor, cyclone, ammonium nitrate cooler, grinders, fines dissolving tank, acid charge tank, and acid heater. We can tear both cycles at once between the charge tank and the acid heater, between the heater and the reactor, or between the reactor and the cyclone. The stream between the reactor and the cyclone involves three variables ($\dot{m}_4$, $\dot{m}_5$, and $\dot{m}_6$), one of which may immediately be eliminated by virtue of the specified percentage excess of ammonia in the reactor feed. Since no other potential tear stream involves fewer variables, we will choose this location as the tear point.

Figure 10.3-2 shows a block diagram of the simulation. Note the following features of the diagram.

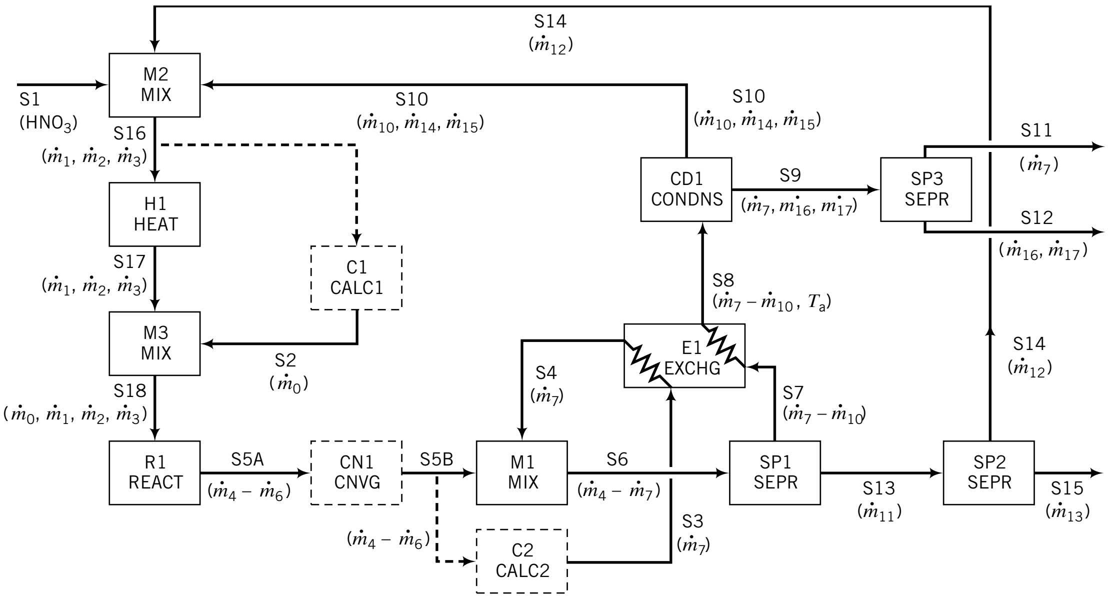


Figure 10.3-2 Block diagram for sequential modular simulation of ammonium nitrate process.

1. Blocks are not included for the fines dissolver and the ammonium nitrate cooler, since both of these units serve simply to pass along a stream of material from one unit to another. If energy balances on these units were required, we would then include blocks for them.
2. Two calculation blocks are included. In the first (`C1`), the value of the ammonia fresh feed rate ($\dot{m}_0$) will be calculated from the known value of the nitric acid feed rate, the calculated quantity of recycled ammonia ($\dot{m}_1$), and the specified percentage excess ammonia in the reactor feed (5%). In the second block (`C2`), the flow rate of air ($\dot{m}_7$) will be calculated from the known mass flow rate of the reactor effluent ($\dot{m}_4 + \dot{m}_5 + \dot{m}_6$) and the specified mass ratio of air to reactor effluent (0.045).
3. The `SEPR` block must be used to simulate the cyclone. However, since this block only accepts a single input stream, the reactor effluent and air feed must first be combined in a `MIX` operation, even though there is no physical mixing stage in the process.

The simulation would begin with a guess at the tear stream variables (`S5B`). The subroutine calling sequence for the simulation would then be as follows.

```
CALL CALC2(C1,S5B,S3)
```

Calculates $\dot{m}_7$, hence streams `S3`, `S4`, and `S11`

```
CALL MIX(M1,S5B,S4,S6)
CALL SEPR(SP1,S6,S7,S13)
```

Takes as input the flow rates of air ($\dot{m}_7$), ammonia ($\dot{m}_4$), ammonium nitrate ($\dot{m}_5$), and water ($\dot{m}_6$) entering the cyclone and the known splits of air, ammonia, water, and ammonium nitrate, and calculates the component flow rates of streams `S7` and `S13` ($\dot{m}_8, \dots, \dot{m}_{11}$).

```
CALL SEPR(SP2,S13,S14,S15)
```

Calculates $\dot{m}_{12}$ and $\dot{m}_{13}$ from the specified fraction of fines in the grinder product.

```
CALL EXCH(E1,S3,S4,S7,S8)
```

Calculates T_a from the known stream flow rates and the three other stream temperatures.

```
CALL CONDS(CD1,S8,S9,S10)
```

Calculates $\dot{m}_{14}, \dots, \dot{m}_{17}$ from the known flow rates of stream `S8` and the equilibrium relations for ammonia and water. If the temperatures of `S9` and `S10` were specified, the subroutine could also determine the required heat duty on the condenser.

At this point in the calculation, we could call `SEPR` for unit `SP3`. However, since this calculation has no bearing on the convergence of the iterative cyclic calculations, we may as well hold off on it and do it only after the iterative procedure has converged.

```
CALL MIX(M2,S1,S10,S14,S16)
```

Calculates $\dot{m}_1$, $\dot{m}_2$, and $\dot{m}_3$. Notice that in previous flowsheet simulation examples, our `MIX` block could only handle two inlet streams. If that were the case here, we would need two block calls—one to mix `S1` and `S14`, and the next to mix the product of the first stage with `S10`.

```
CALL CALC1(C1,S16,S2)
```

Calculates $\dot{m}_0$ from the known value of the nitric acid feed rate, the current value of the ammonia recycle rate ($\dot{m}_1$), and the specified value of 5% excess ammonia in the reactor feed.

We will bypass the call of `HEAT` for the acid heater at this point, for the same reason we did not call `SEPR` for the final condenser. This calculation is not needed to complete the cycle, and so we need only do it after the cyclic calculation has converged.

```
CALL MIX(M3,S2,S17,S18)
```

Calculates the combined feed to the reactor.

```
CALL REACT(R1,S18,S5A)
```

Calculates the reactor effluent (`S5A`) flow rates $\dot{m}_4, \dot{m}_5$, and $\dot{m}_6$ and the required heat duty on the reactor, $\dot{Q}_r$.

```
CALL CONVG(CN1,S5A,S5B)
```

Compares the estimated (`S5B`) and recalculated (`S5A`) values of the tear stream variables. If they do not agree within a specified tolerance, the program generates a new set of estimated values using the Wegstein algorithm and goes back to the first step [`CALL MIX(M1,...)`] to begin a new cycle. If convergence is achieved, the program proceeds to the remaining calculations.

```
CALL SEPR(SP3,S9,S11,S12)
```

Calculates the flow rates of two of the process product streams. If temperatures of `S9`, `S11`, and `S12` were specified, an energy balance could be performed on this unit as well.

```
CALL HEAT(H1,S16,S17)
```

Calculates the required heat duty on the acid heater, $\dot{Q}_h$.

3. ***Equation-based simulation.*** The system equations are presented below. Verify that each set of equations is consistent with the degree-of-freedom analysis for that unit.

Reactor

Nitric acid fed (and reacted) = (6527 kg/h)/(63.0 kg/kmol) = 103.6 kmol/h

Excess ammonia: $$\frac{\dot{m}_0 + \dot{m}_1}{17.0 \text{ kg/kmol}} = 1.05 \times 103.6 \text{ kmol/h}$$

$$\Downarrow$$

$$\dot{m}_0 + \dot{m}_1 = 1849 \text{ kg/h} \qquad \textbf{(1)}$$

Water balance: $\dot{m}_2 = \dot{m}_6$ **(2)**

Ammonium nitrate balance: $\dot{m}_5 = 103.6 \text{ kmol/h formed } (80.0 \text{ kg/kmol})$

$$\Downarrow$$

$$\dot{m}_5 = 8288 \text{ kg/h}$$

Ammonia balance: $m_4 = 1849 \text{ kg/h fed} - (103.6 \text{ kmol/h react})(17.0 \text{ kg/kmol})$

$$\Downarrow$$

$$\dot{m}_4 = 88 \text{ kg/h}$$

Energy balance: $$\dot{Q}_r = \sum_{\text{out}} \dot{m}_i\hat{H}_i - \sum_{\text{in}} \dot{m}_i\hat{H}_i + [103.6 \text{ kmol HNO}_3/\text{h}]\Delta\hat{H}_r^\circ \tag{3}$$

The specified enthalpies of the feed and product components would be calculated in kJ/kg, relative to the components at 25°C (liquid nitric acid, gaseous ammonia, and solid ammonium nitrate), and the standard heat of reaction would be determined in kJ/kmol.

Centrifuge

Air feed: $$\dot{m}_7 = 0.045(\dot{m}_4 + \dot{m}_5 + \dot{m}_6)$$

$$\Big\Downarrow \dot{m}_4 = 88 \text{ kg/h}, \dot{m}_5 = 8288 \text{ kg/h}$$

$$\dot{m}_7 = 0.045\dot{m}_6 + 377 \text{ kg/h} \tag{4}$$

Ammonia balance: $\dot{m}_8 = \dot{m}_4 = 88$ kg/h

Water balance: $$\dot{m}_9 = \dot{m}_6 \tag{5}$$

Ammonium nitrate vaporization: $\dot{m}_{10} = 0.03\dot{m}_5 = 249$ kg/h

Ammonium nitrate balance: $\dot{m}_{11} = \dot{m}_5 - \dot{m}_{10} = (8288 - 249)$ kg/h $= 8039$ kg/h

Grinders

Fines: $\dot{m}_{12} = 0.164\dot{m}_{11} = 1318$ kg/h

Ammonium nitrate balance: $\dot{m}_{13} = \dot{m}_{11} - \dot{m}_{12} = 6721$ kg/h

Air Preheater

Energy balance: $$\left[\sum_i \dot{m}_i C_{pi}\right](233^\circ\text{C} - T_a) = \dot{m}_7 C_{p7}(205^\circ\text{C} - 24^\circ\text{C}) \tag{6}$$

Partial Condenser

$$y_{H_2O} = \dot{m}_{16}/(\dot{m}_7 + \dot{m}_{16} + \dot{m}_{17}) \tag{7}$$

$$y_{NH_3} = \dot{m}_{17}/(\dot{m}_7 + \dot{m}_{16} + \dot{m}_{17}) \tag{8}$$

$$x_{H_2O} = \dot{m}_{15}/(\dot{m}_{10} + \dot{m}_{14} + \dot{m}_{15}) \tag{9}$$

$$x_{NH_3} = \dot{m}_{14}/(\dot{m}_{10} + \dot{m}_{14} + \dot{m}_{15}) \tag{10}$$

$$y_{H_2O} = f_1(x_{H_2O}, x_{NH_3}) \tag{11}$$

$$y_{NH_3} = f_2(x_{H_2O}, x_{NH_3}) \tag{12}$$

NH_3 *balance:* $$\dot{m}_8 = \dot{m}_{14} + \dot{m}_{17} \tag{13}$$

H_2O *balance:* $$\dot{m}_9 = \dot{m}_{15} + \dot{m}_{16} \tag{14}$$

Acid Charge Tank

NH_3 *balance:* $$\dot{m}_{14} = \dot{m}_1 \tag{15}$$

H_2O *balance:* $$4443 \text{ kg/h} + \dot{m}_{15} = \dot{m}_2 \tag{16}$$

Ammonium nitrate balance: $$\dot{m}_{10} + \dot{m}_{12} = \dot{m}_3$$

$$\Big\Downarrow \begin{array}{l} \dot{m}_{10} = 249 \text{ kg/h} \\ \dot{m}_{12} = 1318 \text{ kg/h} \end{array}$$

$$\dot{m}_3 = 1567 \text{ kg/h}$$

Acid heater

Energy balance: $$\dot{Q}_h = \left[\sum_{\text{all species}} \dot{m}_i C_{pi}\right](149^\circ\text{C} - 24^\circ\text{C}) \tag{17}$$

At this point we have 17 equations in 17 unknowns: $\dot{m}_0$, $\dot{m}_1$, $\dot{m}_2$, $\dot{m}_6$, $\dot{m}_7$, $\dot{m}_9$, $\dot{m}_{14}$ to $\dot{m}_{17}$, T_a, $\dot{Q}_r$, $\dot{Q}_h$, and the four mass fractions defined by Equations 7 through 10. The system of equations can be solved by an equation-solving program such as E-Z Solve.

10.4 COMMERCIAL PROCESS SIMULATION PACKAGES

A number of programs have been written to simulate steady-state processes using a sequential modular approach (some with imbedded simultaneous equation solution capability). At the time this text was written, the most frequently used general purpose programs and the companies that distributed them were ASPEN PLUS® (Aspen Tech), CHEMCAD® (Chemstations), HYSYS® (Hyprotech), DESIGN II® (WinSim), and PROVISION® (Simulation Sciences). Other programs have been written specifically for particular process industries, such as the petroleum processing and pulp and paper manufacturing industries.

Besides having provisions for simulating most of the principal types of process equipment, the more extensive of these programs have routines that generate physical properties of hundreds of chemical species, either from built-in data tables or by using estimation formulas. Included in the stored data are boiling and melting points, liquid densities, critical constants, heat capacities, latent heats, solubilities, and vapor pressures.

The simulation program is written so that a block subroutine that requires a physical property automatically retrieves the property from the data bank. In addition, it is possible for the user to have direct access to the data, and it is not uncommon for a simulation program to be used just to generate physical properties of materials without actually carrying out a simulation.

The design of a process unit to achieve a desired output from a specified input normally includes a calculation of the unit size, which is the principal determinant of the installation and operating costs of the unit. A number of general estimation formulas have been proposed to predict the cost of a specific type of unit from a given size-dependent parameter (e.g., volume, heat transfer area, or power rating of a pump). These formulas have been built into some simulation programs. The normal procedure for using them is to solve all system material and energy balances in the manner we have described and then to call the subroutines that determine the sizes and costs of the units.

Equation-based flowsheet simulators have not reached the level of commercialization of their sequential modular counterparts as of the time of this writing, and the development of efficient equation-solving algorithms is the subject of much continuing research.

10.5 FINAL CONSIDERATIONS

This chapter has introduced computer process simulation—using computers to carry out material and energy balance calculations on processes at steady state. When thinking about the chapter material, remember the following points:

- Whether you do process analysis manually or with a spreadsheet or simulation program, you can only determine all unknown process variables associated with a process if the process has zero degrees of freedom. It is therefore always a good idea to perform a degree-of-freedom analysis before attempting to solve the system equations.
- If a process has positive degrees of freedom, you must select as many design variables as there are degrees of freedom, and then solve the system state equations for the remaining (state) variables. Which variables you select as design variables can have a dramatic effect on the difficulty of the subsequent calculations.
- For single-unit processes, it is usually desirable to pick design variables that minimize the number of state equations that must be solved simultaneously. For multiple-unit processes, it is desirable to pick design variables to minimize the number of cycles on the flowchart. When doing calculations for cycles on flowcharts, it is desirable to tear as many cycles as possible with the minimum number of tear stream variables. These rules of thumb may not always lead to the most efficient calculations and they may contradict one another, however, so that finding the best combination of design and tear stream variables may require considerable trial-and-error for complex processes.
- When you first construct a simulation, don't believe any of the initial results it gives you until you have checked as many of them as possible with manual calculations. Once the first set

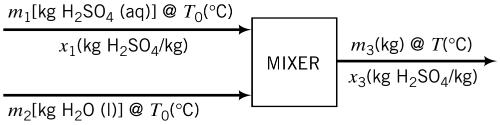
of results has been verified, it is probably safe to believe results for additional cases. (There are never any absolute guarantees, however.)

You are advised at this point to go back over the instructional objectives at the beginning of the chapter and review the chapter material on any objectives you feel you have not yet mastered.

PROBLEMS

10.1. Draw and label a flowchart and determine the number of degrees of freedom for each of the given systems. Give a feasible set of design variables and, if possible, an infeasible set. The solution to part (a) is given as an example.

(a) An aqueous solution of sulfuric acid at temperature T_0 is diluted with pure water at the same temperature in an adiabatic mixer. Calculate the final mixture temperature.



Solution:

$$\begin{array}{rl} & 7 \text{ variables } (m_1, x_1, m_2, m_3, x_3, T_0, T) \\ - & 3 \text{ relations (2 material balances and 1 energy balance)} \\ \hline = & 4 \text{ degrees of freedom} \end{array}$$

One feasible set of design variables (there are others) is

$$\{m_1,\ x_1,\ m_2,\ T_0\}$$

If you are given values of these variables you can calculate m_3 (total mass balance), x_3 (H_2SO_4 balance), and T (energy balance). An infeasible set is

$$\{m_1,\ m_2,\ m_3,\ T_0\}$$

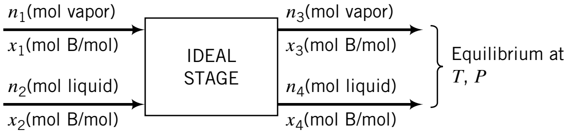
Once m_1 and m_2 have been specified, m_3 is fixed by a total material balance and may not be independently assigned a value.

(b) A natural gas containing methane, ethane, and propane at temperature T_1 is mixed with preheated air at temperature T_2, and the mixture is heated to 200°C. Calculate the required heat input.

(c) A stream containing hexane vapor in nitrogen at temperature T_1 is cooled at constant pressure, condensing 95% of the hexane. Calculate the product temperature.

Equipment Encyclopedia
distillation column

10.2. Benzene (B) and chlorobenzene (C) are being separated in a distillation column. Vapor and liquid streams, each containing both species, are fed to one of the trays of the column, and liquid and vapor streams are taken off the tray. The tray functions as an **ideal stage** (see Problem 6.63): the effluent streams are in equilibrium at temperature T and pressure P, with compositions related by Raoult's law, Equation 6.4-1.



Calculate the number of degrees of freedom. Then specify sets of design variables for which the solution for the remaining state variables would be (a) straightforward, (b) iterative, and (c) impossible.

10.3. Barium sulfate is reduced with carbon as part of the manufacture of lithopone, a white pigment:

$$2\,BaSO_4(s) + 4\,C(s) \rightarrow 2\,BaS(s) + 4\,CO_2(g)$$

A mixture of crushed barite (an ore containing x_B kg $BaSO_4$/kg barite) and coal (containing x_C kg C/kg coal) at temperature T_0(K) is fed to a furnace. Essentially all of the barium sulfate in the feed is converted. As part of the furnace design, you must specify for a basis of 100 kg barite ore the masses of coal fed and of carbon, barium sulfide, carbon dioxide, and other solids emerging from the reactor, as well as the product temperature and required heat input to the furnace.

(a) Draw and label a flowchart, and calculate the degrees of freedom of the process.

(b) Outline the solution procedure (i.e., list in order the equations you would write and the variables you would determine) if you are given values of x_B, x_C, T_0, the percent excess coal fed, and the product temperature. If a solution involves iteration or is impossible, say so.

(c) Repeat part (b), assuming that the specified variables are x_B, x_C, T_0, the mass of BaS produced, and the heat input to the furnace.

(d) Repeat part (b), assuming that the specified variables are x_B, x_C, T_0, the percent excess coal fed, and the heat input to the furnace.

10.4. Ethyl alcohol can be bacterially oxidized to acetic acid in the following two-step fermentation sequence:

$$2\,C_2H_5OH + O_2 \rightarrow 2\,CH_3CHO + 2\,H_2O$$

$$2\,CH_3CHO + O_2 \rightarrow 2\,CH_3COOH$$

If the alcohol-containing feedstock is wine, cider, or a malt solution, the resulting solution is *vinegar.*

An aqueous solution containing ethyl alcohol in water is fermented to produce dilute acetic acid. The feed mixture (the ethanol solution and the bacteria that make the fermentation occur) and air are fed at a temperature T_0. The product solution contains ethanol, acetaldehyde (CH_3CHO), acetic acid, and water. All liquid and gaseous effluents are at temperature T. The variables involved in the process are n_f (mol feed solution), x_{ef} (mol ethanol/mol feed solution), n_{air} (mol air fed), P_{xs} (percent excess air), n_e, n_{ah}, n_{aa}, n_w (gram-moles of ethanol, acetaldehyde, acetic acid, and water, respectively, in the product mixture), n_{ox}, n_n (gram-moles of oxygen and nitrogen, respectively, emerging from the reactor), T_0, T, and Q (kJ heat transferred).

(a) Calculate the number of degrees of freedom of the process. How would the answer differ if the reactor were adiabatic?

(b) Outline the solution procedure to determine all unknown variables from given values of n_f, x_{ef}, P_{xs}, n_e, n_{ah}, T_0, and T.

(c) Specify a set of design variables that would require an iterative solution for the remaining state variables.

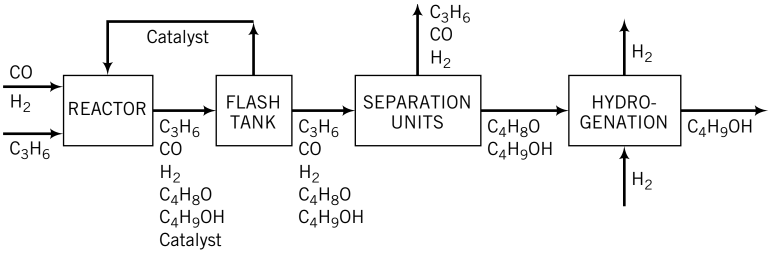
(d) Specify an infeasible set of design variables.

10.5. Propylene is converted to butyraldehyde and n-butanol in the following reaction sequence:

$$C_3H_6 + CO + H_2 \rightarrow C_3H_7CHO \quad \text{(butyraldehyde)}$$

$$C_3H_7CHO + H_2 \rightarrow C_4H_9OH \quad (n\text{-butanol})$$

Liquid propylene, gaseous carbon monoxide and hydrogen, and a soluble cobalt catalyst are fed to a high-pressure catalytic reactor. The reactor effluent goes to a flash tank, where all of the solution constituents are vaporized except the catalyst, which is recycled to the reactor. The reaction products are separated from unconsumed reactants in a multiple-unit process, and the product stream, which contains both butyraldehyde and n-butanol, is subjected to additional hydrogenation with excess hydrogen, converting all of the butyraldehyde to butanol.



(A more detailed flowchart is shown on p. 769 of G. T. Austin, *Shreve's Chemical Process Industries,* 5th Edition, McGraw-Hill, New York, 1984.)

(a) Redraw and label the flowchart, including in the labeling the molar flow rates of all stream components, the temperatures of each stream, and the heat duties ($\dot{Q}$) for each unit. If all of a species entering a process unit leaves in a single product stream, use the same variable label at the inlet and outlet. Calculate the number of degrees of freedom for each subprocess (the reactor, flash tank, separation process, and hydrogenator) and then the number for the entire process. (See Example 10.3-1.)

(b) Why must the catalyst circulation rate be a design variable?

Equipment Encyclopedia
reactor,
distillation
column

10.6. Normal butane is catalytically isomerized to isobutane. A fresh feed stream containing pure *n*-butane at temperature T_1(°C) is mixed adiabatically with a recycle stream containing *n*-butane and isobutane, and the combined stream is fed to the reactor, where some but not all of the *n*-butane in the feed is converted. The reactor effluent is pumped to a distillation column. The overhead distillation product contains primarily isobutane and a small amount of *n*-butane. The bottoms product, which also contains both species, is the stream recycled to the reactor. The streams leaving the distillation column are at different temperatures.

(a) Determine the number of degrees of freedom associated with the feed mixer, the reactor, the distillation column, and the entire process. Include all unknown process stream temperatures and process unit heat duties in your analysis.

(b) Suppose a single-pass conversion of 35.0% is attained in the reactor, the overhead distillation column product contains 88.5 mole% isobutane, and the recycle stream contains 85.0 mole% *n*-butane. Calculate the overall conversion, the recycle ratio (mol recycle/mol fresh feed), and the gram-moles of overhead product produced per 100 mol fresh feed.

(c) Solve the problem of part (b) again, only this time do it as it might be done by a sequential modular simulation of the process. Take a basis of calculation of 100 mol fresh feed and choose n_r (mol recycle) as the tear stream variable. Begin by assuming $n_r = 100$ mol and go through three successive substitution iterations (Appendix A.2). What is the percentage error in the third calculated value of n_r?

(d) Repeat part (c), only perform a Wegstein acceleration step (Appendix A.2) after the first two successive substitution iterations. What is the percentage error in the last calculated value of n_r?

(e) Set up a spreadsheet to do the calculations of parts (c) and (d), using Example 10.2-3 as a model. Proceed to convergence.

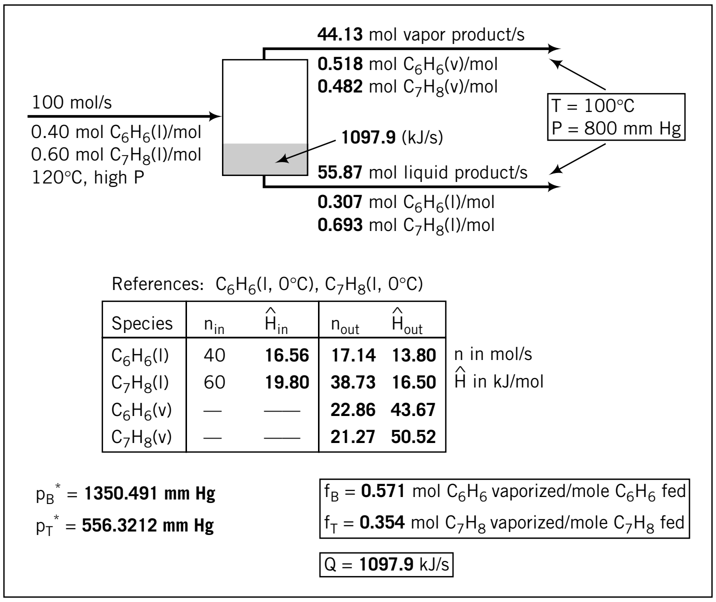
10.7. Simulate a module called `SPLIT`, which takes a feed stream (`SF`) and splits it into two streams (`S1` and `S2`), each having the composition and temperature of the feed stream. A fraction `X1` of the feed stream becomes stream `S1`, and a fraction (1−`X1`) becomes `S2`. Up to four components may be present in the feed stream, so that each stream has associated with it five attributes: four component molar flow rates and the stream temperature. Test your simulation for a feed stream flowing at a rate of 150 mol/h at $T = 315$ K containing 35 mole% *n*-octane (A), 57% iso-octane (B), and the balance a chemically inert species (C), which is to be split into two streams in a 60:40 ratio.

(a) Write a spreadsheet to perform the simulation. Draw a flowchart on the spreadsheet and label each stream with the component flow rates and temperature (see Example 10.2-1). Include the split ratio (`X1`) in a separate cell and vary it to show its effect on the component flow rates in streams `S1` and `S2`.

(b) Write a computer subprogram to simulate the module (see Example 10.2-1). The arguments of the subprogram should be `SF`, `S1`, and `S2` (each five-membered arrays), `X1`, and `N`, the number of components in the feed stream (which may be any number from one to four). `X1`, `N`, and the elements of `SF` are input variables, and the elements of `S1` and `S2` are output variables. Write and run a calling program that assigns the test case values to the input variables, calls the module subprogram, and prints out the attributes of `S1` and `S2`.

10.8. You have been assigned to simulate a flash evaporator that separates a liquid feed stream containing benzene and toluene at temperature T_F(°C) into liquid and vapor product streams in equilibrium at temperature T(°C) and pressure P(mm Hg). The compositions of the product streams are related by Raoult's law (Equation 6.4-1), and the component vapor pressures are expressed by the Antoine equation (Table B.4).

A spreadsheet that performs the required material and energy balances and vapor–liquid equilibrium calculations on this process unit is shown on the next page. In the test case, a 40 mole% benzene–60 mole% toluene mixture is fed to the evaporator at $T_F = 120$°C and a pressure high enough to assure that the feed stream remains in the liquid state. The unit operates at $T = 100$°C and $P = 800$ mm Hg.



44.13 mol vapor product/s
0.518 mol C_6H_6(v)/mol
0.482 mol C_7H_8(v)/mol

100 mol/s
0.40 mol C_6H_6(l)/mol
0.60 mol C_7H_8(l)/mol
120°C, high P

1097.9 (kJ/s)

T = 100°C
P = 800 mm Hg

55.87 mol liquid product/s
0.307 mol C_6H_6(l)/mol
0.693 mol C_7H_8(l)/mol

References: C_6H_6(l, 0°C), C_7H_8(l, 0°C)

Species	n_{in}	$\hat{H}_{in}$	n_{out}	$\hat{H}_{out}$
C_6H_6(l)	40	**16.56**	**17.14**	**13.80**
C_7H_8(l)	60	**19.80**	**38.73**	**16.50**
C_6H_6(v)	—	——	**22.86**	**43.67**
C_7H_8(v)	—	——	**21.27**	**50.52**

n in mol/s
$\hat{H}$ in kJ/mol

p_B^* = **1350.491 mm Hg**
p_T^* = **556.3212 mm Hg**

f_B = **0.571** mol C_6H_6 vaporized/mole C_6H_6 fed
f_T = **0.354** mol C_7H_8 vaporized/mole C_7H_8 fed

Q = **1097.9** kJ/s

The heat capacities of liquid benzene and toluene have been taken to be 0.138 kJ/(mol·°C) and 0.165 kJ/(mol·°C), respectively, and the vapor heat capacities and heats of vaporization of both species are those given in Appendix B.

(a) Derive expressions for the quantities in boldface on the spreadsheet—that is, the flow rates and compositions of the liquid and vapor product streams, the vapor pressures of benzene and toluene at the evaporator temperature, the fractional vaporizations of benzene and toluene, the specific enthalpies of benzene and toluene liquid at T_F and T and of benzene and toluene vapor at T (all relative to the liquid species at 0°C), and the required rate of heat transfer to the evaporator.

(b) Create a spreadsheet that replicates the one shown above, entering the formulas derived in part (a) and, if possible, imbedding the graphics for the streams and the process unit. In the formulas, enter the cell addresses for variables appearing elsewhere on the spreadsheet: for example, if a formula involves the mole fraction of benzene in the feed, do not enter "0.40" but the cell address of this variable on the spreadsheet. In this way, variables like the benzene mole fraction in the feed and the temperature and pressure of the evaporator may be changed and the new values of the calculated variables will be instantly determined. When the spreadsheet is complete, use it to determine the bubble-point and dew-point temperatures of a 40 mole% benzene–60 mole% toluene mixture at P = 800 mm Hg. Print out the spreadsheets for T = 100°C and for the bubble-point and dew-point temperatures.

(c) Write the code for a subprogram called `FLASH` to simulate the evaporator. The input variables should be the attributes of the feed stream (benzene and toluene flow rates and T_F), T, P, and the physical properties of the feed stream species (Antoine constants, heat capacity formula coefficients for liquid and vapor, and heats of vaporization). The output variables are the attributes of the vapor and liquid product streams and $\dot{Q}$. Write and run a calling program that defines the values of the feed stream variables and other input variables (use the test case values), calls the subprogram, and prints out the output variables. The physical properties may be passed to the subprogram either as arguments or through a `COMMON` or `GLOBAL` block.

10.9. You are to simulate a flash evaporator that converts a liquid feed stream (SF) containing N species at a high pressure to liquid and vapor product streams (SL, SV) in equilibrium at temperature T(°C) and pressure P(mm Hg). The compositions of the liquid and vapor product streams are related by Raoult's law (Equation 6.4-1), and the component vapor pressures are expressed by the Antoine equation, Table B.4.

(a) Write the system mass and energy balances and equilibrium relations in terms of the following variables:

`NF,NL,NV`	The molar flow rates (mol/s) of feed, liquid product, and vapor product.

`XF(I)`
`XL(I)`
`XV(I)`
	The mole fractions of the *i*th component in the feed, liquid product, and vapor product, where `I` runs from 1 to $(N - 1)$.

`TF,T,P`	Feed temperature, vaporizer temperature, and pressure, respectively.
`PV(I)`	Vapor pressures of the N species at temperature T, where `I` runs from 1 to N.

`A(I)`
`B(I)`
`C(I)`
	Antoine equation constants for the N species involved in the process (transmitted to the subroutine via a `COMMON` or `GLOBAL` statement).

`CP(I)`	Liquid-phase heat capacities [kJ/(mol·°C)] of the N species (transmitted via `COMMON` or `GLOBAL`). Assume independent of temperature.
`HV(I)`	Heats of vaporization (kJ/mol) of the N species (transmitted via `COMMON` or `GLOBAL`). Assume independent of temperature.
`Q`	The required heat input (kW) to the vaporizer.

Show that the system has $(N + 3)$ degrees of freedom, counting as the system variables three stream flow rates, $3(N - 1)$ mole fractions, N vapor pressures, `TF`, `T`, `P`, and `Q`. Then work out a trial-and-error procedure for determining the product stream flow rates and mole fractions and `Q` from specified values of `TF`, `T`, `P`, and the feed stream molar flow rate and component mole fractions.

(b) Write a module subroutine `FLASHN` to implement the procedure outlined in part (a) for a feed stream containing up to seven components. The arguments of the subroutine should be `N`, `SF`, `SV`, `SL`, `P`, and `Q`, where `SF`, `SV`, and `SL` are eight-membered arrays. The first `N` elements of each array are the component molar flow rates and the (`N` + 1)st element is the stream temperature. The input variables are `SL`(`N` + 1) and `SV` (`N` + 1) (both of which equal the vaporizer temperature), `P`, and the attributes of `SF` (N molar flow rates and the feed temperature), and the outlet variables are `Q` and the remaining attributes of `SV` and `SL`.

(c) Test your code for a feed stream containing 34.8 mole% n-pentane, 30.0 mole% n-hexane, and the balance n-heptane flowing at a rate of 1.00 mol/s which is to be flashed from 363 K and a high pressure to 338 K and 611 mm Hg. The heat capacities of liquid pentane, hexane, and heptane [in kJ/(mol·K)] may be taken to be 0.188, 0.216, and 0.213, respectively, and the heats of vaporization may be taken to have their values at the normal boiling points of these substances. Write and run a calling program that defines the attributes of `SF` and other input parameters (including the heat capacities and heats of vaporization), calls the module subroutine, and prints out the attributes of the product streams and the required heat input.

(d) Use a process simulator to perform the same calculations.

(e) Use an equation-solving program to perform the same calculations.

Equipment Encyclopedia
condenser

10.10. You are to simulate a partial condenser module that converts a vapor feed stream (`SF`) containing a single condensable species at temperature `TF`(K) to liquid and vapor product streams (`SL`, `SV`) in equilibrium at a temperature `T`(K). The process takes place at a constant pressure `P`(atm). The compositions of the liquid and vapor product streams are related by Raoult's law (Equation 6.4-1), and the component vapor pressures are correlated with temperature by the Antoine equation, Table B.4.

The system variables are as follows:

`NF,NL,NV`	mol/s of feed, liquid product, and vapor product.
`XF` `XV`	Mole fractions of the condensable substance in the feed and the vapor product.
`TF,T,P`	Feed temperature (K), condenser temperature (K), and condenser pressure (atm), respectively.
`PV`	Vapor pressure (mm Hg) of the condensable substance at temperature T.
`A,B,C`	Antoine equation constants for the condensable substance.

CPL	Liquid-phase heat capacity [kJ/(mol·K)] of the condensable substance. Assume independent of temperature.
HV	Heat of vaporization (kJ/mol) of the condensable substance. Assume independent of temperature.
CPV CPG	Heat capacities [kJ/(mol·K)] of the condensable vapor and the noncondensable gas. Assume independent of temperature.
Q	Required heat input (kW) to the condenser. (*Q* will be negative.)

(a) Show that the system has five degrees of freedom, counting as the system variables three stream flow rates, two mole fractions, one vapor pressure, TF, T, P, and Q.

(b) The input variables to the module are to be the molar flow rates of the condensable and noncondensable feed stream constituents [SF(1) and SF(2)], the feed temperature [SF(3) = TF], the operating pressure of the condenser (P), and the fraction YC of the condensable species in the feed that is to be condensed. (The heat capacities and heat of vaporization must also be supplied.) The output variables are the molar flow rate of the liquid product stream [SL(1)], the molar flow rates of the vapor product stream constituents [SV(1) and SV(2)], the operating temperature of the condenser [SL(2) = SV(3) = T], and the required heat transfer rate (Q). Outline the required calculations.

(c) Write a spreadsheet to perform the calculations of part (b) for a feed stream flowing at 1.00 mol/s containing methyl alcohol in air at 60°C and 1 atm with a relative saturation of 85%, from which 90% of the methanol is to be removed by partial condensation at constant pressure. The heat capacities in kJ/(mol·K) of liquid methanol, methanol vapor, and air may be taken to be 0.078, 0.050, and 0.030, respectively. After you have generated the solution and recorded the output variable values, use the spreadsheet to generate a plot of condenser temperature (T) versus fractional methanol removal (YC), and briefly explain why the plot looks the way it does.

(d) Use an equation-solving program to perform the calculations outlined in part (c).

(e) Write a computer subprogram CNDNS to implement the procedure of part (b) for the test case of part (c). The subroutine arguments should be SF, SV, SL, P, YC, and Q. Input variables are YC, P, and the attributes of SF, and output variables are Q and the attributes of SV and SL. The values of physical property parameters, A, B, C, CPL, CPV, CPG, and HV should be transmitted to the subprogram either as additional arguments or through a COMMON or GLOBAL statement. Then write and run a calling program that defines the attributes of SF and other input and physical property parameters, calls the subprogram, and prints out the input and output variable values for the test case of part (c).

10.11. You are to simulate a single-phase reactor in which a single reaction takes place. The reaction has the general form.

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \cdots + \nu_m A_m = 0$$

In this equation A_i is the ith reactant or product and ν_i is the stoichiometric coefficient of this species (negative for reactants and positive for products). It is also convenient to define ν_i for each inert species in the feed to the reactor, assigning it a value of 0. The inputs to the module are the feed stream flow rate, composition, and temperature, the fractional conversion of one of the reactants, and the product stream temperature. The module is to calculate the product stream component flow rates and the required heat transfer to the reactor.

The module equations should be written in terms of the following variables:

N	The total number of reactive and inert species present in the feed and product streams.
SF(I),I = 1,...,N+1	The molar flow rates of the feed stream components (mol/s) and the feed stream temperature (K).
SP(I),I = 1,...,N+1	The molar flow rates of the product stream components (mol/s) and the product stream temperature (K).
NU(I),I = 1,...,N	The stoichiometric coefficients of all species (− for reactants, + for products, 0 for inerts).
X	The fractional conversion of one of the reactants.
IX	The number of the reactant for which the fractional conversion is specified.
CP(I),I = 1,...,N	The heat capacities of all species, kJ/(mol·K) (assume constant).

`HF(I),I = 1,...,N`	The standard heats of formation of all species, kJ/mol.
`Q`	The heat input to the reactor, kW. (If Q is negative, heat must be transferred from the reactor.)

(a) Write the equations you would use to calculate `Q` and the first `N` components of `SP` from specified values of all of the other variables defined above.

(b) Write a spreadsheet to perform the calculations of part (a) for a reactor in which propane flowing at a rate of 270 standard cubic meters per hour is burned with 20% excess air. The combined stream enters the reactor at 423 K and the stack gas leaves at 1050 K. Ninety percent of the propane fed is converted, and no CO is contained in the stack gas. Take the heat capacity of each species to be its value at 700 K as calculated from Table B.2 [so that, for example, `CP(1)` = 0.1431 kJ/(mol·K), where (1) refers to propane]. After you have performed the calculations and recorded the output variable values, use the spreadsheet to generate a plot of `Q` versus stack gas temperature and briefly explain why the plot looks the way it does.

(c) Use an equation-solving program to perform the calculations outlined in part (b).

(d) Write a computer subprogram `REACTS` to implement the procedure of part (a). The subprogram arguments should be `SF`, `SP`, `NU`, `N`, `X`, `IX`, and `Q`. The arrays CP and HF should either be transmitted as additional arguments or via a `COMMON` or `GLOBAL` statement. Write and run a calling program that defines the input variables, calls the subprogram, and prints out the required output variables for the test case of part (b). Number the species involved in the process as follows: 1—C_3H_8, 2—O_2, 3—N_2, 4—CO_2, 5—H_2O. For example, `NU(1)` = −1, `NU(2)` = −5, `SF(1)` = 3.348, `SF(3)` = 75.54, `SF(6)` = 423, and `SP(6)` = 1050. (Verify these values as part of your problem solution.)

10.12. You are to simulate a single-phase adiabatic reactor in which a single gas-phase reaction takes place. The reaction has the general form

$$\nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 + \cdots + \nu_m A_m = 0$$

In this equation A_i is the ith reactant or product and ν_i is the stoichiometric coefficient of this species; ν_i is negative for reactants and positive for products. It is also convenient to define ν_i for each inert species in the feed to the reactor, assigning it a value of 0. The inputs to the program are the stoichiometric coefficients, feed stream flow rate, composition, and temperature, and the fractional conversion of one of the reactants. The program is to calculate the product stream component flow rates and temperature.

The program equations should be written in terms of the following variables:

`N`	The total number of reactive and inert species present in the feed and product streams.
`SF(I),1 = I,...,N+1`	The molar flow rates of the feed stream components (mol/s) and the feed stream temperature (K).
`SP(I),1 = I,...,N+1`	The molar flow rates of the product stream components (mol/s) and the product stream temperature (K).
`NU(I),1 = I,...,N`	The stoichiometric coefficients of all species (− for reactants, + for products, 0 for inerts).
`X`	The fractional conversion of one of the reactants.
`IX`	The number of the reactant for which the fractional conversion is specified.

`ACP(I),1 = I,...,N`
`BCP(I),1 = I,...,N`
`CCP(I),1 = I,...,N`
`DCP(I),1 = I,...,N`
	Coefficients of the heat capacity formula C_p[kJ/(mol·°C)] = $a + bT + cT^2 + dT^3$.

`DHF(I),1 = I,...,N`	The standard heats of formation of all species in the gaseous state, kJ/mol.

(a) Write the equations you would use to calculate the attributes of `SP` from specified values of all the other listed variables. The last equation you derive should be a fourth-order equation for the reactor temperature,

$$(\Delta H =)\ \alpha T^4 + \beta T^3 + \gamma T^2 + \delta T + \varepsilon = 0$$

where α, β, γ, δ, and ε involve most of the system variables.

(b) Write a spreadsheet to perform the calculations of part (a) for a reactor in which carbon monoxide is oxidized with 25% excess air at 1 atm to form carbon dioxide. The combined feed stream enters the reactor at 650°C at a rate of 23.0 kmol/h, and a CO conversion of 45% is obtained. Use the goalseek tool to solve the fourth-order energy balance equation. After you have performed the calculations and recorded the output variable values, use the spreadsheet to generate a plot of product gas temperature versus percentage CO conversion and briefly explain why the plot looks the way it does.

(c) Use an equation-solving program to perform the calculations outlined in part (b).

(d) Write a computer subprogram `REACTAD` to implement the procedure of part (a). The subprogram arguments should be `SF`, `SP`, `NU`, `N`, `X`, and `IX`. The arrays ACP, BCP, CCP, DCP, and DHF should either be transmitted as additional arguments or via `COMMON` or `GLOBAL`. All arguments but the attributes of `SP` should be considered input variables. Use Newton's rule (Appendix A.2) to solve the fourth-order energy balance equation. Write and run a calling program that defines the input variables, calls the subprogram, and prints out the required output variables for the test case of part (b). Number the species involved in the process as follows: 1—CO, 2—O_2, 3—N_2, 4—CO_2. For example, `NU`$(1) = -1$, `NU`$(2) = -1/2$, `SF`$(1) = 1.607$, and `SF`$(3) = 3.777$. (Verify these values as part of your problem solution.)

10.13. The following two reactions occur in an ethylene oxide production process:

$$2C_2H_4 + O_2 \rightarrow 2C_2H_4O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

A stream containing equimolar amounts of ethylene and oxygen is joined by a recycle stream containing pure ethylene, and the combined stream is fed to the reactor. The single-pass conversion of ethylene in the reactor and the single-pass ethylene oxide yield based on ethylene consumption are defined as X_{sp} (mol C_2H_4 react/mol C_2H_4 fed) and Y_{sp} (mol C_2H_4O formed/mol C_2H_4 react). The reactor effluent goes through a multiple-unit separation process that has three outlet streams. The first stream, which is sold, is pure ethylene oxide; the second, which is discarded, contains all the carbon dioxide, oxygen, water, and 5% of the unreacted ethylene leaving the reactor; and the third stream, which is the recycle stream, contains the remaining unreacted ethylene.

(a) Taking 100 mol/s fresh feed as a basis of calculation and letting $X_{sp} = 0.20$ and $Y_{sp} = 0.90$, construct a spreadsheet to simulate this process, treating the separation process as a single unit. Use the recycle stream flow rate as a tear stream variable: that is, assume a recycle flow rate entering the recycle–fresh feed mixing point, solve the system balance equations to recalculate the recycle flow rate at the outlet of the separation process and find the assumed value for which the assumed and recalculated values are the same. Determine the overall conversion and yield,

$$X_0 \text{ (mol } C_2H_4 \text{ consumed in process/mol } C_2H_4 \text{ in fresh feed)}$$

$$Y_0 \text{ (mol } C_2H_4O \text{ produced in process/mol } C_2H_4 \text{ in fresh feed)}$$

and the molar flow rate of the recycle stream.

(b) For the given fresh feed and single-pass conversion of ethylene, use the spreadsheet to find the range of single-pass yields that are physically possible. (A value is not possible if it leads to a negative species flow rate at any point in the process.) Note the values of Y_0 and the recycle flow rate at the extremes of this range. Then repeat the calculation for a 30% single-pass conversion of ethylene. Show your results in a table with the following form:

X_{sp}	Y_{sp}	Y_0	n_{rec}
0.2	(Y_{min})		
0.2	(Y_{max})		
0.3	(Y_{min})		
0.3	(Y_{max})		

Explain why a species flow rate becomes negative when Y falls below a certain value.

(c) Summarize the equations that describe the behavior of this system and use an equation-solving program to solve them for the variable values of part (a).

10.14. You are to write the code for a convergence module that can deal with one to three tear stream variables using the Wegstein algorithm, as outlined in Appendix A.2. The object is to determine the values of one, two, or three of the variables x_1, x_2, and x_3 that satisfy the relations

$$
\begin{aligned}
x_1 &= f_1(x_1, x_2, x_3) \\
x_2 &= f_2(x_1, x_2, x_3) \\
x_3 &= f_3(x_1, x_2, x_3)
\end{aligned}
$$

where f_1, f_2, and f_3 may be simple algebraic functions, or they may represent the composite set of calculations involved in proceeding around a cycle of unit operations to recalculate tear stream variables. The calculation consists of assuming values for the tear stream variables $[x_{ia}, i = 1, \ldots, 3]$; computing $[x_{ic} = f_i(x_{1a}, x_{2a}, x_{3a}), i = 1, \ldots, 3]$; determining whether x_{ia} and x_{ic} are within a specified tolerance of each other for each i; and if they are not, using the Wegstein algorithm to estimate the values of x_{1a}, x_{2a}, and x_{3a} to be used in the next iteration.

The module code should be written in terms of the following variables:

`N`	Number of tear stream variables (1, 2, or 3).
`XA(I),I = 1,...,N`	Assumed values of x_i (initially guessed, subsequently calculated by the Wegstein algorithm).
`XC(I),I = 1,...,N`	Recalculated values of x_i obtained from the functions f_i (or by proceeding around a cycle).
`KMAX`	Maximum number of iterations to be allowed.
`EPS`	Relative convergence tolerance (see Equation A.2-9). The difference between `XA(I)` and `XC(I)` divided by the value of `XC(I)` must be less than `EPS` for convergence to be declared.
`IPR`	A printout parameter. The code should be written such that if `IPR = 1` the values of x_i are printed after each iteration, while if `IPR = 0` the printing is suppressed.

(a) Write the code for a module subprogram called `CONVG` that has as its arguments `XA`, `XC`, `N`, `KMAX`, `EPS`, and `IPR`. The values of `N`, `KMAX`, `EPS`, `IPR`, and the elements of `XA` are input variables, and the final estimated values of x_i are to be returned in array `XC`. The code should execute the procedure outline in Section A.2g separately for each of the N variables, up to a maximum of `KMAX` iterations. If this limit is reached and convergence has not been attained, an error message should be printed and the program terminated.

In a real flowchart simulator, the code would be written so that the module could be inserted as a block in the flowchart (see, for example, the flowchart block diagram on p. xxx), and the tear stream variables `XC(I)` would then be recalculated from assumed values of `XA(I)` by proceeding around the cycle. To simplify the coding in this problem, however, have the subprogram call a function-generating subroutine of the form

```
CALL FUNCGEN(N,XA,XC)
```

You will need to write Subroutine `FUNCGEN` to evaluate

`XC(1) =` f_1`[XA(1),XA(2),XA(3)]`

and similarly for `XC(2)` and `XC(3)`.

(b) Apply your code to the problem of Example A.2-2. Build in an upper limit of 20 iterations (`KMAX = 20`).

10.15. Use a commercial flowchart simulation program such as `HYSYS` or `ASPEN` to simulate the ammonium nitrate manufacturing process described in Example 10.3-3.

Chapter 11

Balances on Transient Processes

A system is said to be in a *transient* (or *unsteady-state*) condition if the value of any system variable changes with time. Batch and semibatch process systems are always transient: in a batch system, if nothing is changing with time then nothing is happening, and in a semibatch system (which has an input stream but no output stream or vice versa) at least the mass of the system contents must vary with time. Continuous systems are always transient when they are started up and shut down, and they become transient at other times due to planned or unexpected changes in operating conditions.[1]

The procedures for deriving balances on transient systems are essentially those developed in Chapters 4 (material balances) and 7 (energy balances). The main difference is that transient balances have nonzero accumulation terms that are derivatives, so that instead of algebraic equations the balances are differential equations.

11.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to do the following:

- Derive material balance equations and provide initial conditions for well-mixed transient single-unit processes, and derive energy balance equations and provide initial conditions for well-mixed transient single-unit nonreactive processes.
- Predict transient system behavior by inspecting balance equations. For example, given an equation that has the form $[dC_A/dt = 4 - 2C_A, C_A(0) = 0]$, sketch the expected plot of C_A versus t without integrating the equation.
- Obtain analytical solutions to problems that involve single separable first-order differential balance equations.
- Derive balance equations for systems that involve several dependent variables [e.g., $y_1 = C_A(t), y_2 = C_B(t), y_3 = T(t)$] and express the equations in a form suitable for solution using equation-solving software $[dy_i/dt = f_i(y_1, y_2, \ldots, y_n, t), i = 1, 2, \ldots, n]$.

---

[1] In reality, the concept of a true steady state is fiction, since there are *always* process variable fluctuations in real systems. When you assume steady-state operation, you are assuming that these fluctuations are small enough to be neglected without causing serious errors in calculated values.

11.1 THE GENERAL BALANCE EQUATION…AGAIN

In Section 4.2, the general balance equation (4.2-1) was given as

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption}$$

Two forms of this equation were discussed: differential balances, which relate instantaneous rates of change at a moment in time, and integral balances, which relate changes that occur over a finite time period. We examine in this section the nature of the relationship between these two types of balances; in doing so, we belatedly show why they are called differential and integral.

11.1a Differential Balances

Suppose a species A is involved in a process. Let $\dot{m}_{\text{in}}$(kg/s) and $\dot{m}_{\text{out}}$(kg/s) be the rates at which A enters and leaves the process by crossing the boundaries, and let $\dot{r}_{\text{gen}}$(kg/s) and $\dot{r}_{\text{cons}}$(kg/s) be the rates of generation and consumption of A within the system by chemical reaction. Any or all of the variables $\dot{m}_{\text{in}}$, $\dot{m}_{\text{out}}$, $\dot{r}_{\text{gen}}$, and $\dot{r}_{\text{cons}}$ may vary with time.

Let us now write a balance on A for a period of time from t to $t + \Delta t$, supposing that Δt is small enough for the quantities $\dot{m}_{\text{in}}$, $\dot{m}_{\text{out}}$, $\dot{r}_{\text{gen}}$, and $\dot{r}_{\text{cons}}$ to be considered constant. (Since we will eventually let Δt approach 0, this assumption is not restrictive.) The terms of a balance on A are easily calculated.

$$\begin{aligned} \text{input(kg)} &= \dot{m}_{\text{in}}(\text{kg/s})\,\Delta t(s) \\ \text{output} &= \dot{m}_{\text{out}}\,\Delta t \\ \text{generation} &= \dot{r}_{\text{gen}}\,\Delta t \\ \text{consumption} &= \dot{r}_{\text{cons}}\,\Delta t \end{aligned}$$

We also suppose that the mass of A in the system changes by an amount ΔM(kg) during this small time interval. By definition, ΔM is the accumulation of A in the system. From the balance equation, (4.2-1),

$$\Delta M = (\dot{m}_{\text{in}} + \dot{r}_{\text{gen}} - \dot{m}_{\text{out}} - \dot{r}_{\text{cons}})\,\Delta t \tag{11.1-1}$$

If now we divide by Δt and then let Δt approach 0, the ratio $\Delta M/\Delta t$ becomes the derivative of M with respect to t (dM/dt), and the balance equation becomes

$$\boxed{\frac{dM}{dt} = \dot{m}_{\text{in}} + \dot{r}_{\text{gen}} - \dot{m}_{\text{out}} - \dot{r}_{\text{cons}}} \tag{11.1-2}$$

This is the general differential balance equation: M is the amount of the balanced quantity in the system, and the four terms on the right side are rates that may vary with time.

If Equation 11.1-2 is applied to a continuous system at steady state, the quantity M must be a constant, its time derivative therefore equals zero, and the equation reduces to the familiar equation introduced in Chapter 4:

$$\text{input} + \text{generation} = \text{output} + \text{consumption}$$

However, as long as any term varies with time, the derivative on the left side of Equation 11.1-2 remains part of the equation. We thus conclude that *the balance equation for an unsteady-state system at an instant of time is a differential equation* (hence the term differential balance).

Equation 11.1-2 is an ordinary first-order differential equation. Before it can be solved to yield an expression for $M(t)$, a **boundary condition** must be provided—a specified value of the dependent variable (M) at some value of the independent variable (t). Frequently, the value of M at time $t = 0$ (an "initial condition") is specified. The complete balance equation would be

Equation 11.1-2 followed by

$$t = 0,\ M = \ldots$$

or simply

$$M(0) = \ldots$$

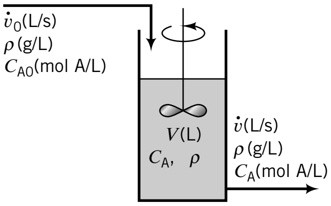
When you analyze a transient system, your analysis is not complete unless every differential equation you derive is accompanied by a boundary condition similar to one of those just given.

EXAMPLE 11.1-1 *Differential Balances on a Chemical Reactor*

Equipment Encyclopedia
reactors-CSTR

A continuous stirred-tank reactor is used to produce a compound R in the liquid-phase reaction A → R. Feed enters the reactor at a rate of $\dot{v}_0$(L/s); the concentration of the reactant in the feed is C_{A0}(mol A/L). The volume of the tank contents is V (L). The vessel may be considered perfectly mixed, so that the concentration of A in the product stream equals that in the tank. For this process the rate of consumption of A equals kC_A[mol/(s·L of reaction volume)]. All fluids (the feed, the tank contents, and the product) may be taken to have the same density, ρ(g/L).

Write differential balances on total mass and on moles of A, expressing the balances in terms of the variables shown on the following diagram:



SOLUTION ***Basis: Given Quantities***

Total Mass Balance (generation = 0, consumption = 0)

$$\text{accumulation} = \text{input} - \text{output}$$

$$\text{Mass in reactor:} \quad M(\text{g}) = V(\text{L})\rho(\text{g/L})$$

$$\Downarrow$$

$$\text{accumulation (g/s)} = \frac{dM}{dt} = \frac{d(V\rho)}{dt} = \rho\frac{dV}{dt} \quad (\text{since } \rho \text{ is constant})$$

$$\text{input (g/s)} = \dot{v}_0(\text{L/s})\rho(\text{g/L})$$

$$\text{output (g/s)} = \dot{v}(\text{L/s})\rho(\text{g/L})$$

$$\Downarrow$$

$$\rho\frac{dV}{dt} = \dot{v}_0\rho - \dot{v}\rho$$

$$\Downarrow \text{cancel } \rho$$

$$\boxed{\begin{aligned} dV/dt &= \dot{v}_0 - \dot{v} \\ t = 0,\quad V &= V_0 \end{aligned}}$$

where V_0 is the initial volume of the tank contents.

Question: If $\dot{v}_0 = \dot{v}$, what does the mass balance tell you?

Balance on A

$$\text{accumulation} = \text{input} - \text{output} - \text{consumption}$$

$$\text{Moles of A in the reactor} = V(\text{L})C_A(\text{mol/L})$$

$$\Downarrow$$

$$\text{accumulation (mol A/s)} = \frac{d(VC_A)}{dt}$$

$$\text{input (mol A/s)} = \dot{v}_0(\text{L/s})C_{A0}(\text{mol A/L})$$

$$\text{output (mol A/s)} = \dot{v}\,(\text{L/s})C_A(\text{mol A/L})$$

$$\text{consumption (mol A/s)} = kC_A[\text{mol A/(s}\cdot\text{L)}]V(\text{L})$$

$$\Downarrow$$

$$\boxed{\begin{gathered}\frac{d(VC_A)}{dt} = \dot{v}_0C_{A0} - \dot{v}C_A - kC_AV\\ t = 0, \quad C_A = C_A(0)\end{gathered}}$$

where $C_A(0)$ is the concentration of A in the initial tank contents. How you would proceed to solve this equation for the output concentration $C_A(t)$ depends on how the quantities $\dot{v}_0$, $\dot{v}$, and C_{A0} vary with time.

11.1b Integral Balances

Let us reconsider the form of the differential balance given in Equation 11.1-3.

$$\frac{dM}{dt} = \dot{m}_{\text{in}} + \dot{r}_{\text{gen}} - \dot{m}_{\text{out}} - \dot{r}_{\text{cons}} \tag{11.1-3}$$

The equation may be rewritten as

$$dM = \dot{m}_{\text{in}}\,dt + \dot{r}_{\text{gen}}\,dt - \dot{m}_{\text{out}}\,dt - \dot{r}_{\text{cons}}\,dt$$

and integrated from an initial time t_0 to a later time t_f, to obtain

$$\int_{t_0}^{t_f} dM = M(t_f) - M(t_0) = \int_{t_0}^{t_f} \dot{m}_{\text{in}}\,dt + \int_{t_0}^{t_f} \dot{r}_{\text{gen}}\,dt - \int_{t_0}^{t_f} \dot{m}_{\text{out}}\,dt - \int_{t_0}^{t_f} \dot{r}_{\text{cons}}\,dt \tag{11.1-4}$$

This is the integral balance equation. The left side is the accumulation of the balanced quantity in the system between t_0 and t_f. The term $(\dot{m}_{\text{in}}\,dt)$ is the amount of the balanced quantity that enters the system in the infinitesimal interval from t to $t + dt$, so that the integral

$$\int_{t_0}^{t_f} \dot{m}_{\text{in}}\,dt$$

is the total amount that enters between t_0 and t_f. Similar reasoning can be applied to the other terms, leading to the conclusion that Equation 11.1-4 is simply another statement of the general balance equation

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption} \tag{11.1-5}$$

only now each term represents an amount of the balanced quantity rather than a rate. For a closed (batch) system, if the balanced quantity is mass (as opposed to energy), $\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = 0$, and the equation may be written

$$M_{\text{initial}} + \int_{t_0}^{t_f} \dot{r}_{\text{generation}}\,dt = M_{\text{final}} + \int_{t_0}^{t_f} \dot{r}_{\text{consumption}}\,dt$$

or

$$\text{initial input} + \text{generation} = \text{final output} + \text{consumption}$$

This is the form of the integral balance equation given in Chapter 4 for a closed system.

The procedure to follow when writing a balance on a transient system is to derive the differential balance equation, integrate it between initial and final times, and solve for the unknown quantity in the resulting equation.

EXAMPLE 11.1-2 *Water Balance on a City Reservoir*

The water level in a municipal reservoir has been decreasing steadily during a dry spell, and there is concern that the drought could continue for another 60 days. The local water company estimates that the consumption rate in the city is approximately 10^7 L/day. The State Conservation Service estimates that rainfall and stream drainage into the reservoir coupled with evaporation from the reservoir should yield a net water input rate of $10^6\exp(-t/100)$ L/day, where t is the time in days from the beginning of the drought, at which time the reservoir contained an estimated 10^9 liters of water.

1. Write a differential balance on the water in the reservoir.
2. Integrate the balance to calculate the reservoir volume at the end of the 60 days of continued drought.

SOLUTION

1. We will write a balance on the mass M(kg) of water in the reservoir, but will express the equation in terms of volumes to make use of the given data, using the relationship $M(\text{kg}) = \rho(\text{kg/L})V(\text{L})$. The differential balance equation is as follows:

$$\frac{dM}{dt} = \dot{m}_{\text{in}} + \dot{r}_{\text{gen}} - \dot{m}_{\text{out}} - r_{\text{cons}} \qquad \text{(each term in kg/day)}$$

$$\Bigg\Downarrow \begin{array}{l} \dfrac{dM}{dt} = \dfrac{d}{dt}(\rho V) = \rho(\text{kg/L})\dfrac{dV}{dt}(\text{L/day}) \qquad \text{(since } \rho \text{ is constant)} \\ \dot{m}_{\text{in}} = \rho(\text{kg/L})[10^6 e^{-t/100}(\text{L/day})] \\ \dot{m}_{\text{out}} = \rho(\text{kg/L})(10^7\ \text{L/day}) \\ \dot{r}_{\text{gen}} = \dot{r}_{\text{cons}} = 0 \qquad \text{(water is not produced or consumed in the reservoir)} \\ \text{Cancel } \rho \end{array}$$

$$\boxed{\begin{array}{c} \dfrac{dV(t)}{dt} = 10^6\exp(-t/100) - 10^7 \\ t = 0, \quad V = 10^9\ \text{L} \end{array}}$$

2. We now separate variables and integrate the differential balance equation from $t = 0$ to $t = 60$ days.

$$\int_{V(0)}^{V(60)} dV = \int_0^{60\ \text{d}} [10^6\exp(-t/100) - 10^7]\,dt$$

$$\Downarrow$$

$$V(60\ \text{days}) - V(0) = \int_0^{60\ \text{d}} 10^6 e^{-t/100}\,dt - \int_0^{60\ \text{d}} 10^7\,dt$$

$$\Downarrow V(0) = 10^9\ \text{liters}$$

$$V(60\ \text{days}) = 10^9 - 10^6(10^2)e^{-t/100}\Big]_0^{60\ \text{d}} - 10^7 t\Big]_0^{60\ \text{d}}$$

$$= \boxed{4.45 \times 10^8\ \text{L}} \quad (\textit{verify})$$

TEST YOURSELF (Answers, p. 662)

A liquid, A, is poured at a rate of 10 kg/h into a tank containing a second liquid, B. The two substances react and A is consumed, but at a lower rate than that at which it is added. Liquid is withdrawn from the reaction vessel at a rate of 10 kg/h.

1. Which terms of the general balance equation

$$\text{accumulation} = \text{input} + \text{generation} - \text{output} - \text{consumption}$$

   do *not* equal zero in each of the following balances on the reaction vessel?
   (a) Total mass. **(b)** Moles of A. **(c)** Moles of B.
2. Write a differential mass balance on the system, letting $m(t)$ be the total mass of the system contents.

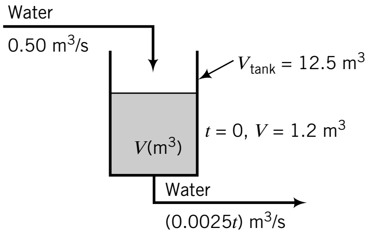
11.2 MATERIAL BALANCES

11.2a Total Mass Balances

A total mass balance necessarily has the form [accumulation = input − output], since mass can neither be generated nor consumed.[2] The accumulation term is always dM/dt, where $M(t)$ is the mass of the system contents. Once you have determined $M(t)$ by solving the differential balance equation, you may have to verify that the mathematical solution remains within the bounds of physical reality—that it does not become negative, for example, or that it does not exceed the total capacity of the system.

EXAMPLE 11.2-1 ***Mass Balance on a Water Storage Tank***

A 12.5-m^3 tank is being filled with water at a rate of 0.050 m^3/s. At a moment when the tank contains 1.20 m^3 of water, a bottom leak develops and gets progressively worse with time. The rate of leakage can be approximated as $0.0025t$ (m^3/s), where t(s) is the time from the moment the leak begins.



1. Write a mass balance on the tank and use it to obtain an expression for dV/dt, where V is the volume of water in the tank at any time. Provide an initial condition for the differential equation.
2. Solve the balance equation to obtain an expression for $V(t)$ and draw a plot of V versus t.

SOLUTION

1. The total mass of the tank contents is $M(\text{kg}) = \rho(\text{kg/m}^3)V(\text{m}^3)$, where $\rho = 1000$ kg/m^3 is the density of liquid water. Then

$$\text{accumulation (kg/s)} = \frac{d(\rho V)}{dt} = \rho\frac{dV}{dt}$$

(The second step follows from the fact that the density of the liquid water in the tank is independent of time and so may be taken out of the derivative.)

$$\text{input (kg/s)} = \rho(\text{kg/m}^3)(0.05\ \text{m}^3/\text{s}) = 0.05\rho$$

$$\text{output (kg/s)} = \rho(\text{kg/m}^3)[0.0025t\ (\text{m}^3/\text{s})] = 0.0025\rho t$$

---

[2] We are excluding nuclear reactions from consideration.

Substituting these terms into the water balance equation (accumulation = input − output) and canceling ρ yields the differential equation

$$\boxed{\begin{aligned}&\frac{dV}{dt} = 0.050\ \text{m}^3/\text{s} - 0.0025t\\ &t = 0, \quad V = 1.2\ \text{m}^3\end{aligned}}$$

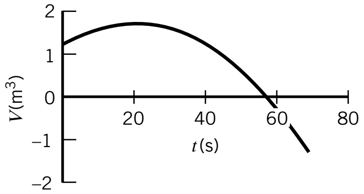
Verify that each term in the equation (including dV/dt) has units of m^3/s.

2. To solve the equation, we separate variables (bring dt to the right-hand side) and integrate from the initial condition ($t = 0$, $V = 1.2\ \text{m}^3$) to an arbitrary time, t, and corresponding volume, V.

$$\begin{aligned}dV(\text{m}^3) = (0.050 - 0.0025t)\,dt &\Longrightarrow \int_{1.2\ \text{m}^3}^{V} dV = \int_0^t (0.050 - 0.0025t)\,dt\\ &\Longrightarrow V\Big]_{1.2\ \text{m}^3}^{V} = \left(0.050t - 0.0025\frac{t^2}{2}\right)\Bigg]_0^t\\ &\Longrightarrow V(\text{m}^3) = 1.2 + 0.050t - 0.00125t^2\end{aligned}$$

Check 1: When $t = 0$, $V = 1.2\ \text{m}^3$ (confirming the given initial condition).
Check 2: $dV/dt = 0.050 - 0.0025t$ [differentiating $V(t)$ yields the original equation for dV/dt].

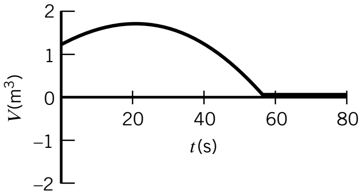
A plot of the derived expression for $V(t)$ is as follows:



Initially, the filling causes the volume of the tank contents to increase, but as the leak gets larger the tank begins to drain. The maximum volume is $1.7\ \text{m}^3$, well below the tank capacity of $12.5\ \text{m}^3$. At about $t = 57$ s the contents drain completely. The mathematical formula for V predicts negative volumes after this time, but physically the volume must remain at zero (the liquid discharges as fast as it is poured in). The actual solution of the balance equation is therefore

$$\boxed{\begin{aligned}V(\text{m}^3) &= 1.2 + 0.050t - 0.00125t^2 && 0 \le t \le 57\ \text{s}\\ &= 0 && t > 57\ \text{s}\end{aligned}}$$

The plot shown above should be changed in the range $t > 57$ s to a line coincident with the t axis.



11.2b A Brief Look Back at Calculus

As you will see, balances on transient systems often lead to differential equations that look like this:

$$\frac{d(VC_A)}{dt} = 1.50 \text{ mol/s} - (\text{s}^{-1})0.200VC_A \qquad \textbf{(11.2-1)}$$

$$C_A(0) = 2.00 \text{ mol/L}$$

In this equation, 1.50 mol/s would be the sum of the input and generation terms in the balance on species A and $0.200C_A$ would be the sum of the output and consumption terms. The goal would be to solve the differential balance to determine the concentration C_A(mol/L) as a function of time t(s), either as an analytical function or in the form of a table or plot.

This section reviews some calculus rules and procedures for solving differential equations like Equation 11.2-1. In what follows, x is an independent variable, $y(x)$ is a dependent variable, and a is a constant.

Rule 1: Derivative of a constant times a function

$$\frac{d(ay)}{dx} = a\frac{dy}{dx} \qquad \textbf{(11.2-2)}$$

If the system volume in Equation 11.2-1 is constant, the equation would become

$$V\frac{dC_A}{dt} = 1.50 \text{ mol/s} - 0.200VC_A$$

We will shortly review how to solve this equation.

Rule 2: Product rule for differentiation

$$\frac{d(y_1y_2)}{dx} = y_1\frac{dy_2}{dx} + y_2\frac{dy_1}{dx} \qquad \textbf{(11.2-3)}$$

If the system volume in Equation 11.2-1 changes with time (e.g., because the tank is being filled or discharged, or the reactor is a cylinder with a moving piston), the product rule yields

$$\frac{d(VC_A)}{dt} = V\frac{dC_A}{dt} + C_A\frac{dV}{dt} = 1.50 \text{ mol/s} - 0.200C_A$$

or

$$\frac{dC_A}{dt} = \frac{1}{V}[1.50 \text{ mol/s} - 0.200C_A] - \frac{C_A}{V}\left(\frac{dV}{dt}\right)$$

If V is constant, this equation reduces to the one given following Rule 1 (convince yourself). To solve for $C_A(t)$, you would have to obtain an independent expression for dV/dt and solve both equations simultaneously. We will discuss problems of this type in Section 11.5.

Rule 3: Solution of separable first-order differential equations

The general form of a first-order differential equation is

$$\frac{dy}{dx} = f(x, y)$$

Consider a specific example:

$$\frac{dy}{dx} = 3xy$$

Novice calculus students are often tempted to solve this equation by doing something like

$$y = \int (3xy)\,dx$$

which is correct but useless, since you cannot evaluate that integral without first substituting for $y(x)$, the function you are trying to determine.

A *separable* first-order differential equation is one that can be written in the form

$$\frac{dy}{dx} = f_1(x)f_2(y)$$
$$x = 0, \quad y = y(0)$$

The procedure for solving a separable equation is to bring all terms involving y (including dy) to one side of the equation and all terms involving x (including dx) to the other side, and then to integrate each side over its respective variable from the initial value [0 for x, $y(0)$ for y] to an arbitrary value:

$$\frac{dy}{dx} = f_1(x)f_2(y) \xrightarrow{\text{separate}} \frac{dy}{f_2(y)} = f_1(x)\,dx \xrightarrow{\text{integrate}} \int_{y(0)}^{y} \frac{dy}{f_2(y)} = \int_0^x f_1(x)\,dx \qquad \textbf{(11.2-4)}$$
$$x = 0, \quad y = y(0)$$

Each integral involves a function of only the variable of integration (y on the left, x on the right), and so both integrals can be evaluated to obtain an expression relating x and y.

Reconsider Equation 11.2-1 once more, letting the system volume V equal 1.00 liter.

$$\left\{\begin{aligned} \frac{dC_A}{dt} &= 1.50 \text{ mol/s} - (0.200\ L/s)C_A \\ t = 0, \quad C_A &= 2.00 \text{ mol/L} \end{aligned}\right\}$$

$$\overset{\text{separate}}{\Longrightarrow} \frac{dC_A}{1.50 - 0.200C_A} = dt \overset{\text{integrate}}{\Longrightarrow} \int_{2.00}^{C_A} \frac{dC_A}{1.50 - 0.200C_A} = \int_0^t dt$$

$$\Longrightarrow -\frac{1}{0.200}\ln(1.50 - 0.200C_A)\Big]_{2.00}^{C_A} = t \Longrightarrow \ln\left(\frac{1.50 - 0.200C_A}{1.50 - 0.400}\right) = -0.200t$$

$$\Longrightarrow \frac{1.50 - 0.200C_A}{1.10} = e^{-0.200t} \Longrightarrow \boxed{C_A(\text{mol/L}) = \frac{1}{0.200}(1.50 - 1.10e^{-0.200t(\text{s})})}$$

Try to follow each step of this procedure. It will be used to solve almost every balance equation in the remainder of this chapter.

TEST YOURSELF (Answers, p. 662)

Separate variables for each of the following equations to obtain integrals of the form of Equation 11.2-4. Then proceed as far as you can to obtain expressions for $y(t)$.

1. $(dy/dt) = 2 - t$, $y(0) = 1$.
2. $(dy/dt) = 2 - y$, $y(0) = 1$.
3. $(dy/dt) = (2 - t)(2 - y)$, $y(0) = 1$.

11.2c Balances on Single Well-Mixed Process Units

Here is the general procedure for writing and solving a transient material balance equation:

1. *Eliminate terms in the general balance equation that equal zero* (input and output for batch systems, generation and consumption for balances on total mass and nonreactive species).
2. *Write an expression for the total amount of the balanced species in the system* [$V(\text{m}^3)\rho(\text{kg/m}^3)$ for total mass, $V(\text{m}^3)C_A(\text{mol A/m}^3)$ or $n_{\text{total}}(\text{mol})x_A(\text{mol A/mol})$ for species A]. *Differentiate the expression with respect to time to obtain the accumulation term in the balance equation.*
3. *Substitute system variables into the remaining terms* (input, generation, output, consumption) *in the balance equation.* Make sure that all terms have the same units (kg/s, lb-mole/h, etc.).

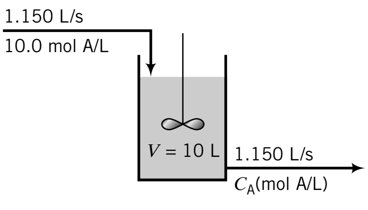
4. *If $y(t)$ is the dependent variable to be determined* (e.g., the mass of the system contents, the concentration of species A, the mole fraction of methane), *rewrite the equation to obtain an explicit expression for dy/dt. Supply a boundary condition*—the value of the dependent variable at a specified time (usually $t = 0$). This condition may be expressed as $[t = 0, y = y_0]$ or simply $[y(0) = y_0]$, where y_0 is a number.
5. *Solve the equation—analytically if possible, otherwise numerically.* In the processes to be analyzed in this chapter, you will generally be able to use separation of variables to obtain the solution analytically.
6. *Check the solution.* You can do so using any (and preferably all) of these methods:
   - **(a)** Substitute $t = 0$ and verify that the known initial condition $[y(0) = y_0]$ is obtained.
   - **(b)** Find the long-time asymptotic (steady-state) value of the dependent variable by setting dy/dt equal to 0 in the original balance equation and solving the resulting algebraic equation for y_{ss}, and then verify that if you let $t \to \infty$ in your solution, $y \to y_{ss}$. (The equation may not have a steady-state solution, in which case this method will not work.)
   - **(c)** Differentiate your solution to obtain an expression for dy/dt, substitute for y and dy/dt in the original differential equation, and verify that the equation is satisfied.
7. *Use your solution to generate a plot or table of y versus t.*

The next example illustrates this procedure.

EXAMPLE 11.2-2 Transient Behavior of a Stirred-Tank Reactor

Equipment Encyclopedia
reactor-CSTR

A liquid-phase reaction with stoichiometry A→B takes place in a continuous well-mixed 10.0-liter stirred-tank reactor. A schematic diagram of the process is shown below.



A ⟶ B, rate = $0.0050C_A$[mol A react/(L·s)]

The reactor may be considered perfectly mixed, so that the contents are uniform and the concentration of A in the product stream equals that inside the tank. The tank is initially filled with a solution that contains 2.00 mol A/L, and the inlet and outlet flows then begin.

1. Write a balance on species A in the tank and provide an initial condition.
2. Calculate C_{AS}, the steady-state concentration of A in the tank (the value approached as $t \to \infty$).
3. Sketch the shape expected for a plot of C_A versus t.
4. Solve the balance equation for $C_A(t)$, check the solution, and draw the actual plot of C_A versus t.

SOLUTION

Compare what follows with the general procedure given prior to this example.

1. The total moles of A in the reactor at any time equals $(10.0\text{ L})[C_A(\text{mol/L})] = 10.0C_A$ (mol A). Therefore,

Accumulation: $$\frac{d(10.0C_A)}{dt} = 10.0\frac{dC_A}{dt}\left(\frac{\text{mol A}}{\text{s}}\right)$$

Input: $(0.150\text{ L/s})(10.0\text{ mol A/L}) = 1.50\text{ mol A/s}$

Output: $(0.150\text{ L/s})[C_A(\text{mol A/L})] = 0.150C_A(\text{mol A/s})$

Generation: 0 mol A/s (A is not a reaction product)

Consumption: $(10.0\text{ L})[0.0050C_A(\text{mol A/(L·s)})] = 0.050C_A$ (mol A/s)

These terms are substituted into the balance equation on A (accumulation = input − output − consumption), which is then divided through by 10.0 to obtain an expression for dC_A/dt. The result along with the initial condition for the equation [$C_A(0) = 2.00$ mol A/L] is

$$\boxed{\begin{gathered}\frac{dC_A}{dt} = 0.150 \text{ mol A/s} - (0.0200 \text{ L/s})C_A \\ t = 0, \quad C_A = 2.00 \text{ mol A/L}\end{gathered}}$$

2. At steady state nothing varies with time, so that the derivative of C_A (and of every other system variable) with respect to time must equal zero. Setting $dC_A/dt = 0$ in the balance equation and letting $C_A = C_{AS}$ (steady state) in the resulting equation yields

$$0 = 0.150 \text{ mol/s} - 0.0200C_{AS} \Longrightarrow \boxed{C_{AS} = 7.50 \text{ mol A/L}}$$

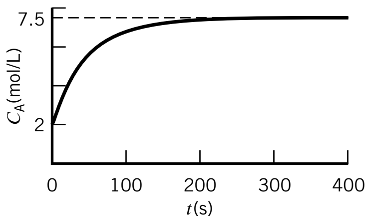
If C_{AS} had not had an asymptotic (steady-state) limit, the equation would not have had a finite solution.

3. We can now deduce quite a lot about the plot of C_A versus t, even though we have not yet solved the differential balance equation. We know a point at $t = 0$ (the initial condition) and the asymptotic value as $t \to \infty$ (the steady-state solution), and we also have an expression for the slope of the plot at any time (dC_A/dt) as a function of the concentration (slope $= 0.150 - 0.0200C_A$). Let us summarize what we can deduce.

- The plot originates at ($t = 0$, $C_A = 2.00$ mol/L).
- At $t = 0$, the slope of the plot is $[0.150 - 0.0200](2.00 \text{ mol/s}) = 0.110$ mol/s. Since it is positive, C_A must increase as t increases.
- As t continues to increase and C_A also increases, the slope of the curve ($0.150 - 0.0200C_A$) gets progressively less positive. The curve must therefore be concave down.

- At long times, the plot asymptotes to $C_A = 7.50$ mol/L.

Combining all these observations leads to the following sketch:



4. We may now solve the differential balance to determine the values of C_A at specific values of t or vice versa. Reconsider the equation

$$\frac{dC_A}{dt} = 0.150 - 0.0200C_A$$

$$t = 0, \quad C_A = 2.00$$

Separating variables and integrating as in Equation 11.2-4 yields

$$\frac{dC_A}{0.150-0.0200C_A}=dt\Longrightarrow\int_{2.00}^{C_A}\frac{dC_A}{0.150-0.0200C_A}=\int_0^t dt=t$$

$$\Longrightarrow -\frac{1}{0.0200}\ln(0.150-0.0200C_A)\Big]_{2.00}^{C_A}=t\Longrightarrow \ln\frac{0.150-0.0200C_A}{0.150-0.0200(2.00)}=-0.0200t$$

$$\Longrightarrow\frac{0.150-0.0200C_A}{0.110}=e^{-0.0200t}\Longrightarrow\boxed{C_A(\text{mol/L})=7.50-5.50e^{-0.0200t}}$$

(Verify each step.)

Whenever you obtain the solution of a differential equation, you should check it as many ways as you can. In this case, we have three ways:

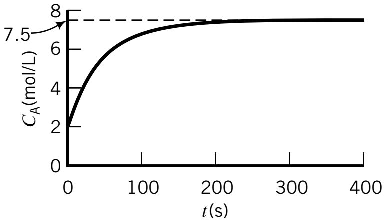
Check 1: Substitute $t=0$ into the solution $\Longrightarrow C_A(0)=2.00$ mol/L (the correct initial value).

Check 2: Substitute $t\to\infty$ into the solution to obtain $C_A(\infty)=7.50$ mol/L (the previously determined steady-state value).

Check 3: Differentiate the equation to obtain an expression for dC_A/dt, and then substitute for both dC_A/dt and $C_A(t)$ in the original equation $[dC_A/dt=1.50-0.200C_A]$ to show that the solution satisfies the equation.

Verify that the derived solution satisfies each of these conditions.

A plot of the solution matches the form of the plot previously sketched.



11.3 ENERGY BALANCES ON SINGLE-PHASE NONREACTIVE PROCESSES

The general energy balance has the form

$$\text{accumulation}=\text{input}-\text{output}\qquad\textbf{(11.3-1)}$$

since energy can neither be generated nor consumed.

Suppose $E_{\text{sys}}(t)$ is the total energy (internal + kinetic + potential) of a system, and $\dot{m}_{\text{in}}$ and $\dot{m}_{\text{out}}$ are the mass flow rates of the system input and output streams. (If the system is closed, these quantities each equal zero.) Proceeding as in the development of the transient mass balance equation, we apply the general energy balance equation (11.3-1) to the system in a small time interval from t to $t+\Delta t$, during which time the properties of the input and output streams remain approximately constant. The terms of the equation are as follows (see Section 7.4):

$$\text{accumulation}=\Delta E_{\text{sys}}=\Delta U_{\text{sys}}+\Delta E_{\text{k,sys}}+\Delta E_{\text{p,sys}}$$

$$\text{input}=\dot{m}_{\text{in}}\left(\hat{H}_{\text{in}}+\frac{u_{\text{in}}^2}{2}+gz_{\text{in}}\right)\Delta t+\dot{Q}\,\Delta t$$

$$\text{output}=\dot{m}_{\text{out}}\left(\hat{H}_{\text{out}}+\frac{u_{\text{out}}^2}{2}+gz_{\text{out}}\right)\Delta t+\dot{W}_s\,\Delta t$$

where the quantities in parentheses are the specific enthalpies, kinetic energies, and potential energies of the input and output streams, and $\dot{Q}$ and $\dot{W}_s$ are the rates of transfer of heat and shaft work. (See Section 7.4c.) Any or all of the variables $\dot{m}$, $\hat{H}$, u, z, $\dot{Q}$, and $\dot{W}_s$ may vary with time.

If we now substitute the given expressions for accumulation, input, and output into Equation 11.3-1, divide by Δt, and let Δt approach zero, we obtain the general differential energy balance:

$$\frac{dU_{\text{sys}}}{dt} + \frac{dE_{\text{k,sys}}}{dt} + \frac{dE_{\text{p,sys}}}{dt} = \dot{m}_{\text{in}}\left(\hat{H}_{\text{in}} + \frac{u_{\text{in}}^2}{2} + gz_{\text{in}}\right) - \dot{m}_{\text{out}}\left(\hat{H}_{\text{out}} + \frac{u_{\text{out}}^2}{2} + gz_{\text{out}}\right) + \dot{Q} - \dot{W}_s \qquad \textbf{(11.3-2)}$$

If there are several input and output streams, a term of the form

$$\dot{m}\left(\hat{H} + \frac{u^2}{2} + gz_{\text{in}}\right)$$

must be included in Equation 11.3-2 for each stream.

It is quite difficult to solve Equation 11.3-2 unless a number of simplifications are made. We will restrict our consideration to systems that satisfy the following conditions:

1. The system has at most a single input stream and a single output stream, each with the same mass flow rate.

$$\dot{m}_{\text{in}} = \dot{m}_{\text{out}} = \dot{m} \qquad \textbf{(11.3-3)}$$

A consequence of this assumption is that the mass of the system contents does not change with time.

2. Kinetic and potential energy changes in the system and between the inlet and outlet streams are negligible.

$$\frac{dE_{\text{k,sys}}}{dt} \approx \frac{dE_{\text{p,sys}}}{dt} \approx 0 \qquad \textbf{(11.3-4)}$$

$$\dot{m}\left(\frac{u_{\text{in}}^2}{2} - \frac{u_{\text{out}}^2}{2}\right) \approx 0 \qquad \textbf{(11.3-5)}$$

$$\dot{m}(gz_{\text{in}} - gz_{\text{out}}) \approx 0 \qquad \textbf{(11.3-6)}$$

Under these conditions, Equation 11.3-2 simplifies to

$$\frac{dU_{\text{sys}}}{dt} = \dot{m}(\hat{H}_{\text{in}} - \hat{H}_{\text{out}}) + \dot{Q} - \dot{W}_s \qquad \textbf{(11.3-7)}$$

If the equation is applied to a closed system, $\dot{m} = 0$, and the rate of transfer of energy as shaft work, $\dot{W}_s$, must be replaced by the total rate of energy transfer as work, $\dot{W}$.

Equation 11.3-7 is simple in appearance, but its solution is still generally difficult to obtain. If, for example, the composition or temperature of the system contents varies with position in the system, it is difficult to express the total internal energy U_{sys} in terms of measurable quantities, and a similar problem occurs if phase changes or chemical reactions take place in the course of the process. To illustrate the solution of energy balance problems without becoming too involved in the thermodynamic complexities, we will impose the additional restrictions that follow.

3. The temperature and composition of the system contents do not vary with position within the system (i.e., the system is perfectly mixed). In consequence, the outlet stream and the system contents must be at the same temperature, or

$$T_{\text{out}} = T_{\text{sys}} = T \qquad \textbf{(11.3-8)}$$

4. No phase changes or chemical reactions take place within the system; $\hat{U}$ and $\hat{H}$ are independent of pressure; and the mean heat capacities C_v and C_p of the system contents (and of the inlet and outlet streams) are independent of composition and temperature, and hence unchanging with time. Then if T_r is a reference temperature at which $\hat{H}$ is defined to be zero and M is the mass (or number of moles) of the system contents,

$$U_{\text{sys}} = M\hat{U}_{\text{sys}} = M[\hat{U}(T_r) + C_v\,(T - T_r)]$$

$$\Big\Downarrow\ M,\ \hat{U}(T_r),\text{ and } C_v \text{ are constant}$$

$$\frac{dU_{\text{sys}}}{dt} = MC_v\,\frac{dT}{dt} \tag{11.3-9}$$

$$\hat{H}_{\text{in}} = C_p(T_{\text{in}} - T_r) \tag{11.3-10}$$

$$\hat{H}_{\text{out}} = C_p(T_{\text{out}} - T_r)$$

$$\Big\Downarrow\ \text{Equation 11.3-8}$$

$$\hat{H}_{\text{out}} = C_p(T - T_r) \tag{11.3-11}$$

Finally, we may substitute the expressions of Equations 11.3-3 through 11.3-11 into the general energy balance (Equation 11.3-2) to obtain for an open system

Open System:

$$\boxed{MC_v\,\frac{dT}{dt} = \dot{m}C_p(T_{\text{in}} - T) + \dot{Q} - \dot{W}_s} \tag{11.3-12}$$

(Verify this result for yourself.) For a closed system, the equation is

Closed System:

$$\boxed{MC_v\,\frac{dT}{dt} = \dot{Q} - \dot{W}} \tag{11.3-13}$$

To summarize, the conditions under which Equations 11.3-12 and 11.3-13 are valid are: (a) negligible kinetic and potential energy changes, (b) no accumulation of mass in the system, (c) pressure independence of $\hat{U}$ and $\hat{H}$, (d) no phase changes or chemical reactions, and (e) a spatially uniform system temperature. Any or all of the variables T, T_{in}, $\dot{Q}$ and $\dot{W}_s$ (or $\dot{W}$) may vary with time, but the system mass, M, the mass throughput rate, $\dot{m}$, and the heat capacities, C_v and C_p, must be constants.

The following example illustrates the derivation and solution of an energy balance on a closed system that satisfies these restrictions.

EXAMPLE 11.3-1 *Startup of a Batch Reactor*

Equipment Encyclopedia
reactor-batch

A well-stirred batch reactor wrapped in an electrical heating mantle is charged with a liquid reaction mixture. The reactants must be heated from an initial temperature of 25°C to 250°C before the reaction can take place at a measurable rate. Use the data given below to determine the time required for this heating to take place.

Reactants: Mass $= 1.50$ kg
$C_v = 0.900$ cal/(g·°C)

Reactor: Mass $= 3.00$ kg
$C_v = 0.120$ cal/(g·°C)

Heating rate: $\dot{Q} = 500.0$ W

Negligible reaction and no phase changes during heating.
Negligible energy added to the system by the stirrer.

SOLUTION

We first note that the conditions of validity of the simplified closed system energy balance equation, Equation 11.3-13, are all satisfied (*verify*); moreover, since the system has constant volume and the energy input due to the stirrer is presumed negligible, $\dot{W} \approx 0$. The equation therefore becomes

$$MC_v \frac{dT}{dt} = \dot{Q}$$
$$t = 0, \quad T_{\text{sys}} = 25°\text{C}$$

The task is now to integrate this equation from the initial state of the system ($t = 0$, $T = 25°\text{C}$) to the final state ($t = t_f$, $T = 250°\text{C}$), and to solve the integrated equation for the heating time t_f. Rearranging the equation,

$$MC_v\,dT = \dot{Q}\,dt$$
$$\Big\Downarrow \text{Integrate}$$
$$\int_{25°\text{C}}^{250°\text{C}} MC_v\,dT = \int_0^{t_f} \dot{Q}\,dt$$
$$\Big\Downarrow \dot{Q}, M, \text{and } C_v \text{ are constant}$$
$$MC_v(250°\text{C} - 25°\text{C}) = \dot{Q}t_f$$
$$\Big\Downarrow$$
$$t_f = \frac{225MC_v}{\dot{Q}}$$

The heat capacity of the system is obtained from Equation 8.3-13 as

$$C_v = \frac{M_{\text{reactants}}}{M}(C_v)_{\text{reactants}} + \frac{M_{\text{reactor}}}{M}(C_v)_{\text{reactor}}$$
$$\Big\Downarrow$$
$$\begin{aligned} MC_v &= (1500\text{ g})\left(0.900\frac{\text{cal}}{\text{g·°C}}\right) + (3000\text{ g})\left(0.120\frac{\text{cal}}{\text{g·°C}}\right) \\ &= (1710\text{ cal/°C})(4.184\text{ J/cal}) \\ &= 7150\text{ J/°C} \end{aligned}$$

The final result is

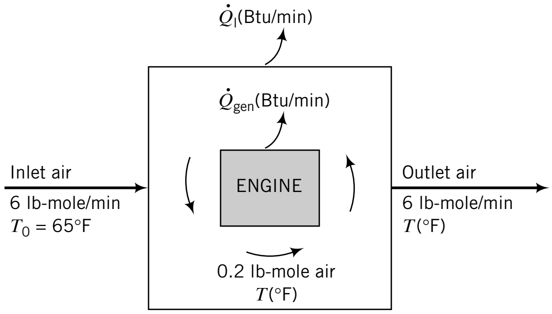
$$t_f = \frac{225MC_v}{\dot{Q}}$$
$$\Big\Downarrow \begin{array}{l} MC_v = 7150\text{ J/°C} \\ \dot{Q} = 500\text{ W} = 500\text{ J/s} \end{array}$$
$$\begin{aligned} t_f &= \frac{7150(\text{J/°C})}{500(\text{J/s})}(225°\text{C}) \\ &= 3220\text{ s} \Longrightarrow \boxed{53.7\text{ min}} \end{aligned}$$

Question: Which restriction on the energy balance (Equation 11.3-13) would probably be violated if the reactants were not stirred?

The final example illustrates a transient energy balance on a continuous system.

EXAMPLE 11.3-2 *Transient Behavior of an Air-Cooling System*

An air-cooled engine generates heat at a constant rate $\dot{Q}_{\text{gen}} = 8530$ Btu/min.



The air in the engine housing is circulated rapidly enough for its temperature to be considered uniform and equal to the temperature of the outlet air. Air passes through the engine housing at a rate of 6.00 lb-mole/min, entering at a temperature of 65°F, and an average of 0.200 lb-mole of air is contained within the engine housing. (We will neglect the variation of this quantity with the changing temperature of the gas.) Heat is lost from the housing to its surroundings at a rate

$$\dot{Q}_{\text{lost}}(\text{Btu/min}) = [33.0\ \text{Btu/(°F·min)}](T - 65\text{°F})$$

Suppose the engine is started with the inside air temperature equal to 65°F.

1. Calculate the steady-state air temperature if the engine runs continuously for an indefinite period of time, assuming

$$C_v = 5.00\ \text{Btu/(lb-mole·°F)}$$

2. Derive a differential equation for the variation of the outlet temperature with the time from startup and solve it.

SOLUTION System = the air within the engine housing.

1. The steady-state energy balance equation may be obtained by setting dT/dt equal to zero in Equation 11.3-12.

$$0 = \dot{m}C_p(T_{\text{in}} - T) + \dot{Q} - \dot{W}_s$$

$$\Bigg\Downarrow \begin{array}{|l} T_{\text{in}} = 65\text{°F (given)} \\ T = T_s(\text{°F}) \quad \text{(steady-state outlet temperature)} \\ \dot{W}_s = 0 \quad \text{(no moving parts)} \\ \dot{Q} = \dot{Q}_{\text{gen}} - \dot{Q}_{\text{lost}} \end{array}$$

$$\dot{m}C_p(T_s - 65.0\text{°F}) = 8530\ \text{Btu/min} - 33.0(T_{ss} - 65.0\text{°F})$$

Assuming ideal gas behavior

$$C_p = C_v + R = (5.00 + 1.99)\text{Btu/(lb-mole·°F)} \quad \text{(Equation 8.3-12)}$$

$$\dot{m}C_p = \frac{6.00\ \text{lb-mole}}{\text{min}}\left|\frac{6.99\ \text{Btu}}{\text{lb-mole·°F}}\right. = 41.9\ \frac{\text{Btu}}{\text{min·°F}}$$

The energy balance equation then becomes

$$41.9(T_s - 65.0\text{°F}) = 8530\ \text{Btu/min} - 33.0(T_s - 65.0\text{°F})$$

$$\Downarrow$$

$$\boxed{T_s = 179\text{°F}}$$

2. The unsteady-state balance equation (11.3-12) is, for our system,

$$MC_v \frac{dT}{dt} = \dot{m}C_p(65°\text{F} - T) + \dot{Q}_{\text{gen}} - \dot{Q}_{\text{lost}}$$

$$\Bigg\Downarrow \begin{array}{l} M = 0.2 \text{ lb-mole} \\ C_v = 5.00 \text{ Btu/(lb-mole·°F)} \\ \dot{m}C_p = 41.9 \text{ Btu/(min·°F)} \quad \text{[from part 1]} \\ \dot{Q}_{\text{gen}} = 8530 \text{ Btu/min} \\ \dot{Q}_{\text{lost}} = 33.0(T - 65)(\text{Btu/min}) \end{array}$$

$$\boxed{\begin{array}{c} \dfrac{dT}{dt} = -74.9T + 13{,}400°\text{C/min} \\ t = 0, \quad T = 65°\text{F} \end{array}}$$

You can check this result by setting $dT/dt = 0$ and solving the resulting equation for the steady-state value of T. The result is $(13{,}400/74.9)$°F $= 179$°F, in agreement with the result of part 1.

The solution of the equation is obtained by separating variables and integrating:

$$\int_{65°\text{F}}^{T} \frac{dT}{13{,}400 - 74.9T} = \int_0^t dt$$

$$\Downarrow$$

$$-\frac{1}{74.9}\ln(13{,}400 - 74.9T)\Big]_{65°\text{F}}^{T} = t$$

$$\Downarrow$$

$$\ln(13{,}400 - 74.9T) = -74.9t + \ln(8530)$$

$$\Downarrow$$

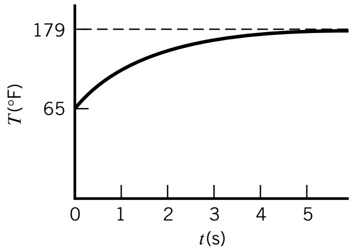
$$13{,}400 - 74.9T = 8530\exp(-74.9t)$$

$$\Downarrow$$

$$\boxed{T(°\text{F}) = 179 - 114\exp(-74.9t)}$$

A check on the solution may be obtained by substituting $t = 0$ and verifying that T equals the specified initial value, 65°F.

If you evaluate T from this equation for a number of values of $t(s)$, a plot would appear as follows:



The plot starts from the initial condition of 65°F and asymptotically approaches the steady-state value of 179°F. It takes 3.8 seconds for the temperature to reach 178°F, one degree short of its final value.

TEST YOURSELF (Answers, p. 662)

1. Under what conditions is the simplified form of the energy balance (Equation 11.3-12) valid?
2. Suppose the heat capacity C_v is a function of T, which varies with time. Where would the derivation of Equation 11.3-12 break down?

11.4 SIMULTANEOUS TRANSIENT BALANCES

Throughout this book, we have seen that when more than one species is involved in a process or when energy balances are required, several balance equations must be derived and solved simultaneously. For steady-state systems the equations are algebraic, but when the systems are transient, simultaneous differential equations must be solved. For the simplest systems, analytical solutions may be obtained by hand, but more commonly numerical solutions are required. Software packages that solve general systems of ordinary differential equations—such as Mathematica®, Maple®, Matlab®, TK-Solver®, Polymath®, and EZ-Solve®—are readily obtained for most computers. Other software packages have been designed specifically to simulate transient chemical processes. Some of these dynamic process simulators run in conjunction with the steady-state flowsheet simulators mentioned in Chapter 10 (e.g., SPEEDUP®, which runs with Aspen Plus, and a dynamic component of HYSYS®) and so have access to physical property databases and thermodynamic correlations.

Suppose $y_1(t), y_2(t), \ldots, y_n(t)$ are dependent variables in a process system (such as species flow rates or concentrations or mole fractions or temperature), and that at time $t = t_0$ (usually but not always 0) these variables have the values $y_{1i}, y_{2i}, \ldots, y_{ni}$. The goal is to derive a set of n differential equations that have the following form:

$$\frac{dy_1}{dt} = f_1(y_1, y_2, \ldots, y_n, t) \qquad \textbf{(11.4-1)}$$

$$y_1(t_0) = y_{1i}$$

$$\frac{dy_2}{dt} = f_2(y_1, y_2, \ldots, y_n, t) \qquad \textbf{(11.4-2)}$$

$$y_2(t_0) = y_{2i}$$

$$\vdots \qquad\qquad \vdots$$

$$\frac{dy_n}{dt} = f_n(y_1, y_2, \ldots, y_n, t) \qquad \textbf{(11.4-}\boldsymbol{n}\textbf{)}$$

$$y_n(t_0) = y_{ni}$$

The functions on the right-hand sides of these equations are derived from the input, output, generation, and consumption terms in the balance equations. The solutions of the equations may be expressed as a table of $y_1, y_2, \ldots, y_n$ for increasing values of t or as plots of y_1 versus t, y_2 versus $t, \ldots, y_n$ versus t. The next example provides an illustration.

EXAMPLE 11.4-1 *Transient Balances on a Semibatch Reactor*

Equipment Encyclopedia
reactor: semi-batch

An aqueous solution containing 0.015 mol/L of species A is fed into a holding tank that initially contains 75 liters of pure water. The reactant decomposes at a rate

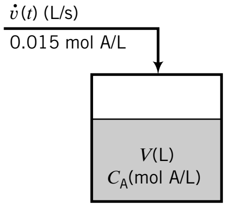
$$r[\text{mol A/(L·s)}] = 0.0375C_A$$

where C_A(mol A/L) is the concentration of A in the tank. The volumetric feed rate of the solution, $\dot{v}(t)$, increases linearly over a 10-second period from 0 to 25 L/s and stays constant at that rate thereafter until the tank is filled to the desired level. The density of the feed stream is constant.

1. Write transient balances for the total mass of the tank contents and the mass of A in the tank. Convert the equations to differential equations for $V(t)$ (the volume of the tank contents) and $C_A(t)$ (the concentration of A in the tank) that have the form of Equations 11.4-1 and 11.4-2, and provide initial conditions.

2. Sketch the shapes of the plots you would expect for the volume of the tank contents, V(L), and the concentration of A in the tank, C_A(mol/L), versus time.
3. Outline how the equations would be solved to derive an expression for $C_A(t)$ for the period from $t = 0$ to $t = 60$ s.

SOLUTION A flowchart of the process is as follows:



The concentration of A in the tank changes with time because both the moles of A in the tank and the volume of the tank contents are changing.

1. ***Total mass balance***: accumulation = input (kg/s). The total mass of the tank contents (kg) at any time is ρ(kg/L)V(L), and the mass flow rate of the feed stream (kg/s) is ρ(kg/L)$\dot{v}$(L/s). The mass balance thus becomes $d(\rho V)/dt = \rho\dot{v}$, or, bringing ρ (which we are told is constant) out of the derivative and canceling it,

$$\boxed{\begin{aligned}\frac{dV}{dt} &= \dot{v}\\ V(0) &= 75.0\text{ L}\end{aligned}} \tag{1}$$

Balance on A: accumulation (mol A/s) = input − consumption. The number of moles of A in the tank at any time equals V(L)C_A(mol A/L). The balance equation therefore becomes

$$\frac{d}{dt}(VC_A) = \dot{v}\left(\frac{\text{L}}{\text{s}}\right)\cdot 0.015\,\frac{\text{mol A}}{\text{L}} - (0.0375C_A)\left(\frac{\text{mol A}}{\text{L·s}}\right)V(\text{L})$$

$$\Big\Downarrow \text{product rule}$$

$$V\frac{dC_A}{dt} + C_A\frac{dV}{dt} = 0.015\dot{v} - 0.0375VC_A$$

$$\Big\Downarrow \text{Substitute for } dV/dt \text{ from Equation 1, solve for } dC_A/dt$$

$$\boxed{\begin{aligned}\frac{dC_A}{dt} &= \frac{\dot{v}}{V}(0.015\text{ mol A/L} - C_A) - 0.0375C_A\\ C_A(0) &= 0\text{ mol A/L}\end{aligned}} \tag{2}$$

The initial condition in Equation 2 follows from the statement that the tank initially contains pure water. In Equations 1 and 2,

$$\dot{v}(t) = 2.5t \qquad 0 \le t \le 10\text{s} \tag{3a}$$

$$= 25\text{ L/s} \qquad t > 10\text{ s} \tag{3b}$$

(Verify Equation 3a.)

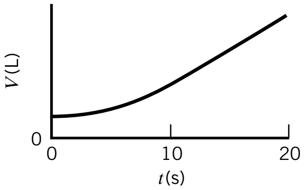
Equations 1 and 2 are two differential equations in two dependent variables that have the form of Equations 11.4-1 and 11.4-2, where V and C_A correspond to y_1 and y_2, respectively. The equations may therefore be solved with any of the computer programs mentioned at the beginning of this section.[3]

---

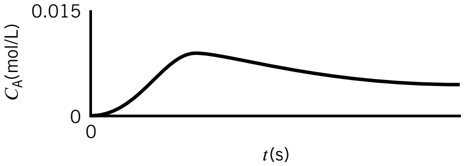
[3] It would be easier in this particular problem to solve Equation 1 analytically and substitute for $V(t)$ in Equation 2. The methods we are illustrating now would work even if an analytical solution to Equation 1 could not be found.

2. To predict the shape of the curve on a plot of V versus t, we need only remember that the slope of the curve is dV/dt, which in turn equals $\dot{v}(t)$ (from Equation 1). Try to follow this chain of reasoning:

- A point on the plot of V versus t is the initial condition ($t = 0, V = 75$ L).
- During the first 10 seconds, $dV/dt = 2.5t$ (from Equations 1 and 3a). The slope of the curve therefore equals zero at $t = 0$ (so that the curve is horizontal at the V axis) and increases over the first 10 seconds (so that the curve is concave up).
- At $t = 10$ seconds, dV/dt reaches a value of 25 L/s and thereafter remains constant at that value. A curve with a constant slope is a straight line. The plot of V versus t for $t \geq 10$ s must therefore be a straight line with a slope of 25 L/s.
- Putting the preceding observations together, we conclude that the plot of V versus t starts horizontally at ($t = 0, V = 75$ L), curves up for 10 seconds, and then becomes a straight line with a slope of 25 L/s. It should have the following appearance:



- The plot of C_A versus t must begin at ($t = 0, C_A = 0$), since the tank initially contains pure water.
- At $t = 0$, the expression of Equation 2 for dC_A/dt equals zero since both t and C_A are zero at this point. (*Verify.*) The plot of C_A versus t is therefore horizontal at the C_A axis. Since we are adding A to the tank, its concentration must increase and so the curve must be concave up.
- As time proceeds, more and more of the tank volume is occupied by fluid in which the A has had a long time to react. We could anticipate that at a *very* long time, the tank would contain a huge volume with very little A in it, and the A being added would be diluted down to a concentration approaching zero. C_A should therefore increase near $t = 0$, rise to a maximum, start decreasing, and approach zero at long times.
- Furthermore, the concentration in the tank can never be greater than that in the feed stream (0.015 mol/L) and, in fact, must always be less than this amount since (a) the feed is diluted by the water initially in the tank and (b) some of the A in the feed reacts once it is in the tank. The maximum value of C_A must therefore be less than 0.015 mol A/L.
- All of these observations combine to predict a plot with the following shape:



3. The system of equations must be solved in two stages—the first from $t = 0$ to $t = 10$ s (when $v = 2.5t$) and the second for $t > 10$ s, when $\dot{v} = 25$ L/s. The procedure is as follows:

- Substitute $2.5t$ for $\dot{v}(t)$ in Equations 1 and 2.

$$\frac{dV}{dt} = 2.5t \tag{1a}$$

$$V(0) = 75.0 \text{ L}$$

$$\frac{dC_A}{dt} = \frac{2.5t}{V}(0.015 - C_A) - 0.0375C_A \tag{2a}$$

$$C_A(0) = 0$$

When this pair of equations is solved for $V(t)$ and $C_A(t)$ (we will omit details of the solution procedure), we determine that $V(10\text{ s}) = 200\text{ L}$ and $C_A(10\text{ s}) = 0.00831\text{ mol A/L}$.

- Substitute $\dot{v}(t) = 25\text{ L/s}$ in Equations 1 and 2 and substitute the dependent variable values at $t = 10$ s for the initial conditions:

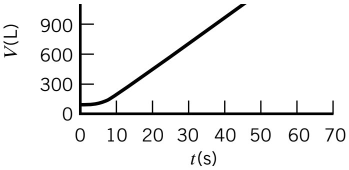
$$\frac{dV}{dt} = 25\text{ L/s} \tag{1b}$$

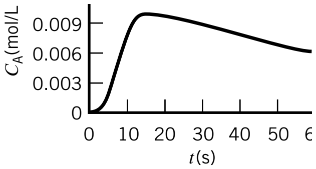
$$V(10) = 200\text{ L}$$

$$\frac{dC_A}{dt} = \frac{25}{V}(0.015 - C_A) - 0.0375C_A \tag{2b}$$

$$C_A(10) = 0.0831\text{ mol A/L}$$

These equations may be solved for $V(t)$ and $C_A(t)$ for $t > 10$ s. These solutions along with the previous solutions for $t \leq 10$ s are shown in the following plots:





11.5 SUMMARY

All batch and semibatch processes are transient, as are continuous processes being started up, shut down, or in transition from one operating state to another. The accumulation terms in balance equations for transient systems are not zero (as they are for steady-state systems) but rather are derivatives of system variables with respect to time, and balance equations are consequently differential rather than algebraic.

The procedure for writing and solving transient balances is as follows:

- Write an expression for the amount of the balanced quantity in the system (mass, moles of a particular species, energy) and set the accumulation term in the balance equation equal to the derivative of that amount with respect to time.
- Substitute for the input, output, generation, and consumption terms in the balance equation, and convert the resulting equation into one with the form

$$\frac{dy}{dt} = f(y, t)$$

$$y(0) = y_0$$

  where $y(t)$ is the dependent system variable to be determined (total mass or volume of the system contents, concentration or mole fraction of a species, temperature) and y_0 is the specified initial value of y.
- Sketch the anticipated plot of y versus t, using the initial condition to locate the starting point and using what you know about the slope (which equals dy/dt) to predict the shape of the curve.
- If the balance equation can be solved analytically (e.g., by separation of variables and integration), do so; otherwise, solve it using differential equation-solving software.
- If the system involves more than one dependent variable (such as a semibatch unit in which both the volume and composition of the system contents vary or a reactor in which several

reactions occur simultaneously), write balance equations for all the dependent variables and convert them to the form

$$\frac{dy_1}{dt} = f_1(y_1, y_2, \ldots, y_n, t)$$

$$y_1(t_0) = y_{1i}$$

$$\vdots$$

$$\frac{dy_n}{dt} = f_n(y_1, y_2, \ldots, y_n, t)$$

$$y_n(t_0) = y_{ni}$$

Differential equation-solving software may then be used to generate tables and/or plots of the dependent variables versus time.

PROBLEMS

Most of the following problems ask you to write one or more transient balances, provide initial conditions for each derived equation, and integrate the equations. Whether or not such a problem explicitly requests it, you should always check your solution by verifying that (a) the initial condition is satisfied, (b) differentiating your solution yields the original balance equation, and (c) the previously determined steady-state solution (if one has been determined) is approached as $t \rightarrow \infty$ in the transient solution.

11.1. A solution containing hydrogen peroxide with a mass fraction x_{p0} (kg H_2O_2/kg solution) is added to a storage tank at a steady rate $\dot{m}_0$(kg/h). During this process, the liquid level reaches a corroded spot in the tank wall and a leak develops. As the filling continues, the leak rate $\dot{m}_1$(kg/h) becomes progressively worse. Moreover, once it is in the tank the peroxide begins to decompose at a rate

$$r_d(\text{kg/h}) = kM_p$$

where M_p(kg) is the mass of peroxide in the tank. The tank contents are well mixed, so that the peroxide concentration is the same at all positions. At a time $t = 0$ the liquid level reaches the corroded spot. Let M_0 and M_{p0} be the total liquid mass and mass of peroxide, respectively, in the tank at that moment, and let $M(t)$ be the total mass of liquid in the tank at any time thereafter.

- **(a)** Show that the leakage rate of hydrogen peroxide at any time is $\dot{m}_1 M_p/M$.
- **(b)** Write differential balances on the total tank contents and on the peroxide in the tank, and provide initial conditions. Your solution should involve only the quantities $\dot{m}_0$, $\dot{m}_1$, x_{p0}, k, M, M_0, M_p, M_{p0}, and t.

11.2. One hundred fifty kmol of an aqueous phosphoric acid solution contains 5.00 mole% H_3PO_4. The solution is concentrated by adding pure phosphoric acid at a rate of 20.0 L/min.

- **(a)** Write a differential mole balance on phosphoric acid and provide an initial condition. [Start by defining n_p(kmol) to be the total quantity of phosphoric acid in the tank at any time.]
- **(b)** Solve the balance to obtain an expression for $n_p(t)$. Use the result to derive an expression for $x_p(t)$, the mole fraction of phosphoric acid in the solution.
- **(c)** How long will it take to concentrate the solution to 15% H_3PO_4?

11.3. Methanol is added to a storage tank at a rate of 1200 kg/h and is simultaneously withdrawn at a rate $\dot{m}_w(t)$ (kg/h) that increases linearly with time. At $t = 0$ the tank contains 750 kg of the liquid and $\dot{m}_w = 750$ kg/h. Five hours later $\dot{m}_w$ equals 1000 kg/h.

- **(a)** Calculate an expression for $\dot{m}_w(t)$, letting $t = 0$ signify the time at which $\dot{m}_w = 750$ kg/h, and incorporate it into a differential methanol balance, letting M(kg) be the mass of methanol in the tank at any time.
- **(b)** Integrate the balance equation to obtain an expression for $M(t)$ and check the solution two ways. (See Example 11.2-1.) For now, assume that the tank has an infinite capacity.
- **(c)** Calculate how long it will take for the mass of methanol in the tank to reach its maximum value, and calculate that value. Then calculate the time it will take to empty the tank.
- **(d)** Now suppose the tank volume is 3.40 m^3. Draw a plot of M versus t, covering the period from $t = 0$ to an hour after the tank is empty. Write expressions for $M(t)$ in each time range when the function changes.

11.4. A 10.0-ft^3 compressed-air tank is being filled. Before the filling begins, the tank is open to the atmosphere. The reading on a Bourdon gauge mounted on the tank increases linearly from an initial value of 0.0 to 100 psi after 15 seconds. The temperature is constant at 72°F, and atmospheric pressure is 1 atm.

(a) Calculate the rate $\dot{n}$(lb-mole/s) at which air is being added to the tank, assuming ideal gas behavior. (*Suggestion:* Start by calculating how much is in the tank at $t = 0$.)

(b) Let $N(t)$ equal the number of lb-moles of air in the tank at any time. Write a differential balance on the air in the tank in terms of N and provide an initial condition.

(c) Integrate the balance to obtain an expression for $N(t)$. Check your solution two ways.

(d) Estimate the number of lb-moles of *oxygen* in the tank after two minutes.

11.5. A gas storage tank with a floating roof receives a steady input of 540 m^3/h of a natural gas. The rate of withdrawal of gas from the tank, $\dot{v}_{\text{w}}$, varies more or less randomly during the day and is recorded at 10-min intervals. At 8:00 a.m. one morning the volume of stored gas is 3.00×10^3 m^3. The withdrawal rate data for the next 4 hours are as follows:

Hour Beginning at	$\dot{v}_{\text{w}}$(m^3/min)
8:00	11.4, 11.9, 12.1, 11.8, 11.5, 11.3
9:00	11.4, 11.1, 10.6, 10.8, 10.4, 10.2
10:00	10.2, 9.8, 9.4, 9.5, 9.3, 9.4
11:00	9.5, 9.3, 9.6, 9.6, 9.4, 9.9
12:00	9.8

The temperature and pressure of the inlet, stored, and outlet gases are equal and nearly constant throughout the given time period.

(a) Write a differential balance on the moles of gas in the tank, and prove that when integrated it yields the following equation for the gas volume:

$$V(t) = 3.00 \times 10^3 + 9.00t - \int_0^t \dot{v}_{\text{w}}\, dt$$

where t(min) is the time elapsed since 8:00 a.m.

(b) Calculate the stored gas volume at noon, using Simpson's rule (Appendix A.3) to evaluate the integral.

(c) Although a running estimate of the tank volume is important to have, in practice it would probably not be obtained in the manner indicated. How would it be obtained? What might you infer if the value estimated in part (b) is greater than that obtained by the more accurate method?

***(d)** Create a spreadsheet or a computer program to read in the data for $\dot{v}_{\text{w}}(t)$ and to estimate and print out the gas volume at each time for which $\dot{v}_{\text{w}}$ is recorded, using the trapezoidal rule (Appendix A.3) to evaluate the integral over each successive 10-min interval. What is the percentage difference between the volumes at noon estimated by Simpson's rule and the trapezoidal rule? Which estimate should be more accurate?

Student Workbook

Equipment Encyclopedia
valve

11.6. Water is added at varying rates to a 300-liter holding tank. When a valve in a discharge line is opened, water flows out at a rate proportional to the height and hence to the volume V of water in the tank. The flow of water into the tank is slowly increased and the level rises in consequence, until at a steady input rate of 60.0 L/min the level just reaches the top but does not spill over. The input rate is then abruptly decreased to 20.0 L/min.

(a) Write the equation that relates the discharge rate, $\dot{v}_{\text{out}}$(L/min), to the volume of water in the tank, V(L), and use it to calculate the steady-state volume when the input rate is 20 L/min.

(b) Write a differential balance on the water in the tank for the period from the moment the input rate is decreased ($t = 0$) to the attainment of steady state ($t \to \infty$), expressing it in the form $dV/dt = \cdots$. Provide an initial condition.

(c) Without integrating the equation, use it to confirm the steady-state value of V calculated in part (a) and then to predict the shape you would anticipate for a plot of V versus t. Explain your reasoning.

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*Computer problem.

(d) Separate variables and integrate the balance equation to derive an expression for $V(t)$. Calculate the time in minutes required for the volume to decrease to within 1% of its steady-state value.

11.7. The production supervisor of a small pharmaceutical firm has observed a decreasing demand for potassium regurgitol (PRG) over a two-month period, and since the plant manager has been throwing up the low sales of this product at the weekly staff meetings, the supervisor decides to discontinue its production immediately. On the day of this decision, the inventory of PRG is 18,000 kg. Based on the orders on hand, the manager projects the following weekly demand for the next six weeks:

Week	1	2	3	4	5	6
Demand $\dot{D}$(kg/wk)	2385	1890	1506	1196	950	755

(a) Use a semilog plot of the projected demand figures to derive an equation for $\dot{D}$ as a function of t(weeks) from the present time.

(b) Write a differential balance on the inventory I(kg) of PRG, and integrate it to determine I as a function of t.

(c) If the demand continues to follow the projected trend of the next six weeks, how much PRG will eventually have to be discarded?

11.8. A ventilation system has been designed for a large laboratory with a volume of 1100 m^3. The volumetric flow rate of ventilation air is 700 m^3/min at 22°C and 1 atm. (The latter two values may also be taken as the temperature and pressure of the room air.) A reactor in the laboratory is capable of emitting as much as 1.50 mol of sulfur dioxide into the room if a seal ruptures. An SO_2 mole fraction in the room air greater than 1.0×10^{-6} (1 ppm) constitutes a health hazard.

(a) Suppose the reactor seal ruptures at a time $t = 0$ and the maximum amount of SO_2 is emitted and spreads uniformly throughout the room almost instantaneously. Assuming that the air flow is sufficient to make the room air composition spatially uniform, write a differential SO_2 balance, letting N be the total moles of gas in the room (assume constant) and $x(t)$ the mole fraction of SO_2 in the laboratory air. Convert the balance into an equation for dx/dt and provide an initial condition. (Assume that all of the SO_2 emitted is in the room at $t = 0$.)

(b) Predict the shape of a plot of x versus t. Explain your reasoning, using the equation of part (a) in your explanation.

(c) Separate variables and integrate the balance to obtain an expression for $x(t)$. Check your solution.

(d) Convert the expression for $x(t)$ into an expression for the concentration of SO_2 in the room, C_{SO_2} (mol SO_2/L). Calculate (i) the concentration of SO_2 in the room two minutes after the rupture occurs, and (ii) the time required for the SO_2 concentration to reach the "safe" level.

(e) Why would it probably not yet be safe to enter the room after the time calculated in part (d)? (*Hint:* One of the assumptions made in the problem is probably not a good one.)

11.9. A gas leak has led to the presence of 1.00 mole% carbon monoxide in a 350-m^3 laboratory.[4] The leak was discovered and sealed, and the laboratory is to be purged with clean air to a point at which the air contains less than the OSHA (Occupational Safety and Health Administration)-specified Permissible Exposure Level (PEL) of 35 ppm (molar basis). Assume that the clean air and the air in the laboratory are at the same temperature and pressure and that the laboratory air is perfectly mixed throughout the purging process.

(a) Let t_r(h) be the time required for the specified reduction in the carbon monoxide concentration. Write a differential CO mole balance, letting N equal the total moles of gas in the room (assume constant), x the mole fraction of CO in the room air, and $\dot{v}_p$(m^3/h) the flow rate of purge air entering the room (and also the flow rate of laboratory air leaving the room). Convert the balance into an equation for dx/dt and provide an initial condition.

(b) Integrate the balance to derive an equation for t_r in terms of $\dot{v}_p$.

(c) If the volumetric flow rate is 700 m^3/h (representing a turnover of two room volumes per hour), how long will the purge take? What would the volumetric flow rate have to be to cut the purge time in half?

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[4] D. A. Crowl, D. W. Hubbard, and R. M. Felder, *Problem Set: Stoichiometry,* AIChE/CCPS, New York, 1993.

(d) Give several reasons why it might not be safe to resume work in the laboratory after the calculated purge time has elapsed? What precautionary steps would you advise taking at this point?

11.10. Ninety kilograms of sodium nitrate is dissolved in 110 kg of water. When the dissolution is complete (at time $t = 0$), pure water is fed to the tank at a constant rate $\dot{m}$(kg/min), and solution is withdrawn from the tank at the same rate. The tank may be considered perfectly mixed.

(a) Write a total mass balance on the tank and use it to prove that the total mass of liquid in the tank remains constant at its initial value.

(b) Write a balance on sodium nitrate, letting $x(t, \dot{m})$ equal the mass fraction of $NaNO_3$ in the tank and outlet stream. Convert the balance into an equation for dx/dt and provide an initial condition.

(c) On a single graph of x versus t, sketch the shapes of the plots you would expect to obtain for $\dot{m} = 50$ kg/min, 100 kg/min, and 200 kg/min. (Don't do any calculations.) Explain your reasoning, using the equation of part (b) in your explanation.

(d) Separate variables and integrate the balance to obtain an expression for $x(t, \dot{m})$. Check your solution. Then generate the plots of x versus t for $\dot{m} = 50$ kg/min, 100 kg/min, and 200 kg/min and show them on a single graph. (A spreadsheet is a convenient tool for carrying out this step.)

(e) If $\dot{m} = 100$ kg/min, how long will it take to flush out 90% of the sodium nitrate originally in the tank? How long to flush out 99%? 99.9%?

11.11. A *tracer* is used to characterize the degree of mixing in a continuous stirred tank. Water enters and leaves the mixer at a rate of $\dot{v}$(m^3/min). Scale has built up on the inside walls of the tank, so that the effective volume V(m^3) of the tank is unknown. At time $t = 0$, a mass m_0(kg) of the tracer is injected into the tank and the tracer concentration in the outlet stream, C(kg/m^3), is monitored.

(a) Write a differential balance on the tracer in the tank in terms of V, C, and $\dot{v}$, assuming that the tank contents are perfectly mixed, and convert the balance into an equation for dC/dt. Provide an initial condition, assuming that the injection is rapid enough so that all of the tracer may be considered to be in the tank at $t = 0$.

(b) Integrate the balance to prove that

$$C(t) = (m_0/V)\exp(-\dot{v}t/V)$$

(c) Suppose the flow rate through the mixer is $\dot{v} = 30.0$ m^3/min and that the following data are taken:

Time from injection, t(min)	1	2	3	4
$C \times 10^3$ (kg/m^3)	0.223	0.050	0.011	0.0025

(For example, at $t = 1$ min, $C = 0.223 \times 10^{-3}$ kg/m^3.) Verify graphically that the tank is functioning as a perfect mixer—that is, that the expression of part (b) fits the data—and determine the effective volume V(m^3) from the slope of your plot.

Student Workbook

11.12. A 40.0-ft^3 oxygen tent initially contains air at 68°F and 14.7 psia. At a time $t = 0$ an enriched air mixture containing 35.0% v/v O_2 and the balance N_2 is fed to the tent at 68°F and 1.3 psig at a rate of 60.0 ft^3/min, and gas is withdrawn from the tent at 68°F and 14.7 psia at a molar flow rate equal to that of the feed gas.

(a) Calculate the total lb-moles of gas ($O_2 + N_2$) in the tent at any time.

(b) Let $x(t)$ equal the mole fraction of oxygen in the outlet stream. Write a differential mole balance on oxygen, assuming that the tent contents are perfectly mixed (so that the temperature, pressure, and composition of the contents are the same as those properties of the exit stream). Convert the balance into an equation for dx/dt and provide an initial condition.

(c) Integrate the equation to obtain an expression for $x(t)$. How long will it take for the mole fraction of oxygen in the tent to reach 0.27?

11.13. A radioactive isotope decays at a rate proportional to its concentration. If the concentration of an isotope is C(mg/L), then its rate of decay may be expressed as

$$r_d[\text{mg/(L·s)}] = kC$$

where k is a constant.

(a) A volume V(L) of a solution of a radioisotope whose concentration is C_0(mg/L) is placed in a closed vessel. Write a balance on the isotope in the vessel and integrate it to prove that the **half-life** $t_{1/2}$ of the isotope—by definition, the time required for the isotope concentration to decrease to half of its initial value—equals $(\ln 2)/k$.

(b) The half-life of ^{56}Mn is 2.6 h. A batch of this isotope that was used in a radiotracing experiment has been collected in a holding tank. The radiation safety officer declares that the activity (which is proportional to the isotope concentration) must decay to 1% of its present value before the solution can be discarded. How long will this take?

Equipment Encyclopedia
reactor-batch

11.14. A chemical reaction with stoichiometry A → products is said to follow an *n^{th}-order rate law* if A is consumed at a rate proportional to the nth power of its concentration in the reaction mixture. If r_A is the rate of consumption of A per unit reactor volume, then

$$r_A[\text{mol/(L·s)}] = kC_A^n$$

where C_A(mol/L) is the reactant concentration, and the constant of proportionality k is the reaction *rate constant.* A reaction that follows this law is referred to as an *n^{th} order reaction.* The rate constant is a strong function of temperature but is independent of the reactant concentration.

(a) Suppose a first-order reaction ($n = 1$) is carried out in an isothermal batch reactor of constant volume V. Write a material balance on A and integrate it to derive the expression

$$C_A = C_{A0}\exp(-kt)$$

where C_{A0} is the concentration of A in the reactor at $t = 0$.

(b) The gas-phase decomposition of sulfuryl chloride

$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$

is thought to follow a first-order rate law. The reaction is carried out in a constant-volume isothermal batch reactor and the concentration of SO_2Cl_2 is measured at several reaction times, with the following results:

t(min)	4.0	21.3	39.5	63.4	120.0	175.6
C_A(mol/L)	0.0279	0.0262	0.0246	0.0226	0.0185	0.0152

Verify the proposed rate law graphically [i.e., demonstrate that the expression given in part (a) fits the data for $C_A(t)$] and determine the rate constant k, giving both its value and its units.

Equipment Encyclopedia
reactor-batch

11.15. A gas-phase decomposition reaction with stoichiometry 2A → 2B + C follows a second-order rate law (see Problem 11.14):

$$r_d[\text{mol/(m}^3\text{·s)}] = kC_A^2$$

where C_A is the reactant concentration in mol/m^3. The rate constant k varies with the reaction temperature according to the **Arrhenius law**

$$k[\text{m}^3\text{/(mol·s)}] = k_0\exp(-E/RT)$$

where

k_0[m^3/(mol·s)] = the *preexponential factor*
E(J/mol) = the reaction *activation energy*
R = the gas constant
T(K) = the reaction temperature

(a) Suppose the reaction is carried out in a batch reactor of constant volume V(m^3) at a constant temperature T(K), beginning with pure A at a concentration C_{A0}. Write a differential balance on A and integrate it to obtain an expression for $C_A(t)$ in terms of C_{A0} and k.

(b) Let P_0(atm) be the initial reactor pressure. Prove that $t_{1/2}$, the time required to achieve a 50% conversion of A in the reactor, equals RT/kP_0, and derive an expression for $P_{1/2}$, the reactor pressure at this point, in terms of P_0. Assume ideal gas behavior.

(c) The decomposition of nitrous oxide (N_2O) to nitrogen and oxygen is carried out in a 5.00-liter batch reactor at a constant temperature of 1015 K, beginning with pure N_2O at several initial pressures. The reactor pressure $P(t)$ is monitored, and the times ($t_{1/2}$) required to achieve 50% conversion of N_2O are noted.

P_0(atm)	0.135	0.286	0.416	0.683
$t_{1/2}$(s)	1060	500	344	209

Use these results to verify that the N_2O decomposition reaction is second-order and determine the value of k at $T = 1015$ K.

(d) The same experiment is performed at several other temperatures at a single initial pressure of 1.00 atm, with the following results:

T(K)	900	950	1000	1050
$t_{1/2}$(s)	5464	1004	219	55

Use a graphical method to determine the Arrhenius law parameters (k_0 and E) for the reaction.

(e) Suppose the reaction is carried out in a batch reactor at $T = 980$ K, beginning with a mixture at 1.20 atm containing 70 mole% N_2O and the balance a chemically inert gas. How long (minutes) will it take to achieve a 90% conversion of N_2O?

11.16. In an enzyme-catalyzed reaction with stoichiometry $A \rightarrow B$, A is consumed at a rate given by an expression of the **Michaelis–Menten** form:

$$r_A[\text{mol/(L·s)}] = \frac{k_1 C_A}{1 + k_2 C_A}$$

where C_A(mol/L) is the reactant concentration, and k_1 and k_2 depend only on temperature.

(a) The reaction is carried out in an isothermal batch reactor with constant reaction mixture volume V (liters), beginning with pure A at a concentration C_{A0}. Write a balance on A and integrate it to obtain an expression for the time required to achieve a specified concentration C_A.

(b) Use the expression of part (a) to devise a graphical method of determining k_1 and k_2 from data for C_A versus t. Your plot should involve fitting a straight line and determining the two parameters from the slope and intercept of the line. (There are several possible solutions.) Then apply your method to determine k_1 and k_2 for the following data taken in a 2.00-liter reactor, beginning with A at a concentration $C_{A0} = 5.00$ mol/L.

t(s)	60.0	120.0	180.0	240.0	480.0
C_A(mol/L)	4.484	4.005	3.561	3.154	1.866

11.17. Phosgene ($COCl_2$) is formed by CO and Cl_2 reacting in the presence of activated charcoal:

$$CO + Cl_2 \rightarrow COCl_2$$

At $T = 303.8$ K the rate of formation of phosgene in the presence of 1 gram of charcoal is

$$R_f(\text{mol/min}) = \frac{8.75 C_{CO} C_{Cl_2}}{(1 + 58.6 C_{Cl_2} + 34.3 C_{COCl_2})^2}$$

where C denotes concentration in mol/L.

(a) Suppose the charge to a 3.00-liter batch reactor is 1.00 g of charcoal and a gas containing 60 mole% CO and 40 mole% Cl_2, and that the initial reactor conditions are 303.8 K and 1 atm. Calculate the initial concentrations (mol/L) of both reactants, neglecting the volume occupied by the charcoal. Then, letting $C_P(t)$ be the concentration of phosgene at an arbitrary time t, derive relations for C_{CO} and C_{Cl_2} in terms of C_P.

(b) Write a differential balance on phosgene and show that it simplifies to

$$\frac{dC_P}{dt} = \frac{2.92(0.02407 - C_P)(0.01605 - C_P)}{(1.941 - 24.3C_P)^2}$$

Provide an initial condition for this equation.

(c) Starting with the equation of part (b), derive an expression for the time required to achieve a 75% conversion of the limiting reactant. *Your solution should have the form t = a definite integral.*

***(d)** The integral you derived in part (c) can be evaluated analytically; however, more complex rate laws than the one given for the phosgene formation reaction would yield an integral that must be evaluated numerically. One procedure is to evaluate the integrand at a number of points between the limits of integration and to use a quadrature formula such as the trapezoidal rule or Simpson's rule (Appendix A.3) to estimate the value of the integral.

Use a spreadsheet or write a computer program to evaluate the integrand of the integral of part (c) at n_p equally spaced points between and including the limits of integration, where n_p is an odd number, and then to evaluate the integral using Simpson's rule. Perform the calculation for $n_p = 5$, 21, and 51, and compare the results with the exact value of the integral.

Equipment Encyclopedia
absorber

11.18. A gas that contains CO_2 is contacted with liquid water in an agitated batch absorber. The equilibrium solubility of CO_2 in water is given by Henry's law (Section 6.4b)

$$C_A = p_A / H_A$$

where
$C_A(\text{mol/cm}^3)$ = concentration of CO_2 in solution
$p_A(\text{atm})$ = partial pressure of CO_2 in the gas phase
$H_A[\text{atm/(mol/cm}^3)]$ = Henry's law constant

The rate of absorption of CO_2 (i.e., the rate of transfer of CO_2 from the gas to the liquid per unit area of gas–liquid interface) is given by the expression

$$r_A[\text{mol/(cm}^2\cdot\text{s)}] = k(C_A^* - C_A)$$

where
C_A = actual concentration of CO_2 in the liquid
C_A^* = concentration of CO_2 that would be in equilibrium with the CO_2 in the gas phase ($C_A^* = p_A/H_A$)
$k(\text{cm/s})$ = a *mass transfer coefficient*

The gas phase is at a total pressure P(atm) and contains y_A(mol CO_2/mol gas), and the liquid phase initially consists of $V(\text{cm}^3)$ of pure water. The agitation of the liquid phase is sufficient for its composition to be considered spatially uniform, and the amount of CO_2 absorbed is low enough for P, V, and y_A to be considered constant throughout the process.

(a) Write a differential balance on CO_2 in the liquid phase and integrate it to derive the relation

$$C_A(t) = C_A^*[1 - \exp(-kSt/V)]$$

where $S(\text{cm}^2)$ is the effective contact area between the gas and liquid phases.

(b) Suppose the system pressure is 20.0 atm, the liquid volume is 5.00 liters, the tank diameter is 10.0 cm, the gas contains 30.0 mole% CO_2, the Henry's law constant is 9230 atm/(mole/cm^3), and the mass transfer coefficient is 0.020 cm/s. Calculate the time required for C_A to reach 0.620 mol/L if the gas-phase properties remain essentially constant.

11.19. A liquid-phase chemical reaction with stoichiometry A → B takes place in a semibatch reactor. The rate of consumption of A per unit volume of the reactor contents is given by the first-order rate expression (see Problem 11.14)

$$r_A[\text{mol/(L}\cdot\text{s)}] = kC_A$$

where C_A (mol A/L) is the reactant concentration. The tank is initially empty. Beginning at a time $t = 0$, a solution containing A at a concentration C_{A0}(mol A/L) is fed to the tank at a steady rate $\dot{v}$(L/s).

(a) Write a differential balance on the total mass of the reactor contents. Assuming that the density of the contents always equals that of the feed stream, convert the balance into an equation for dV/dt, where V is the total volume of the contents, and provide an initial condition. Then write a differential mole balance on the reactant, A, letting $N_A(t)$ equal the total moles of A in the vessel, and provide an initial condition. Your equations should contain only the variables N_A, V, and t and the constants $\dot{v}$ and C_{A0}. (You should be able to eliminate C_A as a variable.)

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*Computer problem.

(b) Without attempting to integrate the equations, derive a formula for the steady-state value of N_A.

(c) Integrate the two equations to derive expressions for $V(t)$ and $N_A(t)$, and then derive an expression for $C_A(t)$. Determine the asymptotic value of N_A as $t \to \infty$ and verify that the steady-state value obtained in part (b) is correct. Briefly explain how it is possible for N_A to reach a steady value when you keep adding A to the reactor and then give two reasons why this value would never be reached in a real reactor.

(d) Determine the limiting value of C_A as $t \to \infty$ from your expressions for $N_A(t)$ and $V(t)$. Then explain why your result makes sense in light of the results of part (c).

11.20. A kettle containing 3.00 liters of water at a temperature of 18°C is placed on an electric stove and begins to boil in four minutes.

(a) Write an energy balance on the water, neglecting evaporation that may occur during the heating.

(b) What is the average rate (W) at which heat is added to the water during this period? (See Example 11.3-1.)

(c) The rate of heat output from the stove element differs significantly from the heating rate calculated in part (b). In which direction, and why?

11.21. An electrical coil is used to heat 20.0 kg of water in a closed well-insulated vessel. The water is initially at 25°C and 1 atm. The coil delivers a steady 2.50 kW of power to the vessel and its contents.

(a) Write a differential energy balance on the water, assuming that 97% of the energy delivered by the coil goes into heating the water. What happens to the other 3%?

(b) Integrate the equation of part (a) to derive an expression for the water temperature as a function of time.

(c) How long will it take for the water to reach the normal boiling point? Will it boil at this temperature? Why not?

11.22. An iron bar 2.00 cm × 3.00 cm × 10.0 cm at a temperature of 95°C is dropped into a barrel of water at 25°C. The barrel is large enough so that the water temperature rises negligibly as the bar cools. The rate at which heat is transferred from the bar to the water is given by the expression

$$\dot{Q}(\text{J/min}) = UA(T_b - T_w)$$

where $U[= 0.050 \text{ J/(min·cm}^2\text{·°C)}]$ is a *heat transfer coefficient,* $A(\text{cm}^2)$ is the exposed surface area of the bar, and T_b(°C) and T_w(°C) are the surface temperature of the bar and the water temperature, respectively.

The heat capacity of the bar is 0.460 J/(g·°C). Heat conduction in iron is rapid enough for the temperature $T_b(t)$ to be considered uniform throughout the bar.

(a) Write an energy balance on the bar, assuming that all six sides are exposed. Your result should be an expression for dT_b/dt and an initial condition.

(b) Without integrating the equation, sketch the expected plot of T_b versus t, labeling the values of T_b at $t = 0$ and $t \to \infty$.

(c) Derive an expression for $T_b(t)$ and check it three ways. How long will it take for the bar to cool to 30°C?

11.23. A steam coil is immersed in a stirred heating tank. Saturated steam at 7.50 bar condenses within the coil, and the condensate emerges at its saturation temperature. A solvent with a heat capacity of 2.30 kJ/(kg·°C) is fed to the tank at a steady rate of 12.0 kg/min and a temperature of 25°C, and the heated solvent is discharged at the same flow rate. The tank is initially filled with 760 kg of solvent at 25°C, at which point the flows of both steam and solvent are commenced. The rate at which heat is transferred from the steam coil to the solvent is given by the expression

$$\dot{Q} = UA(T_{\text{steam}} - T)$$

where UA (the product of a heat transfer coefficient and the coil surface area through which the heat is transferred) equals 11.5 kJ/(min·°C).The tank is well stirred, so that the temperature of the contents is spatially uniform and equals the outlet temperature.

(a) Prove that an energy balance on the tank contents reduces to the equation given below and supply an initial condition.

$$\frac{dT}{dt} = 1.50\text{°C/min} - 0.0224T$$

(b) Without integrating the equation, calculate the steady-state value of T and sketch the expected plot of T versus t, labeling the values of T_b at $t = 0$ and $t \to \infty$.

(c) Integrate the balance equation to obtain an expression for $T(t)$ and calculate the solvent temperature after 40 minutes.

(d) A new stirrer assembly has been installed in the heating tank. The process described above is run again with the same steam conditions, solvent flow rate, and mass of solvent charged to the tank, and the temperature after 40 minutes is 55°C instead of the value calculated in part (c). One of the system variables listed in the problem statement must have changed as a result of the change in the stirrer. Which variable would you guess it to be, and by what percentage of its initial value did it change?

11.24. At 9:30 one morning, a graduate student measures 350 grams of liquid benzene at 20°C into a glass flask dirty enough that its contents cannot be seen, puts the open flask on a bunsen burner, turns the burner on, and goes for a coffee break. The conversation at the break is lively and he doesn't get back until 10:10 a.m. He looks down into the flask, sees the liquid is boiling, turns the burner off, feels a little irritation in his eye and rubs the eye with his hand, picks up the flask, says "Ouch" (or something roughly equivalent), puts the flask down on his laboratory partner's thermodynamics homework, and starts to prepare the next step of the experiment.

(a) Suppose the heat input rate to the flask contents is 40.2 W. Calculate the time at which the benzene temperature reached 40°C. Neglect evaporation of benzene during the heating and take the heat capacity of liquid benzene to be constant at 1.77 J/(g·°C).

(b) Calculate the quantity of benzene left in the flask at 10:10 a.m., assuming that once the benzene starts boiling, the rate of heat input to the flask (40.2 W) equals the rate of vaporization (g/s) times the heat of vaporization (J/g).

(c) The graduate student was lucky. First, neither his supervisor nor the university safety officer came into the laboratory during this episode. More importantly, he was still alive and well at the end of the day. Identify as many of his safety violations as you can, explaining the danger and suggesting for each violation what he should have done instead.

11.25. A steam radiator is used to heat a 60-m^3 room. Saturated steam at 3.0 bar condenses in the radiator and emerges as a liquid at the saturation temperature. Heat is lost from the room to the outside at a rate

$$\dot{Q}(\text{kJ/h}) = 30.0(T - T_0)$$

where T(°C) is the room temperature and $T_0 = 0$°C is the outside temperature. At the moment the radiator is turned on, the temperature in the room is 10°C.

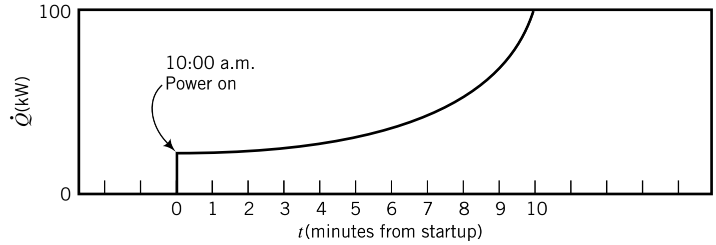
(a) Let $\dot{m}_s$(kg/h) denote the rate at which steam condenses in the radiator and n(kmol) the quantity of air in the room. Write a differential energy balance on the room air, assuming that n remains constant at its initial value, and evaluate all numerical coefficients. Take the heat capacity of air (C_v) to be constant at 20.8 J/(mol·°C).

(b) Write the steady-state energy balance on the room air and use it to calculate the steam condensation rate required to maintain a constant room temperature of 24°C.

(c) Integrate the transient balance to calculate the time required to achieve a temperature of 23°C, assuming that the steam rate is that calculated in part (b).

11.26. An immersed electrical heater is used to raise the temperature of a liquid from 20°C to 60°C in 20.0 min. The combined mass of the liquid and the container is 250 kg, and the mean heat capacity of the system is 4.00 kJ/(kg·°C). The liquid decomposes explosively at 85°C.

At 10.00 a.m. a batch of liquid is poured into the vessel and the operator turns on the heater and leaves to make a phone call. Ten minutes later, his supervisor walks by and looks at the strip chart record of the power input. This what she sees.



The supervisor immediately shuts off the heater and charges off to pass on to the operator several brief observations that come to her mind.

(a) Calculate the required constant power input $\dot{Q}$(kW), neglecting energy losses from the container.

(b) Write and integrate using Simpson's rule (Appendix A.3) an energy balance on the system to estimate the system temperature at the moment the heater is shut off. Use the following data from the recorder chart:

t(s)	0	30	60	90	120	150	180	210	240	270	300
$\dot{Q}$(kW)	33	33	34	35	37	39	41	44	47	50	54

t(s)	330	360	390	420	450	480	510	540	570	600
$\dot{Q}$(kW)	58	62	66	70	75	80	85	90	95	100

(c) Suppose that if the heat had not been shut off, $\dot{Q}$ would have continued to increase linearly at a rate of 10 kW/min. At what time would everyone in the plant realize that something was wrong?

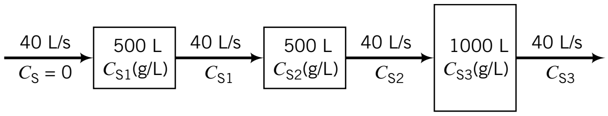
11.27. A 2000-liter tank initially contains 400 liters of pure water. Beginning at $t = 0$, an aqueous solution containing 1.00 g/L of potassium chloride flows into the tank at a rate of 8.00 L/s and an outlet stream simultaneously starts flowing at a rate of 4.00 L/s. The contents of the tank are perfectly mixed, and the density of the feed stream and of the tank solution, ρ(g/L), may be considered constant. Let $V(t)$(L) denote the volume of the tank contents and $C(t)$(g/L) the concentration of potassium chloride in the tank contents and outlet stream.

(a) Write a total mass balance on the tank contents, convert it to an equation for dV/dt, and provide an initial condition. Then write a potassium chloride balance, convert it to an equation of the form $dC/dt = f(C, V)$, and provide an initial condition. (See Example 11.4-1.)

(b) Without solving either equation, sketch the plots you would expect to obtain for V versus t and C versus t. Briefly explain your reasoning.

(c) Solve the mass balance equation to obtain an expression for $V(t)$. Then substitute for V in the potassium chloride balance and solve for $C(t)$. Calculate the KCl concentration in the tank at the moment the tank overflows.

11.28. The diagram below shows three continuous stirred tanks connected in series.



The flow and mixing patterns in this system are studied by dissolving 1500 g of a salt (S) in the first tank, filling each of the other two tanks with pure solvent, and then starting the 40 L/s flow through the system. Each tank outlet stream is monitored with an on-line thermal conductivity detector calibrated to provide instantaneous readings of salt concentration. The data are plotted versus time and the results are compared with the plots that would be expected if the tanks are all perfectly mixed. Your job is to generate the latter plots.

(a) Assuming that pure solvent is fed to the first tank and that each tank is perfectly mixed (so that the salt concentration in a tank is uniform and equal to the concentration in the outlet stream from that tank), write salt balances on each of the three tanks, convert them to expressions for dC_{S1}/dt, dC_{S2}/dt, and dC_{S3}/dt, and provide appropriate initial conditions.

(b) Without doing any calculations, on a single graph sketch the forms of the plots of C_{S1} versus t, C_{S2} versus t, and C_{S3} versus t you would expect to obtain. Briefly explain your reasoning.

***(c)** Use a differential equation-solving program to solve the three equations, proceeding to a time at which C_{S3} has fallen below 0.01 g/L, and plot the results.

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*Computer problems.

11.29. The following chemical reactions take place in a liquid-phase batch reactor of constant volume V.

$$A \rightarrow 2B \qquad r_1[\text{mol A consumed/(L·s)}] = 0.100C_A$$

$$B \rightarrow C \qquad r_2[\text{mol C generated/(L·s)}] = 0.200C_B^2$$

where the concentrations C_A and C_B are in mol/L. The reactor is initially charged with pure A at a concentration of 1.00 mol/L.

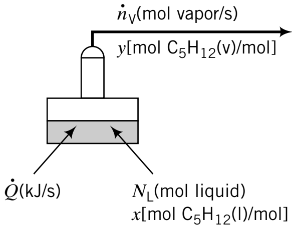
(a) Write expressions for (i) the rate of generation of B in the first reaction and (ii) the rate of consumption of B in the second reaction. (If this takes you more than about 10 seconds, you're missing the point.)

(b) Write mole balances on A, B, and C, convert them into expressions for dC_A/dt, dC_B/dt, and dC_C/dt, and provide boundary conditions.

(c) Without doing any calculations, sketch on a single graph the plots you would expect to obtain of C_A versus t, C_B versus t, and C_C versus t. Clearly show the function values at $t = 0$ and $t \rightarrow \infty$ and the curvature (concave up, concave down, or linear) in the vicinity of $t = 0$. Briefly explain your reasoning.

***(d)** Solve the equations derived in part (b) using a differential equation-solving program. On a single graph, show plots of C_A versus t, C_B versus t, and C_C versus t from $t = 0$ to $t = 50$ s. Verify that your predictions in part (c) were correct. If they were not, change them and revise your explanation.

11.30. A liquid mixture containing 70.0 mol of n-pentane and 30.0 mol of n-hexane initially at 46°C is partially vaporized at $P = 1$ atm in a single-stage distillation apparatus (**Rayleigh still**).



The heat added to the system, $\dot{Q}$, vaporizes liquid at the rate $\dot{n}_V$(mol/s). The vapor product and remaining liquid at a given moment are always in equilibrium with each other. The relationship between the mole fraction of pentane in the liquid (x) and that in the vapor (y) is of the form

$$y = \frac{ax}{x + b}$$

so that the system involves four time-dependent variables—N_L, $\dot{n}_V$, x, and y, where N_L is the total moles of liquid in the still at any time. (We will suppose that the rate of heat transfer to the evaporator, $\dot{Q}$, is constant and known.) Four equations relating the unknowns will be required to determine these variables. The equations are two material balances, an energy balance, and the vapor–liquid equilibrium relationship just given.

(a) When $x = 1$, what must y equal? (Think of the definitions of these quantities.) Use your answer and the vapor–liquid equilibrium expression to derive an equation relating the parameters a and b.

(b) Use Raoult's law (Equation 6.4-1) and the Antoine equation to calculate the mole fraction of pentane in the vapor phase in equilibrium with the 70% pentane–30% hexane feed mixture at the initial system temperature of 46°C and a pressure of 1 atm. Then use this result and that of part (a) to estimate a and b. (We will assume that these values remain the same over the range of compositions and temperatures to be undergone by the system.)

(c) Taking the residual liquid in the still as your system, write a differential balance on total moles to obtain an expression for dN_L/dt. Then write a balance on pentane, recognizing that both N_L and x are functions of time. (*Hint:* Remember the product rule for differentiation.) Prove that the pentane balance can be converted into the following equation:

$$\frac{dx}{dt} = \frac{\dot{n}_V}{N_L}\left(\frac{ax}{x+b} - x\right)$$

Supply initial conditions for your two differential equations.

(d) In part (c), you derived two equations in three unknown dependent variables—$\dot{n}_V(t)$, $N_L(t)$, and $x(t)$. To determine these variables, we need a third relationship. An energy balance provides it.

A rigorous energy balance would take into account the changing composition of the liquid, the slightly different heats of vaporization of pentane and hexane, and the enthalpy changes associated with temperature changes, and would make the problem relatively hard to solve. A reasonable approximation is to assume that (i) the liquid has a constant heat of vaporization of 27.0 kJ/mol, independent of composition and temperature; and (ii) all heat supplied to the still [$\dot{Q}$(kJ/s)] goes to vaporize liquid (i.e., we neglect energy that goes into raising the temperature of the liquid or the vapor). Make these assumptions, consider $\dot{Q}$ to be constant and known, and derive a simple expression for $\dot{n}_V$ that can be used to eliminate this variable in the differential equations of part (c). From there, derive the following expression:

$$\frac{dx}{dt} = -\frac{\dot{Q}/27.0}{100.0\text{ mol} - \dot{Q}t/27.0}\left(\frac{ax}{x+b} - x\right)$$

*__(e)__ Use a differential equation-solving program to calculate x, y, N_L, and $\dot{n}_V$ from $t = 0$ until the time at which the liquid completely evaporates. Do the calculation for (i) $\dot{Q} = 1.5$ kJ/s and (ii) $\dot{Q} = 3.0$ kJ/s. On a single graph, plot x and y versus t, showing curves for both values of $\dot{Q}$.

(f) In a short paragraph, describe what happens to the compositions of the vapor product and residual liquid over the course of a run. Include a statement of what the initial and final vapor compositions are and how the heating rate affects the system behavior.

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*Computer problem.