

بنام خدا

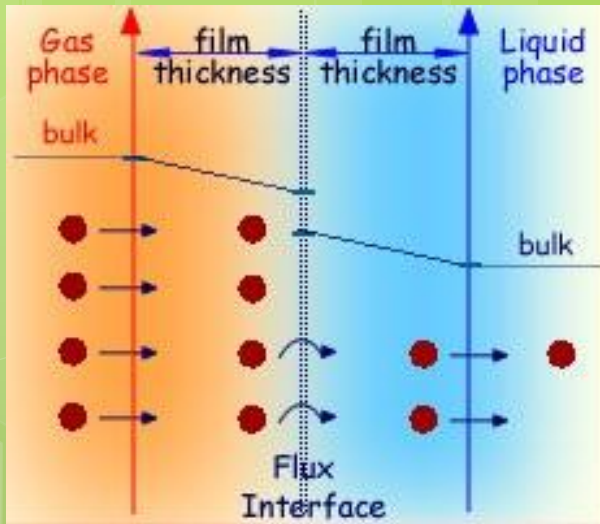
جزوه درس انتقال جرم برای دانشجویان رشته های مهندسی شیمی و مهندسی نفت

مدرس:

دکتر علی اکبری

عضو هیئت علمی دانشکده مهندسی شیمی

دانشگاه صنعتی سهند



نکاتی قبل از شروع درس:

- لزوم حضور در کلاس
- لزوم رعایت نظم و اخلاق

نمرات:

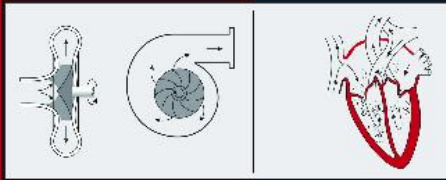
- فعالیت کلاسی (نمره مثبت)
- حضور کامل در کلاسها (۱ نمره مثبت)
- تکالیف و امتحان کلاسی (شفاهی یا کتبی) (۳-۵ نمره)
- میان ترم (شفاهی یا کتبی) (۵-۸ نمره)
- پایان ترم (۹-۱۰ نمره)

سرفصل مطالب:

- مقدمه بر انتقال جرم و ضرایب نفوذ
- معادلات دیفرانسیل انتقال جرم
- نفوذ مولکولی حالت پایا
- نفوذ مولکولی حالت ناپایا
- انتقال جرم جابجایی
- انتقال جرم جابجایی بین فازها
- تجهیزات انتقال جرم

منابع درس

Fundamentals of Momentum, Heat, and Mass Transfer

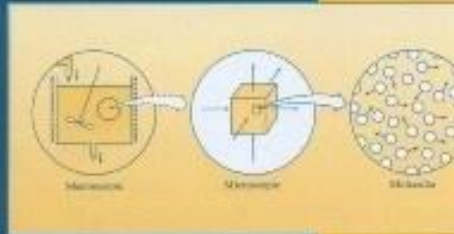


Welty | Wicks | Wilson | Rose

Fifth Edition

Transport Phenomena

Second Edition

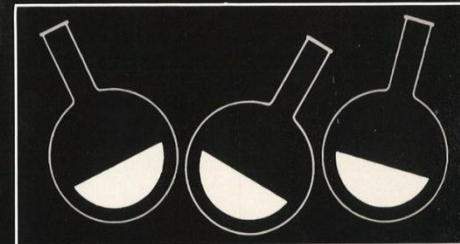


R. Byron Bird • Warren E. Stewart
Edwin N. Lightfoot

MASS-TRANSFER OPERATIONS

Robert E. Treybal

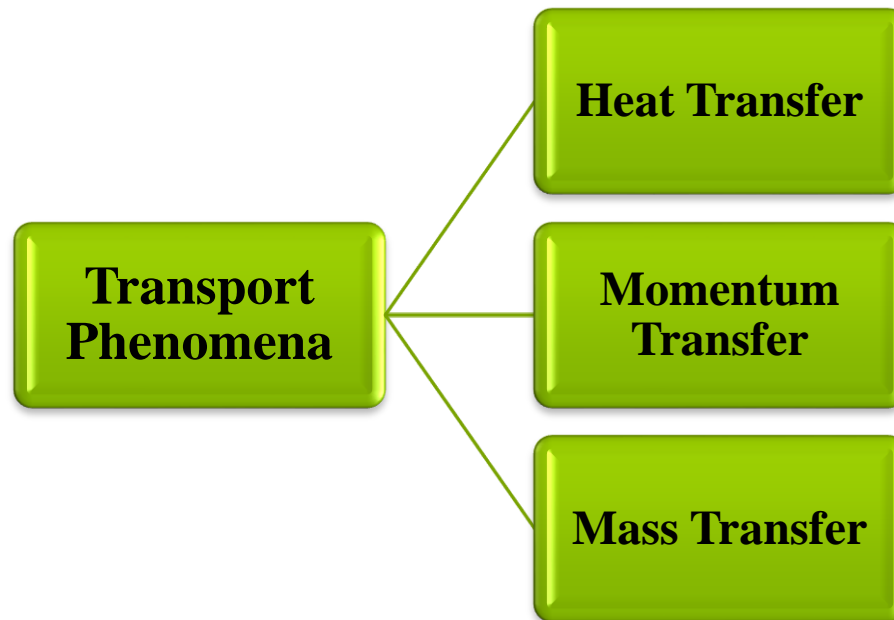
THIRD EDITION



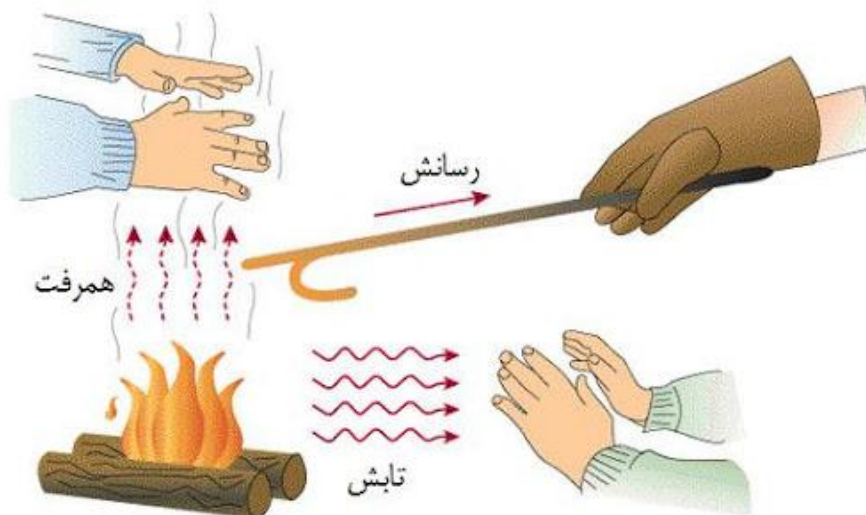
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مقدمه



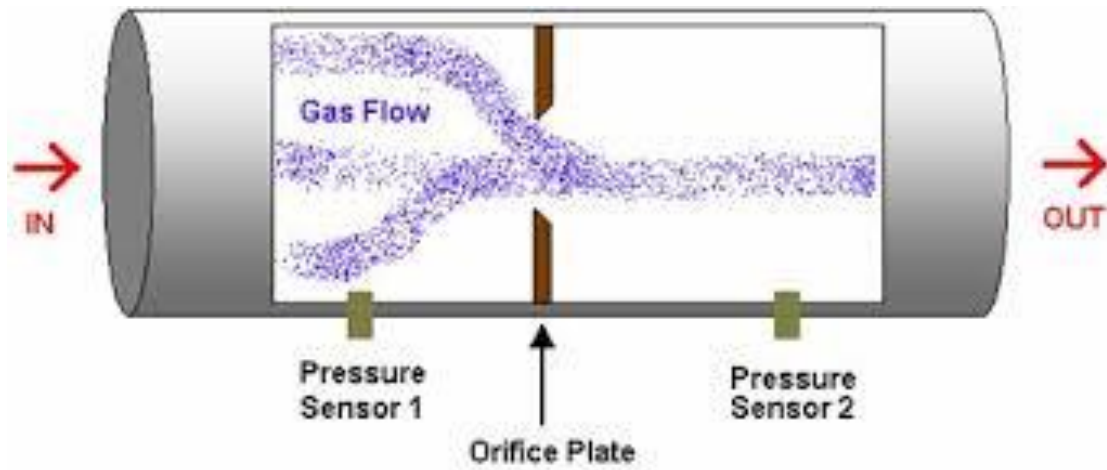
انتقال حرارت (نیرو محرکه: اختلاف دما)



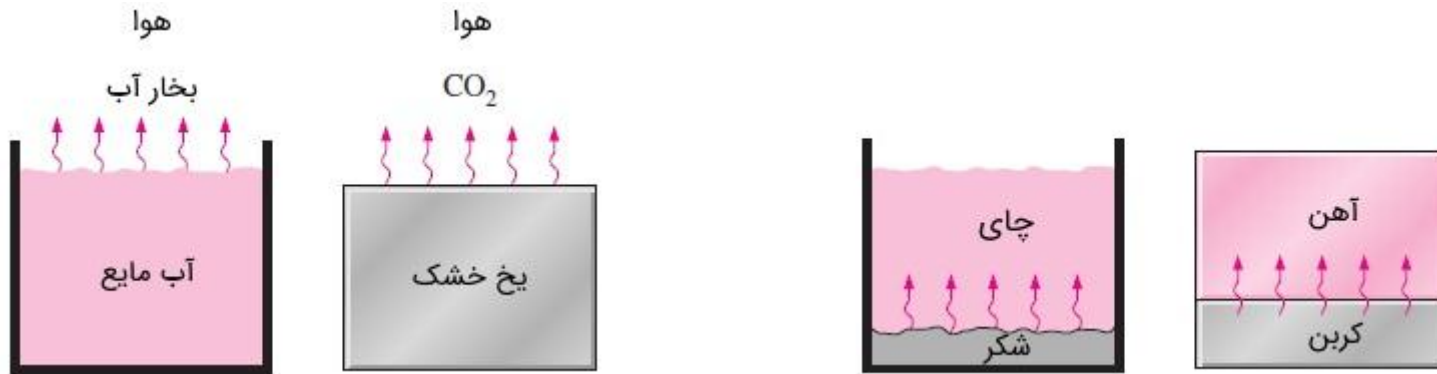
$$Q^{\bullet}_{\text{هدایت}} = -kA \frac{dT}{dx}$$

$$Q^{\bullet} = hA(T_s - T_{\infty})$$

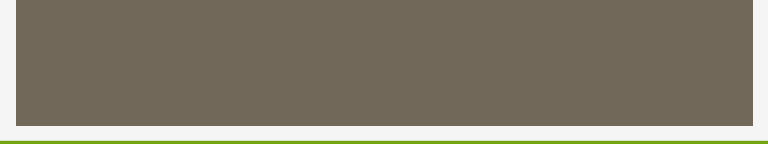
انتقال مومنتوم (فیرو محرکه: اختلاف فشار)



انتقال جرم (نیرو محرکه: اختلاف غلظت)



Diffusion



معرفی پارامترهای انتقال جرم

غلظت:

- غلظت جرمی: غلظت جرمی یک جزء بصورت جرم آن جزء به ازای واحد حجم مخلوط تعریف می شود.

$$\rho_i = \frac{m_i}{V_{mixture}}$$

- غلظت جرمی کل:

$$\rho = \sum_{i=1}^n \rho_i$$

- کسر جرمی:

$$\omega_A = \frac{\rho_A}{\sum_i^n \rho_i} = \frac{\rho_A}{\rho} \qquad \sum_{i=1}^n \omega_i = 1$$

- غلظت مولی: غلظت مولی یک جزء بصورت تعداد مولهای آن جزء به ازای واحد حجم مخلوط تعریف می شود.

$$C_i = \frac{n_i}{V_{mixture}} \quad c_A = \frac{\rho_A}{M_A}$$

- غلظت مولی برای گازهای ایده آل:

$$c_A = \frac{n_A}{V} = \frac{P_A}{RT}$$

- غلظت مولی کل:

$$c = \sum_{i=1}^n c_i$$

- کسر جرمی:

$$x_A = \frac{c_A}{c} \text{ (liquids and solids)}$$

$$y_A = \frac{c_A}{c} \text{ (gases)}$$

$$\sum_{i=1}^n x_i = 1$$

$$\sum_{i=1}^n y_i = 1$$

- کسر جرمی برای گازهای ایده آل (قانون دالتون):

$$y_A = \frac{c_A}{c} = \frac{p_A/RT}{P/RT} = \frac{p_A}{P}$$

$$x_A \quad \text{or} \quad y_A = \frac{\rho_A = c_A M_A}{\omega_A/M_A + \omega_B/M_B}$$
$$\omega_A = \frac{x_A M_A}{x_A M_A + x_B M_B} \quad \text{or} \quad \frac{y_A M_A}{y_A M_A + y_B M_B}$$

Concentrations in a binary mixture of A and B

Mass concentrations

$$\begin{aligned}\rho &= \text{total mass density of the mixture} \\ \rho_A &= \text{mass density of species A} \\ \rho_B &= \text{mass density of species B} \\ \omega_A &= \text{mass fraction of species A} = \rho_A/\rho \\ \omega_B &= \text{mass fraction of species B} = \rho_B/\rho \\ \rho &= \rho_A + \rho_B \\ 1 &= \omega_A + \omega_B\end{aligned}$$

Molar concentrations

Liquid or solid mixture

$$\begin{aligned}c &= \text{molar density of mixture} = n/V \\ c_A &= \text{molar density of species A} = n_A/V \\ c_B &= \text{molar density of species B} = n_B/V \\ x_A &= \text{mole fraction of species A} = c_A/c = n_A/n \\ x_B &= \text{mole fraction of species B} = c_B/c = n_B/n \\ c &= c_A + c_B \\ 1 &= x_A + x_B\end{aligned}$$

Gas mixture

$$\begin{aligned}c &= n/V = P/RT \\ c_A &= n_A/V = p_A/RT \\ c_B &= n_B/V = p_B/RT \\ y_A &= c_A/c = n_A/n = p_A/p \\ y_B &= c_B/c = n_B/n = p_B/p \\ c &= c_A + c_B = \frac{p_A}{RT} + \frac{p_B}{RT} = \frac{P}{RT} \\ 1 &= y_A + y_B\end{aligned}$$

سرعت:

- سرعت متوسط جرمی:

$$\mathbf{v} = \frac{\sum_{i=1}^n \rho_i \mathbf{v}_i}{\sum_{i=1}^n \rho_i} = \frac{\sum_{i=1}^n \rho_i \mathbf{v}_i}{\rho}$$

- سرعت متوسط مولی:

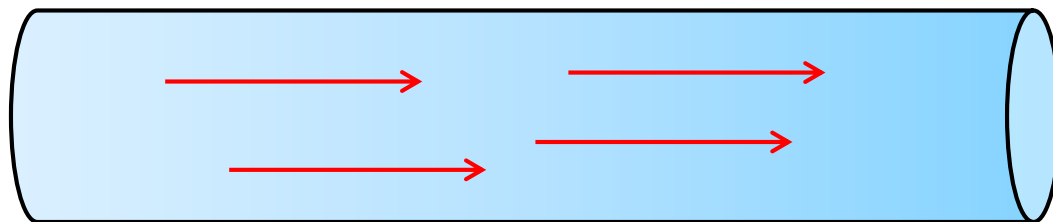
$$\mathbf{V} = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{\sum_{i=1}^n c_i} = \frac{\sum_{i=1}^n c_i \mathbf{v}_i}{c}$$

- سرعت نفوذ: سرعت هر جزء نسبت به سرعت متوسط جرمی و مولی بصورت سرعت نفوذ تعریف می شود.

$\mathbf{v}_i - \mathbf{v}$, the diffusion velocity of species i relative to the mass-average velocity
and

$\mathbf{v}_i - \mathbf{V}$, the diffusion velocity of species i relative to the molar-velocity average

نکته: مطابق با قانون فیک، یک جزء تنها زمانی می تواند دارای سرعتی متفاوت نسبت به سرعت متوسط جرمی یا مولی باشد که اختلاف غلظت داخل سیستم وجود داشته باشد.



شار یا فلاکس:

- شار جرمی: مقدار جرم عبوری به ازای واحد زمان و واحد سطح

$$n_i = \frac{m_i}{A \cdot t}$$

- شار مولی: تعداد مولهای عبوری به ازای واحد زمان و واحد سطح

$$N_i = \frac{n_i}{A \cdot t}$$

- شار نفوذی مولی: بر اساس قانون اول فیک (Fick) در یک سیستم با دما و فشار ثابت، شار نفوذ مولی بصورت زیر تعریف می شود.

$$\mathbf{J}_A = -D_{AB} \nabla c_A$$

For diffusion in only the z direction, the Fick rate equation is

$$J_{A,z} = -D_{AB} \frac{dc_A}{dz}$$

نکته:

A more general flux relation that is not restricted to isothermal, isobaric systems was proposed by de Groot² who chose to write

$$\text{flux} = - \left(\begin{array}{c} \text{overall} \\ \text{density} \end{array} \right) \left(\begin{array}{c} \text{diffusion} \\ \text{coefficient} \end{array} \right) \left(\begin{array}{c} \text{concentration} \\ \text{gradient} \end{array} \right)$$

$$J_{A,z} = -cD_{AB} \frac{dy_A}{dz}$$

$$j_{A,z} = -\rho D_{AB} \frac{d\omega_A}{dz}$$

where $d\omega_A/dz$ is the concentration gradient in terms of the mass fraction. When the density is constant, this relation simplifies to

$$j_{A,z} = -D_{AB} \frac{d\rho_A}{dz}$$

For a binary system with a constant average velocity in the z direction, the molar flux in the z direction relative to the molar-average velocity may also be expressed by

$$J_{A,z} = c_A(v_{A,z} - V_z) \quad (24-18)$$

Equating expressions (24-16) and (24-18), we obtain

$$J_{A,z} = c_A(v_{A,z} - V_z) = -cD_{AB} \frac{dy_A}{dz}$$

which, upon rearrangement, yields

$$c_A v_{A,z} = -cD_{AB} \frac{dy_A}{dz} + c_A V_z$$

For this binary system, V_z can be evaluated by equation (24-14) as

$$V_z = \frac{1}{c}(c_A v_{A,z} + c_B v_{B,z})$$

or

$$c_A V_z = y_A(c_A v_{A,z} + c_B v_{B,z})$$

Substituting this expression into our relation, we obtain

$$c_A v_{A,z} = -cD_{AB} \frac{dy_B}{dz} + y_A(c_A v_{A,z} + c_B v_{B,z}) \quad (24-19)$$

$$\mathbf{N}_A = c_A \mathbf{v}_A$$

$$\mathbf{N}_B = c_B \mathbf{v}_B$$

$$\mathbf{N}_{A,z} = -cD_{AB} \frac{dy_A}{dz} + y_A(\mathbf{N}_{A,z} + \mathbf{N}_{B,z}) \quad (24-20)$$

This relation may be generalized and written in vector form as

$$\mathbf{N}_A = -cD_{AB} \nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B) \quad (24-21)$$

It is important to note that the molar flux, \mathbf{N}_A , is a resultant of the two vector quantities:

$-cD_{AB} \nabla y_A$ the molar flux, J_A , resulting from the concentration gradient. This term is referred to as the *concentration gradient contribution*;

and

$y_A(\mathbf{N}_A + \mathbf{N}_B) = c_A \mathbf{V}$ the molar flux resulting as component A is carried in the bulk flow of the fluid. This flux term is designated the *bulk motion contribution*.

If species A were diffusing in a multicomponent mixture, the expression equivalent to equation (24-21) would be

$$\mathbf{N}_A = -cD_{AM} \nabla y_A + y_A \sum_{i=1}^n \mathbf{N}_i$$

where D_{AM} is the diffusion coefficient of A in the mixture.

The mass flux, \mathbf{n}_A , relative to a fixed spatial coordinate system, is defined for a binary system in terms of mass density and mass fraction by

$$\mathbf{n}_A = -\rho D_{AB} \nabla \omega_A + \omega_A (\mathbf{n}_A + \mathbf{n}_B) \quad (24-22)$$

where

$$\mathbf{n}_A = \rho_A \mathbf{v}_A$$

and

$$\mathbf{n}_B = \rho_B \mathbf{v}_B$$

Under isothermal, isobaric conditions, this relation simplifies to

$$\mathbf{n}_A = -D_{AB} \nabla \rho_A + \omega_A (\mathbf{n}_A + \mathbf{n}_B)$$

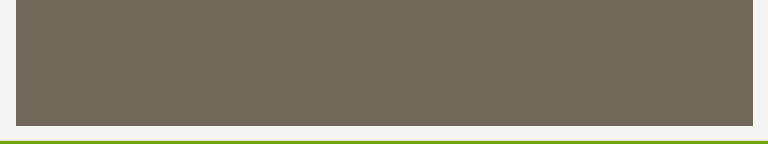
As previously noted, the flux is a resultant of two vector quantities:

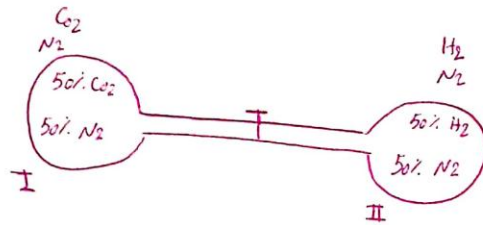
$-D_{AB} \nabla \rho_A$, the mass flux, j_A , resulting from a concentration gradient; the *concentration gradient contribution*.

$\omega_A (\mathbf{n}_A + \mathbf{n}_B) = \rho_A \mathbf{v}$, the mass flux resulting as component A is carried in the bulk flow of the fluid; the *bulk motion contribution*.

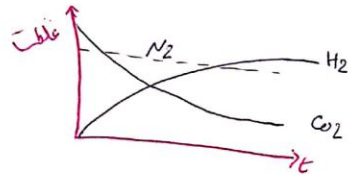
Table 24.2 Equivalent forms of the mass flux equation for binary system *A* and *B*

Flux	Gradient	Fick rate equation	Restrictions
\mathbf{n}_A	$\nabla\omega_A$	$\mathbf{n}_A = -\rho D_{AB} \nabla\omega_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	Constant ρ
	$\nabla\rho_A$	$\mathbf{n}_A = -D_{AB} \nabla\rho_A + \omega_A(\mathbf{n}_A + \mathbf{n}_B)$	
\mathbf{N}_A	∇y_A	$\mathbf{N}_A = -c D_{AB} \nabla y_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	Constant c
	∇c_A	$\mathbf{N}_A = -D_{AB} \nabla c_A + y_A(\mathbf{N}_A + \mathbf{N}_B)$	
\mathbf{j}_A	$\nabla\omega_A$	$\mathbf{j}_A = -\rho D_{AB} \nabla\omega_A$	Constant ρ
	$\nabla\rho_A$	$\mathbf{j}_A = -D_{AB} \nabla\rho_A$	
\mathbf{J}_A	∇y_A	$\mathbf{J}_A = -c D_{AB} \nabla y_A$	Constant c
	∇c_A	$\mathbf{J}_A = -D_{AB} \nabla c_A$	

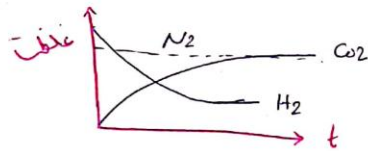




با باز شدن شیر، H_2 و CO_2 در جهت مخالف حرکت می کنند.

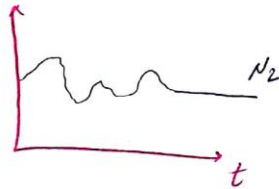


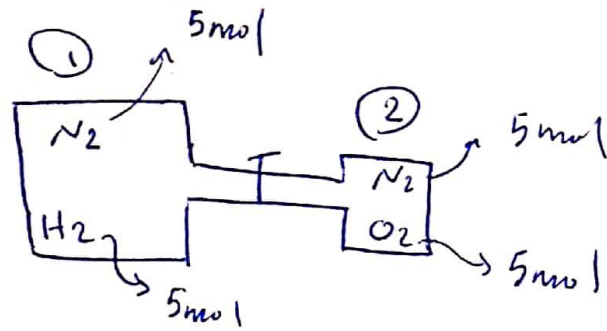
نمونه I



در واقعیت، نبردهای امپلاکی بین مولکولها وجود دارد و مولکولهای با اندازه بزرگتر، مولکولهای کوچک را هل می کنند. اما، در قانون سنیک از این نبردها و همچنین برکنش بین مولکولها صرف نظر می شود. برای این کار نیاز است که غلظت زیاد هل شونده بسیار پایین باشد.

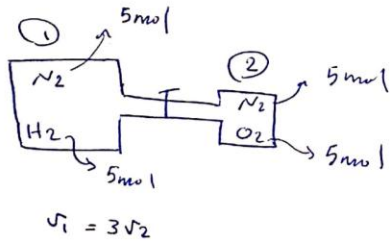
در واقعیت میزان N_2 پس از یک حالت نوسانی در هر دو مخزن به حالت \propto نسبت می رسد.





$$v_1 = 3v_2$$

تعداد اصر لھا کھانی؟



تعداد مولها کفایتی؟

⇒ لحاظ اول

$$\textcircled{1} \begin{cases} C_{N_2} = \frac{5}{V_1} \\ C_{H_2} = \frac{5}{V_1} \end{cases} \quad \textcircled{2} \begin{cases} C_{N_2} = \frac{5}{V_2} \\ C_{O_2} = \frac{5}{V_2} \end{cases}$$

اینها ⇒ $C_{N_2,1} = C_{N_2,2} \Rightarrow \frac{n_{N_2,1}}{V_1} = \frac{n_{N_2,2}}{V_2} \Rightarrow \begin{cases} n_{N_2,2} = 2.5 \text{ mol} \\ n_{N_2,1} = 7.5 \text{ mol} \end{cases}$

$n_{N_2,1} + n_{N_2,2} = 10 \text{ mol}$

$$\begin{cases} n_{H_2,1} = 3.75 \\ n_{H_2,2} = 1.25 \end{cases} \quad \begin{cases} n_{O_2,1} = 3.75 \\ n_{O_2,2} = 1.25 \end{cases}$$

$$C_{T,1} = \frac{7.5 + 3.75 + \frac{3.75}{2}}{V_1} = \frac{15}{V_1} \Rightarrow C_{T,1} = C_{T,2}$$

$$C_{T,2} = \frac{2.5 + 1.25 + 1.25}{V_2} = \frac{5}{V_2} = \frac{15}{V_1}$$

حداکثر در ظروف

$$\begin{aligned} P_1 V_1 &= n_1 R T \Rightarrow P_1 V_1 = 15 R T \\ P_2 V_2 &= n_2 R T \Rightarrow P_2 V_2 = 5 R T \end{aligned} \Rightarrow P_1 = P_2$$

(Dilute solutions)

$$J_{i,x} = -D_{ij} \frac{dc_i}{dx}$$

در حالت کلی $J_i = -D_{ij} \nabla c_i$

$$\Rightarrow N_i = -D_{ij} \nabla c_i + c_i v_s$$

قانون نفوذ نیک برای محلول های رقیق

برای مخلوط های دو جزئی رقیق

خواهیم داشت $D_{ij} = D_{ji}$

نقود در محلول‌های غلیظ

(Diff. in Concentrated solutions)

قانون نرنست بصورت دقیق برای محلول‌های واقعی قابل استفاده است. برای محلول‌های رقیق، تریب نفوذ تابع دماقت است. در این حالت از نفوذ بواسطه برهمکنش‌های حل‌شونده - حلال، حل‌شونده - حل‌شونده و توان مرتب نظر کرد. در نتیجه، تریب نفوذ هم‌مثل از غلظت حل‌شونده می‌باشد. برای محلول‌های غلیظ، قانون نرنست مربوط به محلول‌های در فرقی باید برای حالت رفتار غیر ایده‌آل تفسیر کنند که این غیر ایده‌آلی ناشی از برهمکنش‌های حل‌شونده - حل‌شونده می‌باشد. باید توجه کرد که نیروی محرکه برای فلاکس‌های حل‌شونده در این غلظت نیست، بلکه در این حالت پتانسیل نیم‌آیونی (μ_i) می‌باشد:

$$J_{i,x} = - \frac{D_{ij} C_i}{RT} \nabla \mu_i \quad \text{Nernst - Einstein}$$

$$\mu_i = \mu_i^\circ + RT \ln(\gamma_i x_i)$$

تریب پتانسیل نیم‌آیونی مرجع و γ_i تریب فعالیت مربوط به برهمکنش‌های حل‌شونده - حل‌شونده است. پتانسیل نیم‌آیونی مرجع مستقل از ترکیب می‌باشد و تریب فعالیت تنها تابعی از کم‌مولی است. اگر α_i به مفروضه کند، γ_i عدد کمی خواهد شد. با جایگزین کردن خواهیم داشت:

$$J_{i,x} = -D_{ij} C_i \nabla \ln(\gamma_i x_i)$$

با استفاده از قانون زنجیره‌ای مشتق خواهیم داشت:

$$J_{i,x} = - \frac{D_{ij} C_i}{\gamma_i x_i} \nabla \gamma_i x_i = - \frac{D_{ij} C_i}{\gamma_i x_i} [x_i \nabla \gamma_i + \gamma_i \nabla x_i]$$

بنا بر این بیانکه اگر تابعی از x_i است، با استفاده از قانون زنجیره‌ای خواهیم داشت :

$$\nabla \gamma_i = \frac{d\gamma_i}{dx_i} \nabla x_i$$

با جایگزینی خواهیم داشت : $(C_i = x_i C)$

$$J_{ix} = -\frac{D_{ij} C}{y_i} \left[x_i \frac{dy_i}{dx_i} \nabla x_i + \gamma_i \nabla x_i \right] = -D_{ij} C \left[1 + \frac{d \ln \gamma_i}{d \ln x_i} \right] \nabla x_i$$

برای حلونی با غلظت کم ثابت خواهیم داشت : $C \nabla x_i = \nabla C_i$ فریب نفوذ ماکسول - آنتا

با مقایسه رابطه بالا با رابطه سیک ، فریب نفوذ ظاهری خواهد شد :

$$D_{app} = D_{ij} \left(1 + \frac{d \ln \gamma_i}{d \ln x_i} \right) \quad \text{apparent diffusivity}$$

در وقت بی نهایت (infinite dilution) یعنی $x_i \rightarrow 0$ خواهیم داشت : $D_{app} = D_{ij}^0 = D_{ij}$

محدودیت استفاده از معادله بالا این است که فریب فعالیت معمولاً برای بیاری از حل نرنده ها صحت تابعی از ترکیب نامستقیم است و حتی اگر هم باشد، فریب نفوذ اندازه گیری شده را آزمایشگاهی یکسان نیستند.

غیر ایده‌آلی :

$$\ln \gamma_1 = A x_2^2$$

$$\ln \gamma_2 = A x_1^2$$

دارای فریب (برون استی) $\Rightarrow A = 0$ در حالت ایده‌آل

24.2 THE DIFFUSION COEFFICIENT

Fick's law of proportionality, D_{AB} , is known as the diffusion coefficient. Its fundamental dimensions, which may be obtained from equation (24-15)

$$D_{AB} = \frac{-J_{A,z}}{dc_A/dz} = \left(\frac{M}{L^2 t}\right) \left(\frac{1}{M/L^3 \cdot 1/L}\right) = \frac{L^2}{t}$$

are identical to the fundamental dimensions of the other transport properties: kinematic viscosity, ν , and thermal diffusivity, α , or its equivalent ratio, $k/\rho c_p$. The mass diffusivity has been reported in cm^2/s ; the SI units are m^2/s , which is a factor 10^{-4} smaller. In the English system ft^2/h is commonly used. Conversion between these systems involves the simple relations

$$\begin{aligned} \frac{D_{AB}(\text{cm}^2/\text{s})}{D_{AB}(\text{m}^2/\text{s})} &= 10^4 \\ \frac{D_{AB}(\text{ft}^2/\text{h})}{D_{AB}(\text{cm}^2/\text{s})} &= 3.87 \end{aligned} \tag{24-26}$$

The diffusion coefficient depends upon the pressure, temperature, and composition of the system. Experimental values for the diffusivities of gases, liquids, and solids are tabulated in Appendix Tables J.1, J.2, and J.3, respectively. As one might expect from the consideration of the mobility of the molecules, the diffusion coefficients are generally higher for gases (in the range of 5×10^{-6} to $1 \times 10^{-5} \text{ m}^2/\text{s}$), than for liquids (in the range of 10^{-10} to $10^{-9} \text{ m}^2/\text{s}$), which are higher than the values reported for solids (in the range of 10^{-14} to $10^{-10} \text{ m}^2/\text{s}$).

Mass-Transfer Diffusion Coefficients in Binary Systems

Table J.1 Binary mass diffusivities in gases[†]

System	T (K)	$D_{AB}P$ (cm ² atm/s)	$D_{AB}P$ (m ² Pa/s)
Air			
Ammonia	273	0.198	2.006
Aniline	298	0.0726	0.735
Benzene	298	0.0962	0.974
Bromine	293	0.091	0.923
Carbon dioxide	273	0.136	1.378
Carbon disulfide	273	0.0883	0.894
Chlorine	273	0.124	1.256
Diphenyl	491	0.160	1.621
Ethyl acetate	273	0.0709	0.718
Ethanol	298	0.132	1.337
Ethyl ether	293	0.0896	0.908
Iodine	298	0.0834	0.845
Methanol	298	0.162	1.641
Mercury	614	0.473	4.791
Naphthalene	298	0.0611	0.619
Nitrobenzene	298	0.0868	0.879
<i>n</i> -Octane	298	0.0602	0.610
Oxygen	273	0.175	1.773
Propyl acetate	315	0.092	0.932
Sulfur dioxide	273	0.122	1.236
Toluene	298	0.0844	0.855
Water	298	0.260	2.634
Ammonia			
Ethylene	293	0.177	1.793

Table J.2 Binary mass diffusivities in liquids[†]

Solute <i>A</i>	Solvent <i>B</i>	Temperature (K)	Solute concentration (g mol/L or kg mol/m ³)	Diffusivity (cm ² /s × 10 ⁵ or m ² /s × 10 ⁹)
Chlorine	Water	289	0.12	1.26
Hydrogen chloride	Water	273	9	2.7
			2	1.8
		283	9	3.3
			2.5	2.5
Ammonia	Water	289	0.5	2.44
		278	3.5	1.24
		288	1.0	1.77
Carbon dioxide	Water	283	0	1.46
		293	0	1.77
Sodium chloride	Water	291	0.05	1.26
			0.2	1.21
			1.0	1.24
			3.0	1.36
		5.4	1.54	
Methanol	Water	288	0	1.28
Acetic acid	Water	285.5	1.0	0.82
			0.01	0.91
			1.0	0.96
Ethanol	Water	291	1.0	0.96
		283	3.75	0.50
			0.05	0.83
		289	2.0	0.90
<i>n</i> -Butanol	Water	288	0	0.77
Carbon dioxide	Ethanol	290	0	3.2
Chloroform	Ethanol	293	2.0	1.25

[†]R. E. Treybal, *Mass Transfer Operations*, McGraw-Hill, New York, 1955, p. 25.

Table J.3 Binary diffusivities in solids[†]

Solute	Solid	Temperature (K)	Diffusivity (cm ² /s or m ² /s × 10 ⁴)	Diffusivity (ft ² /h)
Helium	Pyrex	293	4.49×10^{-11}	1.74×10^{-10}
		773	2.00×10^{-8}	7.76×10^{-8}
Hydrogen	Nickel	358	1.16×10^{-8}	4.5×10^{-8}
		438	1.05×10^{-7}	4.07×10^{-7}
Bismuth	Lead	293	1.10×10^{-16}	4.27×10^{-16}
Mercury	Lead	293	2.50×10^{-15}	9.7×10^{-15}
Antimony	Silver	293	3.51×10^{-21}	1.36×10^{-20}
Aluminum	Copper	293	1.30×10^{-30}	5.04×10^{-30}
Cadmium	Copper	293	2.71×10^{-15}	1.05×10^{-14}

[†]R. M. Barrer, *Diffusion In and Through Solids*, Macmillan, New York, 1941.

Gas Mass Diffusivity

Theoretical expressions for the diffusion coefficient in low-density gaseous mixtures as a function of the system's molecular properties were derived by Sutherland,³ Jeans,⁴ and Chapman and Cowling,⁵ based upon the kinetic theory of gases. In the simplest model of gas

$$D_{AB} = \frac{2}{3} \left(\frac{\kappa}{\pi} \right)^{3/2} N^{1/2} T^{3/2} \frac{\left(\frac{1}{2M_A} + \frac{1}{2M_B} \right)^{1/2}}{P \left(\frac{\sigma_A + \sigma_B}{2} \right)^2} \quad (24-31)$$

where M_A is the molecular weight of the diffusing species A, (g/mol), N is Avogadro's number (6.022×10^{23} molecules/mol), P is the system pressure, T is the absolute temperature (K), κ is the Boltzmann constant (1.38×10^{-16} ergs/K), and σ_{AB} is the Lennard–Jones diameter of the spherical molecules.

- an inverse function of total system pressure

$$D_{AB} \propto \frac{1}{P}$$

- a 3/2 power-law function of the absolute temperature

$$D_{AB} \propto T^{3/2}$$

Table K.2 Lennard–Jones force constants calculated from viscosity data[†]

Compound	Formula	ϵ_A/κ , in (K)	σ , in Å
Acetylene	C ₂ H ₂	185	4.221
Air		97	3.617
Argon	A	124	3.418
Arsine	AsH ₃	281	4.06
Benzene	C ₆ H ₆	440	5.270
Bromine	Br ₂	520	4.268
<i>i</i> -Butane	C ₄ H ₁₀	313	5.341
<i>n</i> -Butane	C ₄ H ₁₀	410	4.997
Carbon dioxide	CO ₂	190	3.996
Carbon disulfide	CS ₂	488	4.438
Carbon monoxide	CO	110	3.590
Carbon tetrachloride	CCl ₄	327	5.881
Carbonyl sulfide	COS	335	4.13
Chlorine	Cl ₂	357	4.115
Chloroform	CHCl ₃	327	5.430
Cyanogen	C ₂ N ₂	339	4.38
Cyclohexane	C ₆ H ₁₂	324	6.093
Ethane	C ₂ H ₆	230	4.418
Ethanol	C ₂ H ₅ OH	391	4.455
Ethylene	C ₂ H ₄	205	4.232
Fluorine	F ₂	112	3.653
Helium	He	10.22	2.576
<i>n</i> -Heptane	C ₇ H ₁₆	282 [‡]	8.88 ³
<i>n</i> -Hexane	C ₆ H ₁₄	413	5.909
Hydrogen	H ₂	33.3	2.968
Hydrogen chloride	HCl	360	3.305

[†] R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 1958.[‡] Calculated from virial coefficients.¹

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

Modern versions of the kinetic theory have been attempted to account for forces of attraction and repulsion between the molecules. Hirschfelder et al. (1949),⁶ using the Lennard–Jones potential to evaluate the influence of the molecular forces, presented an equation for the diffusion coefficient for gas pairs of nonpolar, nonreacting molecules:

$$D_{AB} = \frac{0.001858T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P\sigma_{AB}^2\Omega_D} \quad (24-33)$$

where D_{AB} is the mass diffusivity of A through B , in cm^2/s ; T is the absolute temperature, in K ; M_A , M_B are the molecular weights of A and B , respectively; P is the absolute pressure, in atmospheres; σ_{AB} is the “collision diameter,” a Lennard–Jones parameter, in \AA ; and Ω_D is the “collision integral” for molecular diffusion, a dimensionless function of the temperature and of the intermolecular potential field for one molecule of A and one molecule of B . Appendix Table K.1 lists Ω_D as a function of $\kappa T/\varepsilon_{AB}$, k is the Boltzmann constant, which is 1.38×10^{-16} ergs/ K , and ε_{AB} is the energy of molecular interaction for the binary system A and B , a Lennard–Jones parameter, in ergs, see equation (24-31).

$$D_{AB_{T_2, P_1}} = D_{AB_{T_1, P_1}} \left(\frac{P_1}{P_2} \right) \left(\frac{T_2}{T_1} \right)^{3/2} \frac{\Omega_D|_{T_1}}{\Omega_D|_{T_2}}$$

Lennard–Jones Constants

Table K.1 The collision integrals, Ω_μ and Ω_D based on the Lennard–Jones potential[†]

$\kappa T/\epsilon$	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)	kT/ϵ	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D (for mass diffusivity)
			1.75	1.234	1.128
0.30	2.785	2.662	1.80	1.221	1.116
0.35	2.628	2.476	1.85	1.209	1.105
0.40	2.492	2.318	1.90	1.197	1.094
0.45	2.368	2.184	1.95	1.186	1.084
0.50	2.257	2.066	2.00	1.175	1.075
0.55	2.156	1.966	2.10	1.156	1.057
0.60	2.065	1.877	2.20	1.138	1.041
0.65	1.982	1.798	2.30	1.122	1.026
0.70	1.908	1.729	2.40	1.107	1.012
0.75	1.841	1.667	2.50	1.093	0.9996
0.80	1.780	1.612	2.60	1.081	0.9878
0.85	1.725	1.562	2.70	1.069	0.9770
0.90	1.675	1.517	2.80	1.058	0.9672
0.95	1.629	1.476	2.90	1.048	0.9576
1.00	1.587	1.439	3.00	1.039	0.9490
1.05	1.549	1.406	3.10	1.030	0.9406
1.10	1.514	1.375	3.20	1.022	0.9328
1.15	1.482	1.346	3.30	1.014	0.9256
1.20	1.452	1.320	3.40	1.007	0.9186
1.25	1.424	1.296	3.50	0.9999	0.9120
1.30	1.399	1.273	3.60	0.9932	0.9058
1.35	1.375	1.253	3.70	0.9870	0.8998
1.40	1.353	1.233	3.80	0.9811	0.8942

EXAMPLE 2

Evaluate the diffusion coefficient of carbon dioxide in air at 20°C and atmospheric pressure. Compare this value with the experimental value reported in appendix table J.1.

From Appendix Table K.2, the values of s and elk are obtained

	σ , in Å	ε_A/κ , in K
Carbon dioxide	3.996	190
Air	3.617	97

The various parameters for equation (24-33) may be evaluated as follows:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} = \frac{3.996 + 3.617}{2} = 3.806 \text{ Å}$$

$$\varepsilon_{AB}/\kappa = \sqrt{(\varepsilon_A/\kappa)(\varepsilon_B/\kappa)} = \sqrt{(190)(97)} = 136$$

$$T = 20 + 273 = 293 \text{ K}$$

$$P = 1 \text{ atm}$$

$$\frac{\varepsilon_{AB}}{\kappa T} = \frac{136}{293} = 0.463$$

$$\frac{\kappa T}{\varepsilon_{AB}} = 2.16$$

$$\Omega_D \text{ (Table K.1)} = 1.047$$

$$M_{\text{CO}_2} = 44$$

and

$$M_{\text{Air}} = 29$$

Substituting these values into equation (24-33), we obtain

$$\begin{aligned} D_{AB} &= \frac{0.001858 T^{3/2} (1/M_A + 1/M_B)^{1/2}}{P \sigma_{AB}^2 \Omega_D} \\ &= \frac{(0.001858)(293)^{3/2} (1/44 + 1/29)^{1/2}}{(1)(3.806)^2 (1.047)} = 0.147 \text{ cm}^2/\text{s} \end{aligned}$$

From Appendix Table J.1 for CO₂ in air at 273 K, 1 atm, we have

$$D_{AB} = 0.136 \text{ cm}^2/\text{s}$$

Equation (24-41) will be used to correct for the differences in temperature

$$\frac{D_{AB,T_1}}{D_{AB,T_2}} = \left(\frac{T_1}{T_2}\right)^{3/2} \left(\frac{\Omega_D|T_2}{\Omega_D|T_1}\right)$$

Values for Ω_D may be evaluated as follows:

$$\text{at } T_2 = 273 \quad \varepsilon_{AB}/\kappa T = \frac{136}{273} = 0.498 \quad \Omega_D|_{T_2} = 1.074$$

$$\text{at } T_1 = 293 \quad \Omega_D|_{T_1} = 1.074 \quad (\text{previous calculations})$$

The corrected value for the diffusion coefficient at 20°C is

$$D_{AB,T_1} = \left(\frac{293}{273}\right)^{3/2} \left(\frac{1.074}{1.047}\right)(0.136) = 0.155 \text{ cm}^2/\text{s} \quad (1.55 \times 10^{-5} \text{ m}^2/\text{s})$$

سوال ۱:

ضریب نفوذ گاز دی اکسید کربن درون هوا در دمای ۳۰ درجه سانتیگراد و فشار ۱.۲ اتمسفر را با استفاده از سه روش داده های جدولی، مدل کره سخت و تئوری سینتیک مدرن را محاسبه کنید.

سوال ۲:

نشان دهید تنها یک ضریب نفوذ برای توصیف رفتار نفوذ در یک سیستم دو جزئی گازی نیاز است.

$$D_{AB} = D_{BA}$$

$$D_{1-\text{mixture}} = \frac{1}{y'_2/D_{1-2} + y'_3/D_{1-3} + \cdots + y'_n/D_{1-n}} \quad (24-49)$$

where $D_{1-\text{mixture}}$ is the mass diffusivity for component 1 in the gas mixture; D_{1-n} is the mass diffusivity for the binary pair, component 1 diffusing through component n ; and y'_n is the mole fraction of component n in the gas mixture evaluated on a component-1-free basis, that is

$$y'_2 = \frac{y_2}{y_2 + y_3 + \cdots + y_n} = \frac{y_2}{1 - y_1}$$

Liquid-Mass Diffusivity

properties. Wilke and Chang¹⁶ have proposed the following correlation for nonelectrolytes in an infinitely dilute solution:

$$\frac{D_{AB}\mu_B}{T} = \frac{7.4 \times 10^{-8}(\Phi_B M_B)^{1/2}}{V_A^{0.6}} \quad (24-52)$$

where D_{AB} is the mass diffusivity of A diffusing through liquid solvent B , in cm^2/s ; μ_B is the viscosity of the solution, in centipoises; T is absolute temperature, in K; M_B is the molecular weight of the solvent; V_A is the molal volume of solute at normal boiling point, in $\text{cm}^3/\text{g mol}$; and Φ_B is the “association” parameter for solvent B .

Table 24.4 Molecular volumes at normal boiling point for some commonly encountered compounds

Compound	Molecular volume, in $\text{cm}^3/\text{g mol}$	Compound	Molecular volume, in $\text{cm}^3/\text{g mol}$
Hydrogen, H_2	14.3	Nitric oxide, NO	23.6
Oxygen, O_2	25.6	Nitrous oxide, N_2O	36.4
Nitrogen, N_2	31.2	Ammonia, NH_3	25.8
Air	29.9	Water, H_2O	18.9
Carbon monoxide, CO	30.7	Hydrogen sulfide, H_2S	32.9
Carbon dioxide, CO_2	34.0	Bromine, Br_2	53.2
Carbonyl sulfide, COS	51.5	Chlorine, Cl_2	48.4
Sulfur dioxide, SO_2	44.8	Iodine, I_2	71.5

Table 24.5 Atomic volumes for complex molecular volumes for simple substances[†]

Element	Atomic volume, in cm ³ /g mol	Element	Atomic volume, in cm ³ /g mol
Bromine	27.0	Oxygen, except as noted below	7.4
Carbon	14.8	Oxygen, in methyl esters	9.1
Chlorine	21.6	Oxygen, in methyl ethers	9.9
Hydrogen	3.7	Oxygen, in higher ethers and other esters	11.0
Iodine	37.0	Oxygen, in acids	12.0
Nitrogen, double bond	15.6	Sulfur	25.6
Nitrogen, in primary amines	10.5		
Nitrogen, in secondary amines	12.0		

[†]G. Le Bas, *The Molecular Volumes of Liquid Chemical Compounds*, Longmans, Green & Company, Ltd., London, 1915.

Recommended values of the association parameter, Φ_B , are given below for a few common solvents.

Solvent	Φ_B
Water	2.26 ¹⁷
Methanol	1.9
Ethanol	1.5
Benzene, ether, heptane, and other unassociated solvents	1.0

Appendix I

Physical Properties of Gases and Liquids¹

Liquids									
T (°F)	ρ (lb _m /ft ³)	c_p (Btu/lb _m °F)	$\mu \times 10^3$ (lb _m /ft s)	$\nu \times 10^5$ (ft ² /s)	k (Btu/h ft °F)	$\alpha \times 10^3$ (ft ² /h)	Pr	$\beta \times 10^4$ (1/°F)	$g\beta\rho^2/\mu^2 \times 10^{-6}$ (1/°F · ft ³)
Water									
32	62.4	1.01	1.20	1.93	0.319	5.06	13.7	-0.350	
60	62.3	1.00	0.760	1.22	0.340	5.45	8.07	0.800	17.2
80	62.2	0.999	0.578	0.929	0.353	5.67	5.89	1.30	48.3
100	62.1	0.999	0.458	0.736	0.364	5.87	4.51	1.80	107
150	61.3	1.00	0.290	0.474	0.383	6.26	2.72	2.80	403
200	60.1	1.01	0.206	0.342	0.392	6.46	1.91	3.70	1,010
250	58.9	1.02	0.160	0.272	0.395	6.60	1.49	4.70	2,045
300	57.3	1.03	0.130	0.227	0.395	6.70	1.22	5.60	3,510
400	53.6	1.08	0.0930	0.174	0.382	6.58	0.950	7.80	8,350
500	49.0	1.19	0.0700	0.143	0.349	5.98	0.859	11.0	17,350
600	42.4	1.51	0.0579	0.137	0.293	4.58	1.07	17.5	30,300

EXAMPLE 5

Estimate the liquid diffusion coefficient of ethanol, C_2H_5OH , in a dilute solution of water at $10^\circ C$. The molecular volume of ethanol may be evaluated by using values from Table 24.5 as follows:

$$V_{C_2H_5OH} = 2V_C + 6V_H + V_O$$

$$V_{C_2H_5OH} = 2(14.8) + 6(3.7) + 7.4 = 59.2 \text{ cm}^3/\text{mol}$$

At $10^\circ C$, the viscosity of a solution containing 0.05 mol of alcohol/liter of water is 1.45 centipoises; the remaining parameters to be used are

$$T = 283 \text{ K}$$

$$\Phi_B \text{ for water} = 2.26$$

and

$$M_B \text{ for water} = 18$$

Substituting these values into equation (24-52), we obtain

$$\begin{aligned} D_{C_2H_5OH-H_2O} &= \left(\frac{7.4 \times 10^{-8} (2.26 \times 18)^{1/2}}{(59.2)^{0.6}} \right) \left(\frac{283}{1.45} \right) \\ &= 7.96 \times 10^{-6} \text{ cm}^2/\text{s} \quad (7.96 \times 10^{-10} \text{ m}^2/\text{s}) \end{aligned}$$

This value is in good agreement with the experimental value of $8.3 \times 10^{-10} \text{ m}^2/\text{s}$ reported in Appendix J.

Pore Diffusivity

Knudsen diffusion. Consider the diffusion of gas molecules through very small capillary pores. If the pore diameter is smaller than the mean free path of the diffusing gas molecules and the density of the gas is low, the gas molecules will collide with the pore walls more frequently than with each other. This process is known as Knudsen flow or *Knudsen diffusion*. The gas flux is reduced by the wall collisions.

The Knudsen number, Kn , given by

$$Kn = \frac{\lambda}{d_{\text{pore}}} = \frac{\text{mean free path length of the diffusing species}}{\text{pore diameter}}$$

instance, the Knudsen diffusivity for diffusing species A , D_{KA} , is

$$D_{KA} = \frac{d_{\text{pore}}}{3} u = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8kNT}{\pi M_A}} \quad (24-58)$$
$$D_{KA} = \frac{d_{\text{pore}}}{3} \sqrt{\frac{8}{\pi} \left(1.38 \cdot 10^{-16} \frac{\text{g} \cdot \text{cm}}{\text{s}^2 \text{K}} \right) \left(6.023 \cdot 10^{23} \frac{\text{molecules}}{\text{mol}} \right) \sqrt{\frac{T}{M_A}}}$$
$$= 4850 d_{\text{pore}} \sqrt{\frac{T}{M_A}}$$

This simplified equation requires that d_{pore} has units of cm, M_A has units of g/mol, and temperature T has units of K. The Knudsen diffusivity, D_{KA} , is dependent on the pore diameter, species A molecular weight, and temperature. We can make two comparisons of D_{KA} to the binary gas phase diffusivity, D_{AB} . First, it is not a function of absolute pressure P , or the presence of species B in the binary gas mixture. Second, the temperature dependence for the Knudsen diffusivity is $D_{KA} \propto T^{1/2}$, vs. $D_{AB} \propto T^{3/2}$ for the binary gas phase diffusivity.

Generally, the Knudsen process is significant only at low pressure and small pore diameter. However, there are instances where both Knudsen diffusion and molecular diffusion (D_{AB}) can be important. If we consider that Knudsen diffusion and molecular diffusion compete with one another by a “resistances in series” approach, then the effective diffusivity of species A in a binary mixture of A and B , D_{Ae} , is determined by

$$\frac{1}{D_{Ae}} = \frac{1 - \alpha y_A}{D_{AB}} + \frac{1}{D_{KA}} \quad (24-59)$$

with

$$\alpha = 1 + \frac{N_B}{N_A}$$

For cases where $\alpha = 0$ ($N_A = -N_B$), or where y_A is close to zero, equation (24-59) reduces to

$$\frac{1}{D_{Ae}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}} \quad (24-60)$$

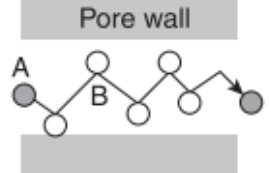
The above relationships for the effective diffusion coefficient are based on diffusion within straight, cylindrical pores aligned in a parallel array. However, in most porous materials, pores of various diameters are twisted and interconnected with one another, and the path for diffusion of the gas molecule within the pores is “tortuous.” For these materials, if an average pore diameter is assumed, a reasonable approximation for the effective diffusion coefficient in random pores is

$$D'_{Ae} = \varepsilon^2 D_{Ae} \quad (24-61)$$

where $\varepsilon = \frac{\text{the volume occupied by pores within the porous solid}}{\text{total volume of porous solid (solid + pores)}}$

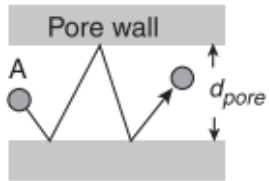
ε is the volume void fraction of the porous volume within the porous material. This “void fraction” is usually experimentally determined for a specific material.

Pure molecular diffusion



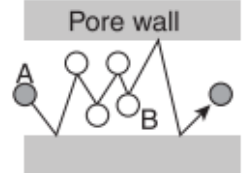
$$D_{AB} = \frac{0.001858T^{3/2} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^{1/2}}{P \sigma_{AB}^2 \Omega_D}$$

Pure knudsen diffusion




$$D_{KA} = \frac{d_{pore}}{3} \sqrt{\frac{8 \kappa N T}{\pi M_A}}$$

Knudsen + molecular diffusion



$$\frac{1}{D_{Ae}} \cong \frac{1}{D_{AB}} + \frac{1}{D_{KA}}$$

Random porous material



$$D'_{Ae} = \varepsilon^2 D_{Ae}$$

Figure 24.3 Types of porous diffusion. Shaded areas represent nonporous solids.