Module 4:

Multicomponent Transport

Lecture 34:

Binary Systems

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For Binary Systems: $D_{AB} = D_{BA}$

Using $(d\overline{G_A})_{T,P} = RTd(\ln a_A)$ (where a_A is the activity of A) and

defining thermal diffusion ratio as $k_T = \dfrac{\rho}{C^2 M_A M_B} \dfrac{D_A^T}{D_{AB}}$,

equation (3.7.11)-(3.7.15) yields

$$j_A = -j_B = -\left(\frac{C^2}{\rho}\right) M_A M_B D_{AB} \left[\begin{array}{l} \left(\dfrac{\partial \ln a_A}{\partial \ln x_A}\right)_{T,P} \nabla x_A - \dfrac{M_A \rho_B x_A}{\rho RT}\left(\underline{g}_A - \underline{g}_B\right) \\[2ex] + \dfrac{M_A x_A}{RT}\left(\dfrac{\overline{V_A}}{MA} - \dfrac{1}{\rho}\right)\nabla p + k_T \nabla \ln T \end{array} \right]$$

(3.7.16)

Note: When k_T is positive, component A moves to the colder region; when k_T is negative, component A moves to the warmer region.

EXPERIMENTAL THERMAL DIFFUSION RATIOS FOR LIQUIDS AND LOW-DENSITY GASES

Liquids[a]				Gases[b]			
Component				**Component**			
$A - B$	$T(°K)$	x_A	k_T	$A - B$	$T(°K)$	x_A	k_T
$C_2H_2Cl_4 - n - C_6H_{14}$	298	0.5	1.08	$N_e - H_e$	330	0.20	0.0531
$C_2H_4Br_2 - C_2H_4Cl_2$	298	0.5	0.225			0.60	0.1004
$C_2H_2Cl_4 - CCl_4$	298	0.5	0.060	$N_2 - H_2$	264	0.294	0.0542

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$CBr_4 - CCl_4$	298	0.09	0.129			0.775	0.0663
$CCl_4 - CH_3OH$	313	0.5	1.23	$D_2 - H_2$	327	0.10	0.0145
$CH_3OH - H_2O$	313	0.5	-0.137			0.50	0.0432
Cyclo- $C_6H_{12} - C_6H_6$	313	0.5	0.100			0.90	0.0166

[a] Abstracted from R. L. Saxton, E. L. Dougherty, and H. G. Drickamer, J. Chem. Phys, 22, 1166-1168 (1954); R. L. Saxton and H. G. Drickamer, ibid., 1287-1288; L. J. Tichacek, W. S. Kmak, and H. G. Drickamer, J. Phys. Chem., 60,660-665 (1956).

[b] Abstracted from, tables givenby J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, Wiley New York (1954), §.4.

Let's consider ordinary diffusion for a moment

$$j_A^{(x)} = -\frac{C^2}{\rho} M_A M_B D_{AB} \left(\frac{\partial \ln a_A}{\partial \ln x_A} \right)_{T,P} \nabla x_A \qquad (3.7.17)$$

Compare with the "usual" form

$$j_A^{(x)} = -\frac{C^2}{\rho} M_A M_B \mathbf{D}_{AB} \nabla x_A \qquad (3.7.18)$$

Thus,

$$\mathbf{D}_{AB} = D_{AB} \left(\frac{\partial \ln a_A}{\partial \ln x_A} \right)_{T,P}$$

For ideal systems (activity proportional to mole fraction), implying

$$\mathbf{D}_{AB} = D_{AB}$$

For liquid systems, $\mathbf{D}_{AB}$ has a stronger dependence on concentration than D_{AB}

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Ordinary Diffusion in Ideal Gas Mixtures

For an ideal gas mixture, eq., (3.7.12) becomes

$$\underline{j_i} = \frac{C^2}{\rho} \sum_{j=1}^{n} M_i M_j D_{ij} \nabla x_j \quad , where\ i=1,2,3,...,n \qquad (3.7.20)$$

Note: In this subsection we are interested in ordinary (concentration) diffusion only. Items superscript (X) has been dropped in (3.7.20).

For ideal gas mixtures, the relation between D_{ij} (the diffusivity of pair *i-j* in the <u>multi component</u>

mixture) and $\mathbf{D}_{ij}$ (the diffusivity of the pair *i-j* in a <u>binary</u> mixture) is known.

Stefan – Maxwell equation

It can be shown that equation (3.7.20) can be turned around as

$$\nabla x_i = \sum_{j=1}^{n} \frac{C_i C_j}{C^2 D_{ij}} \left(v_j - v_i \right) = \sum_{j=1}^{n} \frac{1}{CD_{ij}} \left(x_i \underline{N}_j - x_j \underline{N}_i \right) \qquad (3.7.21)$$

These are known as the <u>Stefan – Maxwell equation.</u>

The advantages of using (3.7.21) over (3.7.20) is that D_{ij} <u>is virtual independent of gas composition</u>

<u>(which is not the case with</u> $\mathbf{D}_{ij}$)

Note: From kinetic theory of gases

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$$D_{ij} = 0.0018583 \frac{\sqrt{T^3 \left(\dfrac{1}{M_i} + \dfrac{1}{M_j} \right)}}{p\sigma_{ij}\Omega_{D,ij}}, \tag{3.7.22}$$

where D_{ij} is in cm^2/s, p is in atm and σ_{ij} is in A^0.

For some calculation it is convenient to define an effective binary diffusivity D_{im} for diffusion of component i into mixture m.

$$\underline{N}_i = -CD_{im}\nabla x_i + x_i \sum_{j=1}^{n} \underline{N}_j \tag{3.7.23}$$

Solving (3.7.23) for ∇x_i and using (3.7.21) one obtains

$$\frac{1}{CD_{im}} = \frac{\displaystyle\sum_{j=1}^{n} \frac{1}{CD_{ij}} \left(x_j \underline{N}_i - x_i \underline{N}_j \right)}{\underline{N}_i - x_i \displaystyle\sum_{j=1}^{n} \underline{N}_j} \tag{3.7.24}$$

Equation (3.7.24) is in general difficult to use because D_{im} depend on position. For certain simplified cases, however, D_{im} becomes particularly simple. For example,

a) Trace components 2,3,………n in nearly pure component 1.

$$D_{im} = D_{i1}$$

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b) D_{ij} are all the same => $D_{im} = D_{ij}$

c) 2,3,.......,n more with the same velocity =>

$$\frac{1-x_1}{D_{1m}} = \sum_{j=2}^{n} \frac{x_j}{D_{1j}}$$
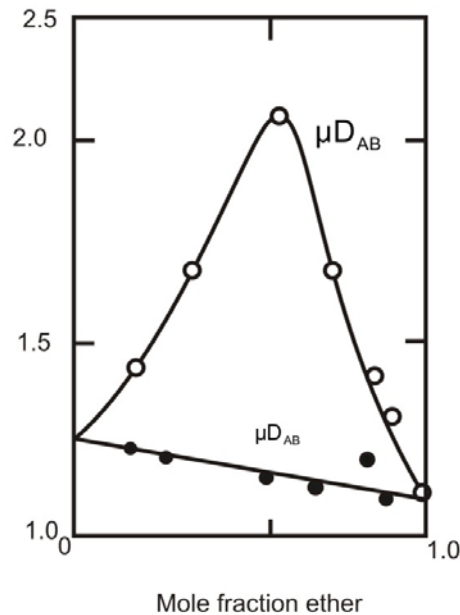
(3.7.25)

Figure showing the effect of activity on the product of viscosity and diffusivity for liquid mixtures chloroform and ether. [Adapted from R. E. Powell, W. L. Roseveare, and Henry Eyring. Ind. Eng. Chem. 33, 430-435 (1941)]