types of stability behavior further underscoring the richness of the dynamic behavior of this system.

NOTATION

B = dimensionless adiabatic temperature rise
m_1, m_2 = roots of the determinant of the stability matrix
s_1, s_2 = roots of the trace of the stability matrix
X_{1s} = dimensionless steady-state conversion
X_{2s} = dimensionless steady-state temperature
Da = Damkohler number
β = dimensionless heat transfer coefficient
γ = dimensionless activation energy
δ_1, δ_2 = parameters defined by Uppal et al. (1974)

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Diaphragm Diffusion Cell: Simpler Cell Design and New Equation to Calculate Diffusivities

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Since Northrop and Anson (1929), made the first diaphragm diffusion cell, the method proposed by them for measuring liquid diffusivities has become well established. The diaphragm cell design has undergone several modifications over the years, mainly with the purpose of eliminating various sources of error (e.g., Stokes, 1950; Dullien and Shemilt, 1961; Albright and Mills, 1965).

The first point of this note is the diaphragm cell design, Figure 1, due to Asfour (1979), which is far simpler than the most sophisticated design known to the authors, Albright and Mills (1965), but notwithstanding its simplicity, yields results of comparable precision. Both the top and the bottom plugs of the cell are made of teflon; there is a capillary bore in the top plug which permits volume changes of the liquid in the upper compartment, while the stainless-steel (SS) screw cap prevents evaporation losses. There is no bore in the bottom plug. The brass bottom cap, threaded on the inside, screws onto the brass ring glued on the extension of the lower compartment, and it assures a water-tight seal. The bottom cap fits into a mount at the bottom of the constant temperature bath containing oil, thus allowing the cells to be placed in the bath reproducibly and in a fixed position. As shown in Figure 1, each compartment contains a magnetic stirrer which in actual operation lightly touch the diaphragm. Sampling is done with the help of a hypodermic syringe fitted with a thin teflon tubing. First the upper compartment then; after inverting the cell, in the bath, the lower compartment is sampled as quickly as possible.

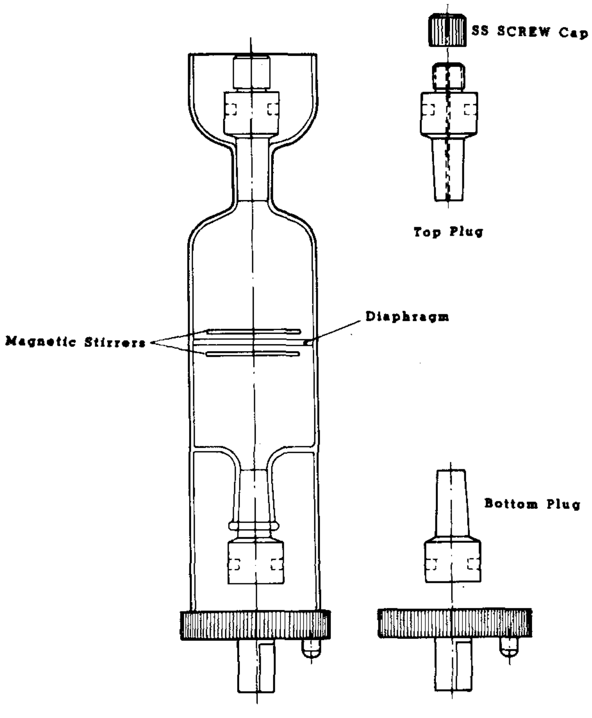

Figure 1. Diaphragm cell.

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Both the KCl solutions used in the calibration runs and the organic solutions used in the actual runs are analyzed by measuring their densities, using an Anton Paar K.G., Model No. DMA 02C density meter.

The second point made in this note is that in the customary formula used to calculate the "integral" diffusion coefficient $\overline{D}_{AB}$:

$$\overline{D}_{AB} = \frac{1}{\beta_c t} \ln \frac{C_L^i - C_U^i}{C_L^f - C_U^f} \tag{1}$$

(β_c is the "cell constant," t the diffusion time, C the concentration of either component, L and U refer to the lower and the upper compartments and i and f refer to the initial and the final conditions, respectively), replacing the concentrations C with the corresponding densities ρ will, in most cases, introduce only a completely negligible error. It can easily be ascertained that this is indeed the case, provided that in the concentration range covered by the diffusion run ρ is a monotonously increasing or decreasing function of C, and the relationship between C and ρ is sufficiently well approximated by a polynomial of the form

$$C = \sum_{i=0}^{n} A_i \rho^i \tag{2}$$

In the diaphragm diffusion experiments the initial concentrations C_U^i and C_L^i customarily are chosen to be fairly close to one another to minimize the effect of volume changes on mixing. Hence, the dependence of C on ρ over the range of values of C covered in one and the same diffusion experiment is always closely approximated by a linear relationship (i.e., $n = 1$). Nevertheless, to avoid limiting our discussion of the validity of the simplification introduced by substituting ρ for C in Eq. 1 to the case of a strictly linear relationship between C and ρ, the more general case of $n = 4$ is considered here. A fourth degree polynomial is usually sufficient to fit the C vs. ρ data over the entire composition range of a binary system.

For the case when $n = 4$, substitution of Eq. 2 into Eq. 1 yields

$$\overline{D}_{AB} = \frac{1}{\beta_c t} \ln \frac{\rho_L^i - \rho_U^i}{\rho_L^f - \rho_U^f} \cdot \zeta \tag{3}$$

with

$$\zeta = \frac{A_1 + A_2\Sigma + A_3\Sigma^2 + A_4\Sigma^3 - \rho_L^i\rho_U^i[A_3 + 2A_4\Sigma]}{A_1 + A_2\Sigma_1 + A_3\Sigma_1^2 + A_4\Sigma_1^3 - \rho_L^f\rho_U^f[A_3 + 2A_4\Sigma_1]} \tag{4}$$

where

$$\Sigma = \rho_L^i + \rho_U^i, \text{ and } \Sigma_1 = \rho_L^f + \rho_U^f.$$

It is evident from Eq. 4 that, for the special case of a linear relationship between C and ρ, ζ is equal to unity, exactly. Linearity between C and ρ, however, also corresponds to no volume change on mixing, i.e., to the very same assumption on which Eq. 1 is based. Conversely, nonlinearity of Eq. 2 implies volume changes on mixing; therefore, in this case Eq. 1 is in error. It is easy to show that the extent to which ζ deviates from unity is determined primarily by the extent of the volume change on mixing. Using data obtained on a large number of binary systems investigated by one of the authors (Dullien) over a period of over 20 years, including ethanol-water (Dullien and Shemilt, 1961), n-octane-methylcyclohexane, n-octane-cyclohexanone, n-heptanol-methylcyclohexane (Robinson et al., 1966), n-octane-carbontetrachloride, n-decane-carbontetrachloride, n-dodecane-carbontetrachloride (Wedlake and Dullien, 1974), n-hexane-carbontetrachloride, toluene-carbontetrachloride (Ghai and Dullien, 1974), benzene-toluene, and chloroform-toluene (Asfour, 1979), for a typical diaphragm diffusion cell experiment an estimate of ζ in the range of 1 to 1.00001 is obtained. Hence, there follows that the error introduced by equating ζ to unity is less by at least two orders of magnitude than the error committed in the diffusivity calculated by Eq. 1.

Having thus shown that ρ may be substituted for C in Eq. 1 without introducing any significant error into $\overline{D}_{AB}$ obtained in a typical diaphragm diffusion cell experiment, there remains to be demonstrated what the advantages are of making this substitution.

The relative standard deviation of the diffusion coefficient obtained by the diaphragm cell method can be expressed by (Robinson et al., 1965):

$$\frac{S_D}{\overline{D}_{AB}} = \frac{S_c}{(C_L^i - C_U^i)\ln R_c} \sqrt{2(R_c^2 + 3)} \tag{5a}$$

where S_c is the standard deviation of the concentration determination, and $R_c = C_L^i - C_U^i/C_L^f - C_U^f$, or by:

$$\frac{S_D}{\overline{D}_{AB}} = \frac{S_\rho}{(\rho_L^i - \rho_U^i)\ln R_\rho} \sqrt{2(R_\rho^2 + 3)} \tag{5b}$$

where S_ρ is the standard deviation of the density determination, and $R_\rho = \rho_L^i - \rho_U^i/\rho_L^f - \rho_U^f \simeq R_c$.

Now, by virtue of the essentially linear relationship between C and ρ over the range of concentrations covered in a typical diffusion run, one can write

$$S_c \simeq \frac{C_L^i - C_U^i}{\rho_L^i - \rho_U^i} S_\rho \tag{6}$$

whence there follows the equivalence of Eqs. 5a and 5b.

Using typical data of $\rho = 0.85$ g/mL, $R = 3$, $\rho_L^i - \rho_U^i = 0.86 - 0.84 = 0.02$ g/mL, and $S_\rho = 1 \times 10^{-5}$ g/mL, one obtains $S_D/\overline{D}_{AB} = 2.2 \times 10^{-3}$ which, on comparison with $S_\rho/\rho = 1.2 \times 10^{-5}$, shows a hundredfold magnification of the error of density determination. In view of this great magnification of error, the densities of representative samples taken from the diffusion cell must be determined with the greatest possible precision. It is *not* necessary, however, to assign a concentration to the measured density with a similar precision, because the densities may be used directly to calculate $\overline{D}_{AB}$. When the recommended new procedure is used the density-concentration relationship is required only for the purpose of assigning the appropriate concentrations to the diffusion coefficients. As the uncertainty of the value of a measured diffusion coefficient is seldom less than 0.2%, it is satisfactory to know the corresponding concentration to within ± 0.1%. In past high precision work, however, often efforts were made to calculate C much more accurately than ± 0.1%. A great deal of painstaking effort was required to achieve such a precision, while still leaving a great deal of doubt as to the question whether an equal accuracy was also achieved.

When the new method of calculating diffusivities is used, only a high precision of the density readings taken on representative samples is of importance to assure a high precision of the diffusivities. The concentrations corresponding to the diffusion coefficients may be found with a sufficient accuracy using customary density tables with the densities given to four significant places.

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NOTATION

A = constant, Eqs. 2 and 4
C = concentration
D_{AB} = mutual diffusivity
R = ratio
S = standard deviation
t = diffusion time

Greek Letters

β = constant
ρ = density
Σ = $\rho_L^i + \rho_U^i$
ζ = defined by Eq. 4

Superscripts

f = final
i = initial

Subscripts

C = cell or concentration
D = diffusivity
L = lower compartment of diaphragm cell
U = upper compartment of diaphragm cell

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BOOKS

Classical Thermodynamics of Nonelectrolyte Solutions, H. C. Van Ness and M. M. Abbott, McGraw-Hill 1982, 482 pp. $39.50.

This book gives a detailed account of the classical approach to the thermodynamics of mixtures, and particularly fluid phase equilibria. It is assumed that the reader has had a course in thermodynamics, but the fundamentals are well reviewed in the early chapters, so that readers whose knowledge is rusty will find the book self-contained. After an initial review chapter, there are two chapters giving the thermodynamic equations and introducing the necessary functions (fugacities, activity coefficients, etc.). This is followed by a chapter on behavior of pure fluids and equations of state for pure and mixed fluids. There are particularly useful accounts of the corresponding states correlations, virial expansion and cubic equations of state, with advice on when to use each. The final two chapters cover property changes on mixing and applications to phase equilibria. This last chapter is the longest in the book (138 pages), and is the most useful to chemical engineers. There are also several useful Appendices covering mathematical techniques, conversion factors, residual function calculations, critical constants, Newton's method, G^E equations, and flash calculations. As in other books by these authors, the text is lucid and easy to read, there are many worked examples, and a very good collection of problems at the end of the book.

Although the authors state clearly at the beginning that they will limit themselves to a purely classical approach, the omission of any molecular interpretation seems to me to restrict the book's appeal as a graduate level text. The inclusion of some statistical thermodynamics gives the reader a feeling for the relation between molecular and macroscopic fluid behavior. Without it the reader cannot appreciate the significance of the virial equation of state or local composition concept, for example, and the all-important mixing and combining rules appear as *ad hoc* constructions. Some of the more complex problems that chemical engineers encounter are included and well treated, for instance, Henry's constants for mixed solvents and ternary phase equilibria. However, as in other texts, a number of the more complex areas are omitted or given scant mention. These include detailed discussions of high pressure phase equilibria (particularly highly nonideal mixtures), calculations for mixture critical points, the nonanalytic behavior of thermodynamic properties near critical points (important in supercritical fluid operations), and the use of group contribution methods.

This book will be useful as a reference and as a text for a second thermodynamics course.

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Industrial Heat Exchangers: A Basic Guide by G. Walker, Hemisphere Publ. Corp. Washington DC, 1982, $41.50, 408 pg.

Recently a number of books started to appear in the, until now, largely neglected area of heat exchanger technology. Practically all such texts are directed to the already experienced reader. The author is correct in stating that this is a "different" book, aimed at the forgotten non-specialist user of heat exchangers as an elementary guide. Within such restrictions it fulfills it's objective very well indeed.

The book starts with a brief summary of heat transfer processes, useful for a novice. The main body of the book contains a concise survey of most industrial heat exchanger types, their principles of operation, areas of application, advantages and limitations and various related comments. Included are standard tubular exchangers, air exchangers, plate and spiral, compact, non-metallic and cryogenic types. Separate sections are devoted to regenerators and boilers, very hard to find elsewhere in such a concise form. Numerous well selected illustrations make the book a good source for self-education or as a supplementary text for heat transfer courses where heat exchangers are usually treated only from academic point of view.

Of special interest even to the more experienced heat exchanger user are the sections on corrosion and erosion, hard to find in general reivew texts. Codes and Standards,