need such a correction for all compounds other than normal paraffins.

EXTRAPOLATION TO LOW TEMPERATURES

Heat capacities at low reduced temperatures are often needed in process calculations. An evaluation of the two methods discussed above was made to see how the correlations perform when extrapolated to low temperatures. The results of these extrapolations for 1-butene and ethyl mercaptan are shown in Figures 1 and 2. The Lyman-Danner predictions, like most empirical correlations, deviate dramatically when extrapolated outside the recommended reduced temperature range $0.35 < T_r < 0.96$. This illustrates clearly why such extrapolations should generally not be made.

On the other hand, extrapolations of the present correlation are reasonably well behaved. For the low temperature data set consisting of 217 experimental points for forty-three compounds, Equation (5) gave an average deviation of only 4.2%, which indicates that this equation may be extrapolated with little loss in accuracy.

The success of the present correlation upon extrapolation to lower temperatures is attributable to two factors. Firstly, a semitheoretical equation, Equation (1), was employed to get an approximate form of the fitting function. Secondly, the new correlation represents a more appropriate and physically meaningful choice of parameters. The fourth parameter κ, used by Lyman and Danner, assumes both positive and negative values. This renders it mathematically difficult to obtain suitable functions that contain odd powers of κ (the same term could add or subtract, depending on whether κ is positive or negative).

The results of this study further demonstrate the usefulness and superiority of the new set of parameters in correlating configurational properties of fluids.

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NOTATION

$C_p{}^o$ = isobaric heat capacity of ideal gas
C_σ = saturation heat capacity of the liquid
P_r = reduced pressure
R = gas constant
$\overline{R}$ = radius of gyration, Å
T = temperature
T_c = critical temperature
T_r = reduced temperature
δ = Rowlinson's third parameter
κ = Passut fourth parameter, used by Lyman and Danner
Φ = newly developed fourth parameter
ω = Pitzer acentric factor

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Quantum Effects in the Diffusion of Gases in Liquids

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Measurements of diffusion coefficients is important both for industrial use and fundamental research. It is of major use in testing current models of the liquid state and for formulating models of mass transfer. Our understanding of industrially important, complex chemical reactions, where combined kinetic and diffusional effects determine product distribution, will depend on our knowledge of the diffusional process.

Diffusion in liquids has been studied for many years beginning with the Stokes-Einstein equation in 1905. Since then, many equations have appeared in the literature. Available expressions have only been partially successful. The problem of accurately predicting diffusion coefficients still remains to be solved.

Previous predictive relationships for gas-liquid diffusivities have been derived from four main theoretical approaches: hydrodynamical theories, kinetic theory, absolute rate theory, and semiempirical expressions based on the first two theories. Among all available equations, the absolute rate theory approach of Akgerman and Gainer (1972) seems to be most successful. This model of the liquid state assumes that liquids contain holes in their structure and solute molecules move into these holes in the process of diffusion.

TABLE 1. QUANTUM PARAMETER AND GAS-LIQUID DIFFUSIVITIES

Solute	Λ^*	$(1 + \Lambda^{*2})$	σ $\times 10^8$ cm	$D\sigma^2_{CCl_4}$* $\times 10^{21}$ cm²/s	Ratio $D\sigma^2/D\sigma^2$ (argon)	$D\sigma^2_{(C_4F_9)_3N}$* $\times 10^{21}$ cm²/s	Ratio $D\sigma^2/D\sigma^2$ (argon)	$D\sigma^2$ water† $\times 10^{21}$ cm²/s	Ratio $D\sigma^2/D\sigma^2$ (argon)
He	2.67	8.13	2.57	132	3.07	86	2.68	59.11	3.01
H_2	1.729	4	2.96	86	2	58	1.81	39.25	1.99
D_2	1.223	2.49	2.96	67	1.56	48	1.5	—	—
N_e	0.593	1.35	2.75	47	1.09	40	1.25	22.7	1.15
CH_4	0.239	1.06	3.81	43	1.0	—	—	34.83	1.77
N_2	0.226	1.05	3.7	47	1.09	32	1.0	22.7	1.15
O_2	0.201	1.04	3.43	45	1.05	—	—	23.52	1.19
Ar	0.186	1.035	3.42	43	1.0	32	1.0	19.65	1

* See Nakanishi et al. (1965).
† See Akgerman and Gainer (1972).

Hildebrand (1971) and Alder and Hildebrand (1973) have criticized theories based on such a model. They hold that vacancies that exist in crystals disappear upon melting and become randomly distributed as intermolecular space. Self-diffusion studies on carbon tetrachloride (Watts et al., 1955) yielded molecular jump lengths much smaller than mean molecular diameters. The work of Alder and Einwohner (1965) shows, using hard sphere calculations, that the probability of mean free paths as long as one molecular diameter is extremely low.

On the basis of these results, Hildebrand (1971) claimed that there is no basis for using an activation energy concept to describe diffusion in liquids. Liquids are remarkably fluid, even when the relative expansion is very small. The relative expansion is based on the intrinsic volume, the volume at zero fluidity. This leads to a model of the liquid state where molecules are moving in a random walk in paths short compared to the molecular diameter.

Assuming that diffusion coefficients are inversely proportional to the square of the solute molecular diameter, Sridhar and Potter (1977) derived an equation for predicting gas liquid diffusivities:

$$D_{AB} = 0.088 \frac{V_B^{*4/3}}{N^{2/3}} \frac{RT}{\mu V_o} \frac{1}{V_A^{*2/3}} \qquad (1)$$

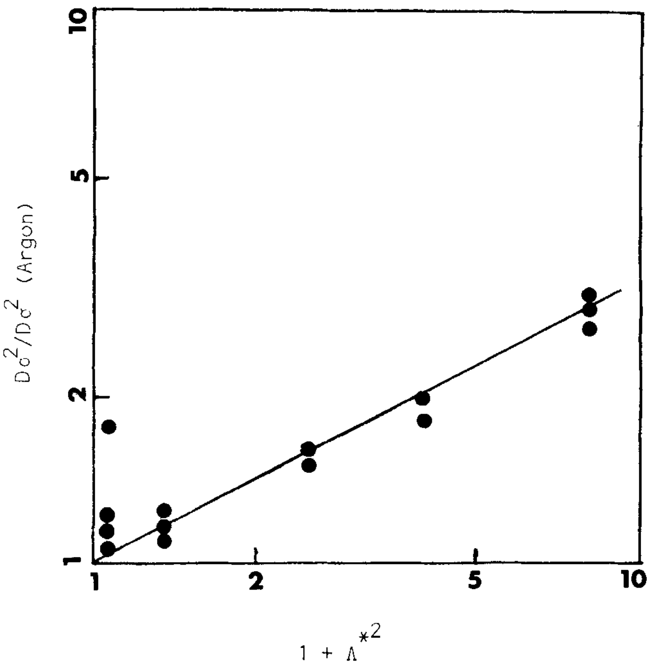

Fig. 1. Enhancement of diffusion due to quantum effect.

TABLE 2. COMPARISON OF EQUATIONS

Solute	Solvent	T°C	Experimental* $\times 10^5$ cm²/s	Predicted by equation (3) $\times 10^5$cm²/s	Predicted by Akgerman-Gainer equation $\times 10^5$ cm²/s
H_2	Water	10	4.34-4.6	4.59	4.07
		25	4.8-7.07	5.24	6.24
		60	13.1	12.44	13.5
He	Water	20	6.84-8.95	7.08	6.78
		25	6.3-9.5	8.09	7.78
		40	8.8	11.6	11.09
		60	14.9	17.2	16.54
H_2	CCl_4	25	9.75	8.5	11.69
Ne	Water	20	3	3.48	2.7
		40	5.39	5.86	4.3
		60	8.08	8.7	6.3
H_2	*n*-hexane	25.4	16.36-62.8	30.1	17.2
H_2	Cyclohexane	25.4	7.08-22.4	9	8.3
H_2	Ethanol	20	15.1	5.55	5.0
H_2	Methanol	20	16.5	10	7.92
H_2	*n*-propanol	25	11.9-12.84	3.71	4.4
H_2	*i*-butanol	20	7.9	3.5	3.4

* Experimental values are as compiled by Sovova (1975), where more than one value is available the range of values is shown.

This equation gives reasonable predictions for both gas-liquid and liquid-liquid systems. The above form of the equation is not applicable to gases like hydrogen and helium owing to quantum effects (Nakanishi et al., 1965). It is the purpose of this note to extend the above equation to quantum gases also.

It is known (Ferrell and Himmelblau, 1967) that quantum effects in diffusion are related to the square of de Boer's quantum mechanical parameter Λ^*, defined as

$$\Lambda^* = \frac{h}{\sigma (m\epsilon)^{1/2}} \tag{2}$$

This dimensionless parameter Λ^* was devised by de Boer and co-workers (de Boer and Bird, 1964) as a measure of the quantum effects in gases and liquids.

In Table 1, the product of diffusion coefficient, D, and square of solute molecular diameter σ is shown for different gases in CCl_4, $(C_4F_9)_3N$, and water at 20°C. The quantum parameter for each gas is also listed. To relate the quantum parameter to the diffusion coefficient, we have chosen argon as a reference gas since it has a small quantum parameter. Alongside the values of $D\sigma^2$ are shown the relative values compared to argon, that is, $D\sigma^2/D\sigma^2$ for argon. It can be seen that this ratio is a constant for a given solute gas. In Figure 1 this ratio is plotted against the parameter $(1 + \Lambda^{*2})$. From this figure it can be seen that diffusion coefficients are directly related to $(1 + \Lambda^{*2})^{0.5}$. This, then, gives an indication of the magnitude of quantum effects. For example, hydrogen diffuses twice as fast as any similar sized molecules.

Thus, Equation (1) is modified to

$$D_{AB} = 0.088 \frac{V_B^{*4/3}}{N^{2/3}} \frac{RT}{\mu V_o} \frac{(1 + \Lambda^{*2})^{1/2}}{V_A^{*2/3}} \tag{3}$$

Table 2 compares the predictions of Equation (3) with experimental data and the Akgerman-Gainer equation. This equation has been found more suitable than other equations (Akgerman and Gainer, 1972). It is seen that both equations give very similar predictions.

The Akgerman-Gainer equation uses molar volumes of the solute at their normal boiling point. The molar volume is computed in an additive fashion from individual atoms. These values differ considerably (Sovova, 1976). Equation (3) uses critical molar volumes and is more convenient to use.

The scatter in experimental data is rather large. Owing to its low solubility, the measurement of diffusivity of hydrogen is difficult. Some experimental data carry considerable error as seen from the values for cyclohexane and n-hexane. More accurate diffusion data are needed to test these theories of the liquid state. Perhaps the only way to choose among the available equations is to compare their predictions over a wide range of temperatures. Such data are, at present, unavailable.

NOTATION

D = diffusion coefficient
h = Planck's constant
m = molecular mass
N = Avogadro number
R = universal gas constant
T = temperature
V^* = critical molal volume
V_o = intrinsic molal volume = $0.31\ V_B^*$
ϵ = force constant
Λ^* = de Boer quantum parameter
μ = solvent viscosity
σ = force constant in Lennard-Jones 6-12 potential

Subscripts

A = solute
B = solvent

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Analytical Model Reduction of Large Scale Linear Dynamic Systems

A class of dynamic model approximation techniques based on a frequency domain Taylor series expansion is presented. These methods yield low-order models and are analytical rather than computational in nature; that is, one can retain important parameters (which may be time varying) from the original model in functional form in the low-order model. This feature is very attractive for on-line updating of the simplified model and subsequent control of the process. An example for a tenth-order original model has shown that the analytical low-order models provide excellent approximations to the step response of the original system.

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The physical models for reaction, separation, and heat exchange processes exhibit a rather strong dependence upon parameters which may vary during operation. For example, variations in flow rate influence the residence time of the above processes and thus have a significant effect on the system dynamics. High performance control

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