

where  $g(\xi)$  is a weak function of  $\xi$ , and  $g(1) \rightarrow 1$ . Combining (8) and (9), we find a relation between drawing rate and viscosity

$$\frac{V}{\nu} R \frac{f(\xi)}{(\xi - 1)} \geq 1 \quad (11)$$

where  $\xi$  and  $T$  are related through (10).

We may state the following conclusions.

1. Deryaguin's method for computing the maximum film thickness has been confirmed.

2. In both open-bath and die coating, the growth rate of a disturbance decreases with increased pulling speed at a fixed thickness. For any given pulling speed, open-bath coating is relatively more unstable than die coating.

3. There is apparently an optimum coating speed in open-bath coating.

4. In die coating, the onset of waves is dependent mainly upon coating viscosity. In open-bath drawing, the criterion is the ratio of drawing speed to viscosity. Increases in  $V$  or decreases in  $\nu$  lead to wave inception.

There is a great need for experiments to substantiate these predictions.

#### NOTATION

$c$	= wave or shock speed, dimensionless
$Ca$	= capillary number
$g$	= acceleration of gravity, m/s <sup>2</sup>
$Go$	= Goucher number
$h$	= radial location of film surface, m
$Q$	= volumetric flux, dimensionless
$R$	= cylinder radius, m
$Re$	= Reynolds number
$Re'$	= modified Reynolds number
$T$	= inverse pulling speed, dimensionless
$u$	= velocity, dimensionless
$V$	= cylinder velocity, m/s
$z$	= axial distance, dimensionless

#### Greek Letters

$\alpha$	= wave number, dimensionless
$\eta$	= wave amplitude, dimensionless
$\mu$	= fluid viscosity, N/s m <sup>2</sup>
$\nu$	= kinematic viscosity, m <sup>2</sup> /s
$\rho$	= fluid density, kg/m <sup>3</sup>
$\sigma$	= surface tension, N/m
$\xi$	= radial location of film surface, dimensionless

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## Predicting Diffusion Coefficients

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Lynch (1974) showed that most available correlations for predicting diffusion coefficients underestimate the magnitude. It is clear that there is a need for a simple expression which can predict gas-liquid diffusivities with confidence.

Hildebrand (1971), following the work of Batschinski (1913), has shown that liquid molal expansion is, in reality, very small, and therefore conventional theories for the liquid state are likely to be unrealistic. When applied to diffusivity, this means that there is little basis for using an Arrhenius type of relationship for the temperature dependence of diffusion coefficients, especially at lower temperatures.

In this note we use this concept of Hildebrand to arrive

at an equation for gas liquid diffusivities. Following Hildebrand, we write

$$D_{AB} = D_{BB} \left( \frac{V_B^*}{V_A^*} \right)^{2/3} \quad (1)$$

where  $D_{BB}$  is the solvent self-diffusion coefficient, and  $V_B^*$  and  $V_A^*$  are the critical molal volumes for solvent and solute, respectively.

Dullien (1972), using the effective molecular diameters in liquids, has developed an equation for predicting self-diffusion coefficients in liquids:

$$D_{BB} = 0.088 \left( \frac{V_B^*}{N} \right)^{2/3} \frac{RT}{\mu V_B} \quad (2)$$

TABLE 1. GAS-LIQUID SYSTEMS

System	Temperature, °C	Experimental,* $\frac{\text{cm}^2}{\text{s}} \times 10^5$	Predicted by equation (5), $\frac{\text{cm}^2}{\text{s}} \times 10^5$	Predicted by Akgerman-Gainer, $\frac{\text{cm}^2}{\text{s}} \times 10^5$
CO <sub>2</sub> -water	20	1.62-1.77	1.8	1.79
	25	1.85-1.98	2.05	2.03
	40	2.75-2.8	2.94	2.83
O <sub>2</sub> -water	20	2.01-2.3	2.1	2.11
	25	2.07-2.6	2.4	2.4
	40	3.33-3.8	3.44	3.36
N <sub>2</sub> -water	60	5.7	5.1	4.95
	20	1.66-2.6	1.85	2.11
	25	1.8-2.25	2.11	2.37
Ne-water	40	2.83-4.3	3.02	3.4
	60	6.5	4.5	4.94
Cl <sub>2</sub> -water	20	3.0	3.08	2.7
	40	5.39	5.05	4.3
	60	8.08	7.49	6.3
CO-water	20	1.22	1.49	1.4
	25	1.4-1.51	1.7	1.6
	40	2.03	1.81	2.11
SO <sub>2</sub> -water	40	3.62	2.96	3.4
	60	5.68	4.39	5.0
	20	1.4-1.66	1.51	1.48
CO <sub>2</sub> -ethanol	25	1.83-2.04	1.72	1.69
	40	2.59	2.47	2.38
	6.4	2.45	1.59	1.22
N <sub>2</sub> -benzene	25	3.42	2.45	1.81
O <sub>2</sub> -cyclohexane	25	6.93	5.38	3.74
Methane-carbon tetrachloride	29.6	5.31	4.74	3.88
	25	2.89	3.31	5.89

\* Experimental values are as listed by Akgerman-Gainer (1972b). Where more than one experimental value is available, the range is shown.

Using Equation (2) in Equation (1), we get

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

Equation (3) should predict gas-liquid diffusion coefficients in systems where the molal volume expansion with temperature is negligible. For other systems, a correction factor would be necessary. Such a correction factor is the

ratio of molal volume  $V_B$  at any temperature to the intrinsic volume  $V_o$ . This correction factor is chosen in the simplest possible form, but theoretical justification for this form is lacking. It reflects the decrease in attractive potential with expansion and the consequent enhancement of diffusivity (Hildebrand and Lamoreaux, 1974). The intrinsic volume  $V_o$  is related to the critical molal volume (Hildebrand, 1971):

TABLE 2. LIQUID-LIQUID SYSTEMS

Solute	Solvent	Temperature, °C	Experimental* $\times 10^5 \text{ cm}^2/\text{s}$	Equation (5) $\times 10^5 \text{ cm}^2/\text{s}$	Wilke-Chang equation $\times 10^5 \text{ cm}^2/\text{s}$
Hexane	Benzene	15	1.78	1.71	1.42
Methanol	Water	15	1.28	1.27	1.36
Methanol	CCl <sub>4</sub>	25	2.61	2.97	3.2
Ethanol	CCl <sub>4</sub>	25	1.95	2.36	2.54
Acetone	CCl <sub>4</sub>	25	1.7	2.02	2.23
Benzene	CCl <sub>4</sub>	25	1.54	1.76	1.96
Cyclohexane	Hexane	25	3.77	5.3	3.98
Decane	Hexane	25	3.02	3.39	2.68
2-methylbutane	Hexane	25	4.4	5.3	3.98
Phenol	CCl <sub>4</sub>	25	1.37	1.74	1.82
Pentane	CCl <sub>4</sub>	25	1.57	1.56	1.73
Benzene	Hexane	25	4.64	5.94	4.49
2-methylbutane	CCl <sub>4</sub>	25	1.49	1.57	1.73
Toluene	CCl <sub>4</sub>	25	1.4	1.54	1.74
Cyclohexane	CCl <sub>4</sub>	25	1.27	1.57	1.73
Eicosane	CCl <sub>4</sub>	25	0.664	0.634	0.78
Decane	CCl <sub>4</sub>	25	1.09	1.0	1.16

\* Experimental values are as listed by Hayduk and Buckley (1972).

$$V_o = 0.31 V_B^* \quad (4)$$

If the equation for diffusion coefficient is multiplied by  $V_B/V_o$ , then

$$D_{AB} = 0.088 \frac{V_B^{*4/3}}{N^{2/3}} \frac{RT}{\mu V_o} \frac{1}{V_A^{*2/3}} \quad (5)$$

Akgerman and Gainer (1972a) have proposed a correlation for diffusion coefficients using absolute rate theory. This equation contains an exponential temperature dependence of the Arrhenius type. Akgerman and Gainer (1972b) compared this equation with that of Wilke-Chang (1955) and other available correlations and claimed that in most cases their (Akgerman-Gainer) correlation gives better predictions than all other correlations. In Table 1, Equation (5) is compared with experimental data and the Akgerman-Gainer correlation. It is clear that Equation (5) predicts diffusion coefficients with reasonable accuracy. This is especially true with solvents like cyclohexane and benzene, where there is quite significant increase in molal volume as the temperature increases. It should be noted that Equation (5) is much simpler to use than the Akgerman-Gainer equation. It should also be mentioned that Equation (5) should not be used for gases like hydrogen and helium (Hildebrand, 1971).

Equation (5) has also been tested on liquid-liquid systems, and the predictions are shown in Table 2. Unfortunately, the Akgerman-Gainer correlation is not very suitable for liquid-liquid systems (Akgerman-Gainer, 1972a); hence, comparison is made with the Wilke-Chang correlation which gives better predictions for liquid-liquid systems. The predictions are of reasonable accuracy. Hence, Equation (5) can be used for both gas-liquid and liquid-liquid systems.

The aim of the present work has been to derive an equation for predicting diffusion coefficients. It is preferable to use experimental values of viscosity rather than trying to correlate viscosity to molal volumes through the Batschinski equation. The derived equation is reasonably successful at lower temperatures. It is quite possible that at higher temperatures this simplified approach may not be entirely correct and that contributions from an entirely different mechanism may become important. Ertl and Dullien (1973) show that diffusion depends to a greater extent than viscous flow on volume expansion. The work of Gotoh (1976) on free volumes in liquids shows that the pore dimensions in water are less than the solute molecular diameter. In such cases, an activation energy concept may

be necessary. This is entirely speculative, and further experimental work, especially at higher pressures and temperatures, is necessary to delineate these mechanisms.

## NOTATION

$D$	= diffusion coefficient
$N$	= Avagadro number
$R$	= universal gas constant
$T$	= temperature
$V$	= molal volume

## Greek Letters

$\mu$	= viscosity
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## Subscripts

$A$	= solute
$B$	= solvent
$o$	= intrinsic value

## Superscript

$*$	= critical property
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# Adsorption Rates of Oxygen in Aqueous Slurries of Activated Carbon

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A method has recently been developed (Niiyama and Smith, 1976) for evaluating mass transfer and adsorption rates in three-phase slurry reactors by analyzing breakthrough curves in the effluent gas stream. Since slurry systems have been proposed for removing pollutants by oxidation with gaseous oxygen, and since the rate of oxygen adsorption can significantly influence the rate of oxidation (Komiya and Smith, 1975), we have used the new

method to determine mass transport and intrinsic adsorption rate parameters for oxygen in aqueous slurries of carbon particles. The same apparatus and experimental techniques were employed as used in the earlier work, where the theory was developed and applied to data for adsorption of nitric oxide in carbon slurries. Hence, this note emphasizes only the results, which show that bubble-to-liquid mass transfer, intraparticle diffusion, and intrinsic adsorption at an interior site can all affect the overall ad-

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