ments, the heat of formation of thorium dioxide, and an estimated uncertainty for the correction for the impurities. The value given here for ThC agrees with that of Aronson (1). This work agrees with Westrum's second law calculation for $\mathrm{ThC}_{1.93}$ (*12*). The thorium carbides are somewhat more stable than the corresponding uranium carbides [$\Delta H_f^\circ {}_{298^\circ}(\mathrm{UC}_{1.00}) = -23.2 \pm 0.7$ kcal. per mole; $\Delta H_f^\circ {}_{298^\circ}(\mathrm{UC}_{1.93}) = -20.5$ kcal. per mole] (*3*).

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Diffusion Coefficient of Ethylene Gas in Water

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Data on ethylene diffusivity obtained by absorbing the gas in a laminar jet of pure water at temperatures of 20°, 25°, and 30° C. are presented and compared with those quoted in the literature. The experimentally determined diffusion coefficients are consistent with results already reported. Various correlations describing the variation of diffusivity with temperature are reviewed and a convenient means of correlating ethylene gas diffusivity with temperature is presented.

As part of an investigation into the reactions of ethylene gas with aqueous solutions of bromine, measurements were made of the diffusivity of the gas in water. The values of the diffusion coefficient, determined from a laminar jet absorber, were compared with data quoted in the literature and a certain amount of discrepancy was found between the various sources (*2, 5, 6, 23*). The purpose of this paper is to present the available data, to examine them critically, and to put forward a convenient correlation for estimating diffusion coefficients over a range of temperature from 20° to 30° C.

The background of diffusion or molecular transport has been discussed in detail by Longwell and Sage (*15*) and need not be reviewed here. It is desirable for practical purposes to define the proportionality constant between the flux density of the diffusing species and the gradient of the appropriate potential. Coefficients based on concentration gradient are now almost universally employed for both gas and liquid system. Diffusion in a binary system, like ethylene-water, is described by the mutual diffusion coefficient, often called the Chapman-Cowling coefficient (*4*), of the binary system.

THEORY

Absorption of gas by a liquid jet was used to measure the diffusivities of ethylene in pure water at various temperatures and at atmospheric pressure. Absorption into the jet may be analyzed using the "penetration theory" provided that the gas molecules penetrate only a short distance into the jet in comparison with its radius, and the velocity across the jet is uniform. The first condition is satisfied in the normal range of contact times and the flow pattern of the jet is very nearly, but not exactly, uniform. This is due to: frictional drag exerted by the inside surface of the nozzle, causing the velocity to be reduced in the boundary layer near the surface; drag of the surrounding gas on the surface; acceleration of the fluid motion due to gravity; and occurrence of ripples together with a stagnant surface at the receiver, where the jet terminates.

The drag of the surrounding gas on the jet surface and the receiver end effects are small and may be neglected; the nozzle drag and gravity effects have been studied in detail by Scriven (*20*) and Beek (*3*).

The diffusion equation and the boundary conditions describing the absorption process are:

$$U \frac{\partial c}{\partial x} + V \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \tag{1}$$

$$c(o, y) = c(x, \infty) = c_i,\; c(x, o) = c_e \tag{2}$$

For a jet in which the velocity throughout is constant, and equal to U_{av}, the instantaneous absorption rate is given by:

$$n^* = (c_e - c_i) \left[\frac{D\, U_{\mathrm{av}}}{x}\right]^{1/2} \tag{3}$$

In an actual jet the instantaneous absorption flux is:

$$n = n^* \, (1 + \Delta) \tag{4}$$

where Δ is a correction factor which takes into account the combined effect of the sources of error discussed above and evaluated by Scriven (*20*). The total absorption rate, N, is obtained by integrating over the entire jet length (*20*),

$$N = \int_0^h n\pi d \, dx$$

$$= (c_e - c_i) \, (\pi D)^{1/2} \int_0^h (1 + \Delta) \left[\frac{U_{\mathrm{av}}}{x} \right]^{1/2} d \, dx \tag{5}$$

EXPERIMENTAL

The apparatus consisted of an absorption chamber, a jet nozzle and receiver, liquid and gas feed systems, constant temperature bath, and a constant head water reservoir. The jet nozzle, jet receiver, and absorption chamber were similar to those used by Scriven and Pigford (*21*). The absorption runs were made with jet lengths varying from 2 to 15.5 cm. and at liquid flow rates varying from 10 to 12 cc. per second. The jet issued from a Perspex nozzle 1.992 mm. I.D. and terminated in a glass capillary receiver 2.02 mm. I.D. Between the nozzle and the receiver, the jet surface was exposed to an atmosphere of solute gas confined within a Perspex chamber. It was possible to collect the entire jet in the receiver for prolonged periods of operation with no entrainment or splashing by carefully aligning the nozzle and the receiver and adjusting the resistance to flow downstream of the receiver. Strong vibrations were eliminated. The solvent liquid passed from the constant-head tank into the absorption chamber via a glass capillary resistance. The ethylene gas, supplied from a cylinder and reducing valve to a water saturator, flowed to the chamber first through a glass capillary resistance to damp out pressure fluctuations caused by bubbling and then through a soap film flowmeter. The flowmeter was a modified buret; at the low flow rates encountered (1 to 2 cc. per minute) this flowmeter combined high accuracy with a low pressure drop. The absorption chamber, 5.72 cm. in diameter and 25.4 cm. in length was placed in a constant temperature water jacket.

Jet length and diameter were measured by a cathetometer with an accuracy of 0.005 cm. Liquid flow rate was measured by collecting a measured volume of liquid in a timed interval. The accuracy in measuring liquid and gas flow rates was 0.02 and 0.01 cc., respectively. Temperatures of the liquid entering and of gas entering the jet chamber were measured to an accuracy of 0.01° C.

RESULTS AND DISCUSSION

The diffusion coefficient, D, was obtained from a linear form of Equation 5 by linear regression. The c_e values can be calculated from the Henry's law constant H. Since errors in the solubility can be more significant than errors in the diffusion data (an error of 1% in the value of equilibrium concentration causes an error of about 2% in the diffusion coefficient), very accurate solubility data are needed to get accurate values of D. The solubility of ethylene gas in aqueous solutions, based on Ramm's data given in Hobler (*12*) used in this investigation, is: 5.24×10^{-6} gram mole per. cc. at 20° C., 4.66×10^{-6} at 25° C., and 4.20×10^{-6} at 30° C.

The data in Table I give experimentally determined absorption rates at a constant liquid rate of 12.52 cc. per second for a series of experiments at 25° C. and 1 atm. The agreement of replicate measurements is, with few exceptions, excellent. The absorption rates can be correlated with the jet length by a straight line with a slope proportional to $(D)^{1/2}$. The line is displaced from the origin. The displacement parallel to, and below, the line for an ideal jet is due to the nonideal behavior of the jet and can be corrected for by Equation 5, in which the correction term Δ, allowing for boundary layer and gravitational corrections, has been evaluated by the method of Scriven (*20*). These methods require that the thickness of the boundary layer in the jet emerging from the nozzle be known; in this investigation, it was estimated from measurements of the profile of the liquid jet actually employed. The magnitude of correction factor Δ is given in Table II.

Values of the diffusion coefficient, with 95% confidence limits, are given in Table III with other quoted values.

Table I. Ethylene Gas Absorption into Water at 25° C., 12.52 Cc./Sec. and 1 Atm.

Jet Length, h, Cm.	Absorption Rate, $N \times 10^7$, Gram Mole/Sec.
2.50	3.18
3.50	3.89
4.00	4.22
5.00	4.83
6.00	5.40
7.00	5.91
8.10	6.37
9.00	6.79
10.00	7.19
15.00	9.22

Table II. Correction Factor, Δ, for Nonideal Jet

Flow, Gram Cc./Sec.	Distance, x, Cm.	Δ	Boundary Layer Thickness, δ, Cm.
12.52	7.0	0.0038	0.0070
	8.0	0.0084	
	9.0	0.0128	
	10.0	0.0172	
	15.5	0.0399	
10.42	6.0	−0.0004	0.0082
	7.0	0.0061	
	10.0	0.0245	
	13.0	0.0417	
	15.5	0.0550	

Table III. Experimental Diffusion Coefficient of Ethylene Gas into Water

Investigator	Date	Method	$D \times 10^5$ Sq. Cm. Sec.$^{-1}$ 20° C.	25° C.	30° C.
Baird and Davidson (*2*)	1962	Annular jet	1.32	1.59	. . .
Baird and Davidson (*2*)	1962	Wetted sphere	1.68	2.00	. . .
Dun (*5*)	1964	Wetted wall	1.36 ± 0.05	1.50 ± 0.30	1.76 ± 0.05
Dun and Wood (*6*)	1966	column			
Unver and Himmelblau (*23*)	1964	Laminar jet	0.88	1.09	1.23
This investigation			1.41 ± 0.07	1.51 ± 0.36	1.78 ± 0.71

The experimentally determined diffusion coefficient of ethylene into water at 20°, 25°, and 30° C. agree closely with those determined by Baird and Davidson (*2*) in the annular jet apparatus, and by Dun (*5*) and Dun and Wood (*6*) in a wetted wall column. The diffusivities obtained by Baird and Davidson in an experiment with a wetted sphere absorber are higher than the others, while those reported by Unver and Himmelblau (*23*) in a laminar jet absorber are far below the experimental results of this investigation and the results reported by other authors. Baird and Davidson concluded that the annular jet determinations were in error, owing to a hydrodynamic entry effect, such as has been taken into account herein, and to a small interfacial resistance which would otherwise be negligible for the wetted sphere absorber. The above comparison is in contradiction to their conclusion. The exceedingly low diffusivity of Unver and Himmelblau is very hard to explain.

Several semiempirical methods have been proposed to predict diffusivities as a function of temperature. Table IV gives values of the diffusion coefficient as determined

Table IV. Predicted Diffusion Coefficient of Ethylene Gas into Water as Determined by Different Correlations

	$D \times 10^5$ Sq. Cm. Sec.$^{-1}$		
Correlation	20° C.	25° C.	30° C.
Einstein (*7*)	1.03	1.17	1.33
Eyring (*8*)	12.81	14.65	16.63
Ferrell and Himmelblau (*10, 11*)	1.45	1.65	1.87
Houghton (*13*)	2.16	2.47	2.80
Longuet-Higgins and Pople (*14*)	1.39	1.58	1.80
Othmer and Thakar (*17*)	1.34	1.53	1.72
Ree, Ree and Eyring (*18*)	2.17	2.48	2.81
Unver and Himmelblau (*23*)	0.93	1.07	1.21
Wilke and Chang (*24*)	1.42	1.63	1.85
This investigation : experimental	1.41 ± 0.07	1.51 ± 0.36	1.78 ± 0.71
Equation 6	1.41	1.53	1.76

Table V. Theoretical Correlations and Physical Parameters used to Predict Diffusion Coefficients given in Table IV

Name	Symbol	Relation	Parameter and Value	Ref.
Einstein (*7*)	D_{E_I}	$= \frac{KT}{6\pi a\mu}$ (*7*)	$a = 2.0815 \times 10^{-8}$	(*22*)
Eyring (*8*)	D_{E_Y}	$= \frac{KT}{\mu}\,\frac{\lambda_1}{\lambda_2\lambda_3}$ (*8*)	$\frac{\lambda_1}{\lambda_2\lambda_3} = \left(\frac{No}{V}\right)^{1/3}$ (*9*)	(*9*)
			$V = 18.7$	(*19*)
Ferrell and Himmelblau (*10, 11*)	D_F	$= \frac{4.8 \times 10^{-7}}{\mu^{\alpha}}\left[\frac{1+\lambda^{*2}}{V_m}\right]^{0.6}$ (*10*)	$\alpha = \sigma\frac{N}{V_m}^{1/3}$ (*11*)	(*10, 11*)
			$\lambda^* = \frac{K}{\sigma(m\epsilon)^{1/2}}$ (*12*)	(*10, 11*)
			$\sigma = 4.163 \times 10^{-8}$	(*22*)
			$\epsilon = 3.10193 \times 10^{-14}$	(*22*)
Houghton (*13*)	D_H	$= \frac{No\rho\beta^2KT}{24M\mu}$ (*13*)	$\beta = 3\left(\frac{V'}{No}\right)^{1/3}$ (*14*)	(*25*)
			$V' = M/\rho$ (*15*)	(*25*)
Longuet-Higgins and Pople (*14*)	D_P	$= \frac{3bKT}{10\pi a\mu}$ (*16*)	$b = 0.75$	(*16*)
			$a = 2.085 \times 10^{-8}$	(*22*)
Othmer and Thaker (*17*)	D_o	$= \frac{14.0 \times 10^{-5}}{\mu^{1.1}\,V_m^{0.6}}$ (*17*)	$V_m = 49.4$	(*19*)
Ree, Ree, and Eyring (*18*)	D_R	$= \frac{1}{6}\left(\frac{N}{(2)^{1/2}V_s}\right)^{1/3}\frac{KT}{\mu}$ (*18*)	$V_s = 1.6\ Vo$ (*19*)	(*1*)
			$V_o = \frac{No\ dm^3}{(2)^{1/2}}$ (*20*)	(*1*)
			$d_m = 2.6554 \times 10^{-8}$	(*22*)
Unver and Himmelblau (*23*)	D_U	$= (A + Bt + Ct^2)\ 10^{-5}$ (*21*)	$A = 0.53815$	(*23*)
			$B = 1.4781 \times 10^{-2}$	(*23*)
			$C = 2.5657 \times 10^{-4}$	(*23*)
Wilkie and Chang (*24*)	D_W	$= \frac{7.4 \times 10^{-8}\,(2.6M)^{1/2}\,T}{\mu\,V_m^{0.6}}$ (*22*)	$V_m = 49.4$	(*19*)

by different correlations. Table V lists the correlations and the physical parameters employed in the various equations. The Einstein equation (*7*) yields diffusivities which are about 40% less than the experimental diffusivities but do exhibit the experimentally observed inverse variation of diffusivities with solute molecule size (*25*). The diffusivities of Longuet-Higgins and Pople (*14*) are 30% higher than those of Einstein and give better agreement with the experimental diffusion coefficients while still providing an inverse proportionality between diffusivity and solute molecule size (*25*). Eyring's equation (*8*) predicts diffusivities which are about 10 times those found experimentally and so cannot be taken to give reasonably accurate predication of the variation of diffusion coefficient with temperatures. Similar comments may be made of diffusivities predicted by Ree, Ree, and Eyring (*18*) and Houghton (*13*), which are almost double the experimental values, although solute diffusion is simulated by self-diffusion in these models, so that there can be no influence of solute molecule size. Unver and Himmelblau's theory gives diffusivities much less than those determined experimentally. The Wilke-Chang (*24*), the Othmer-Thaker (*17*), and the Ferrell-Himmelblau (*10, 11*) correlations appear to represent more closely the over-all experimental results for ethylene gas diffusion in water than any other proposed methods within acceptable limits of their accuracy (*19*).

CONCLUSION

Diffusion coefficients of ethylene gas in water can be correlated with temperature over a range of temperatures from 20° to 30° C. in the form of a quadratic equation by the method of least squares as follows:

$$D = (2.26428 \times 10^{-3} t^2 - 7.8 \times 10^{-2} t + 2.0628) \times 10^{-5} \qquad (6)$$

Diffusivities calculated with this equation are all within ± 10% of the known experimental values.

NOMENCLATURE

A = empirical constant in Equation 21, sq. cm. sec.$^{-1}$
a = molecular radius, cm.
B = empirical constant in Equation 21, sq. cm. sec.$^{-1}$ °C.$^{-1}$
b = volume fraction occupied by molecules, dimensionless
C = empirical constant in Equation 21, sq. cm. sec.$^{-1}$ °C.$^{-2}$
c = concentration of gas in liquid, g. mole cc.$^{-1}$
D = diffusion coefficient, sq. cm. sec.$^{-1}$
d = jet diameter, cm.
d_m = molecular diameter, cm.
H = Henry's law constant, mm. of Hg
h = length of jet, cm.
K = Boltmann's constant, 1.38048×10^{-16} erg °K.$^{-1}$
M = molecular weight of solvent
m = mass of molecule
N = total absorption rate, g. mole sec.$^{-1}$
N_o = Avogadro's number 6.02×10^{23} molecules mole^{-1}
n = instantaneous rate of absorption, g. mole (sq. cm.)$^{-1}$ sec.$^{-1}$
q = liquid flow rate, cc. sec.$^{-1}$
T = absolute temperature, °K.
t = temperature, °C.
U = axial component of velocity, cm. sec.$^{-1}$
V = radial component of velocity, cm. sec.$^{-1}$
v = molecular volume, cc. mole^{-1}
x = axial coordinate
y = radial coordinate

Subscripts

Ei = Einstein
Ey = Eyring
F = Ferrell-Himmelblau
H = Houghton
O = Othmer-Thakar
P = Longuet-Higgins-Pople
R = Ree-Ree-Eyring
U = Unver-Himmelblau
W = Wilke-Chang
e = equilibrium
i = initial
m = solute at its normal boiling point
o = closest packed solvent molecule at the melting point
S = solvent at the melting point

Superscripts

$'$ = solvent at the normal boiling point
$*$ = jet with uniform velocity throughout

Greek Letters

α = exponent in Equation 10, defined by Equation 11, dimensionless
β = dimension of cubic multi-molecular lattice or cell, cm.
Δ = departure from ideal jet, dimensionless
δ = boundary layer thickness, cm.
λ^* = quantum parameter of solute, defined by Equation 12, dimensionles
$\lambda_1,\lambda_2,\lambda_3$ = dimensions of single molecule cell, cm.
μ = solvent viscosity, poise
π = numerical constant 3.14159265
ρ = solvent density, g. cc.$^{-1}$
ϵ,σ = force constants based on Lennard-Jones 6–12 potential

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