Diffusivities of Slightly Soluble Gases in Water

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Reliable knowledge of the diffusivities of various slightly soluble gases in water is required for investigations of the mechanism of gas-liquid mass transfer in liquid phase controlled systems. Several publications have appeared recently which report measurements of such diffusivities (*2*, *3*, *6*, *7*). It is the purpose of this communication to report a set of values obtained under different circumstances and to endeavor to resolve differences between the various published results.

The diaphragm cell technique was employed to measure the diffusivities of helium, hydrogen, oxygen, carbon dioxide, and propylene in water solution at 25°C. The cells were suspended in a constant temperature bath. No mixing other than natural convection was employed within the cells, but the absence of any significant effect due to incomplete mixing was confirmed by noting the lack of any change in the measured rates of diffusion when vibration was transmitted to a cell throughout a run. The bath temperature varied cyclically over a range of 0.2°C.; this was sufficient to generate natural convection currents within either side of the cell but caused no significant thermal pumping within the diaphragm itself.

The cells were calibrated before and after use with potassium chloride solutions. Oxygen analyses were made by the Winkler technique, and carbon dioxide analyses by the standard titration with barium hydroxide. Helium, hydrogen, and propylene analyses were performed by separating the dissolved gas from a water sample in a vacuum spray device and then injecting the extracted gas into a gas chromatograph.

The results of the measurements are presented in Table 1, along with an indication of the reproducibility. Further details of the experimental technique, analytical procedures, and individual results are available elsewhere (*9*, *12*).

The results for oxygen and carbon dioxide agree well with those of other investigators, and there have been no previous measurements reported for propylene in water. On the other hand there are discrepancies between previous reported diffusivities for helium and hydrogen, and these two are of great interest for mass transfer mechanism studies. Table 2 compares the present data with the results of others. Measurements not taken at 25°C. have been corrected to 25°C. by holding the group $\left(\frac{D\mu}{T}\right)$ constant, as is suggested by various theories. Several scattering earlier values for hydrogen are omitted, as is a value of 10.37×10^{-3} for helium at 25°C. reported by Smith, et al. (*10*) and considered by them to be highly improbable.

The measurements of Houghton et al. (*7*) were made by observing the rates of dissolution of small stationary bubbles within stagnant water, a method which should give a transfer coefficient varying with the first power of diffusivity. The measurements of Baird and Davidson (*2*) and of Davidson and Cullen (*3*) were made by observing the rate of pickup of solute gas by water flowing over a sphere, a method which should give a transfer coefficient varying with the one-half power of diffusivity. In theory neither of these methods requires calibration, but both methods do rely upon accurate knowledge of the solubility of the gas in water and upon one's ability to correct for the effect of the wall on bubble dissolution or for end effects or rippling in the flow over a sphere. The wetted sphere methods have involved the metering of very small flow rates of the solute gases, and, as Baird and Davidson point out (*2*), extraneous factors, such as aberrations of the temperature within the gas space, can affect the apparent flow rates. Leakage would also be important. These problems would be most serious for the least soluble gases, and examination of the results of Davidson and Cullen and of Baird and Davidson reveals

Table 1. Diffusivities of Slightly Soluble Gases in Water at 25°C.

Gas	Number of measurements*	Median diffusivity $\times 10^5$ (sq. cm./sec.)	Standard deviation
Helium	9	6.3	10%
Hydrogen	4	4.8	4%
Oxygen	7	2.41	3%
Carbon dioxide	4	2.00	3.5%
Propylene	5	1.44	5%

* Measurements rejected statistically with 90% confidence are not included.

Table 2. Comparison of Reported Diffusivities of Hydrogen and Helium in Water

Method	Diffusivity $\times 10^5$ (sq. cm./sec.)	Reference
	Helium	
Diaphragm cell	6.3	Present
Dissolution of bubbles	6.3*	Houghton et al. (*7*)
Wetted sphere	9.5	Baird and Davidson (*2*)
Rising bubble	4.8	Gertz and Loeschcke (*6*)
	Hydrogen	
Diaphragm cell	4.8	Present
Dissolution of bubbles	4.9†	Houghton et al. (*7*)
Wetted sphere	5.3	Baird and Davidson (*2*)
Wetted sphere	7.0	Davidson and Cullen (*3*)
Rising bubble	4.1	Gertz and Loeschcke (*6*)
Polarography	4.1-4.8**	Aikazyan and Federova (*1*)
Layer	3.2††	Ipatieff and Teodorovich (*8*)
Gel	4.0	Tammann and Jessen (*11*)

* Corrected from 22.1°C.
† Corrected from 24.5°C.
** Corrected from 23.0°C and for viscosity alteration due to ionic content.
†† Corrected from 20°C.

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This communication to the editor introduces the article on page 221.

that the amount of deviation from the present results and those of Houghton et al. increases uniformly as the solubility of the gas decreases.

Gertz and Loeschcke (6) derived diffusivities from an experiment in which they passed water down through a downwardly divergent tube, 2.1 to 2.8 mm. in diameter and 30 cm. long. Bubbles of solute gas were introduced at the bottom of the tube and rose as dissolution took place. The rate of rise of the bubble gave a mass transfer coefficient, taken by Gertz and Loeschcke to be proportional to the first power of diffusivity. Calibration of the device was made by accepting the diffusivity given by Tammann and Jessen for hydrogen in water at 29°C.

A variation with the first power of diffusivity is unlikely in a system where there is flow around a bubble. More likely would be a variation with the 2/3 power of diffusivity, which is the case for flow of this magnitude about a solid sphere or a noncirculating bubble (5). The bubble rise time in all cases was over 30 sec., and it has been found by Deindorfer and Humphrey (4) and others recently that this should be more than time enough for cessation of circulation through accumulation of surfactant molecules or other causes. Figure 1 shows the reported diffusivities of Gertz and Loeschcke at 21°, 25°, 29°, 33°, and 37°C. plotted against the present values for helium, hydrogen, oxygen, and carbon dioxide and against the value of Houghton et al. (7) for nitrogen. The present diffusivities and that of Houghton et al. have been corrected for temperature by holding the group $(D\mu/T)$ constant. It is apparent that the reported diffusivities of Gertz and Loeschcke correlate well with the 2/3 power of the present diffusivities. There is no apparent temperature effect other than that due to diffusivity, a fact in accord with predictions (5). Thus if one of the present values is used for calibration, and laminar boundary-layer theory for flow about a noncirculating spherical bubble is used for interpretation, the results of Gertz and Loeschcke agree well with the present diffusivities and those reported by Houghton et al.

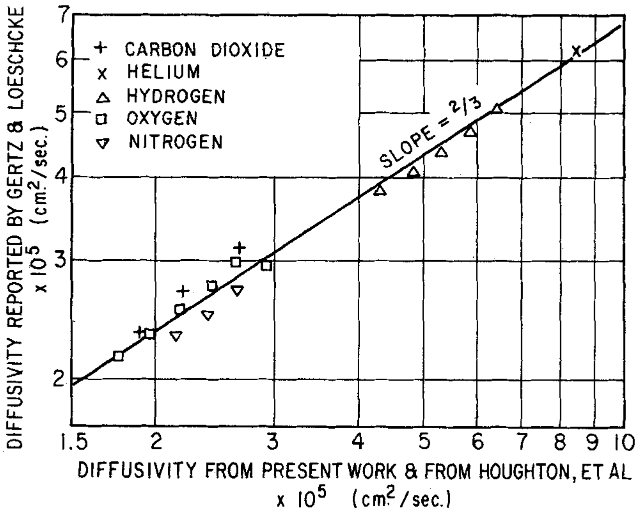

Fig. 1. Diffusivities reported by Gertz and Loeschcke (6).

LITERATURE CITED

1. Aikazyan, E. A., and A. I. Federova, *Dokl. Acad. Nauk. S.S.S.R.*, **86**, 1187 (1952).
2. Baird, M. H. I., and J. F. Davidson, *Chem. Eng. Sci.*, **17**, 473 (1962).
3. Davidson, J. F., and E. J. Cullen, *Trans. Inst. Chem. Engrs.*, **35**, 51 (1957).
4. Deindorfer, F. H., and A. E. Humphrey, *Ind. Eng. Chem.*, **53**, 755 (1961).
5. Friedlander, S. K., *A.I.Ch.E. Journal*, 7, 347 (1961).
6. Gertz, K. H., and H. H. Loeschcke, *Z. Naturforsch.*, **9b**, 1 (1954); **11b**, 61 (1956).
7. Houghton, G., P. D. Ritchie, and J. A. Thomson, *Chem. Eng. Sci.*, **17**, 221 (1962).
8. Ipatieff, V. V., and V. P. Teodorovich, *Zh. Fiz. Khim.*, **10**, 712 (1937).
9. King, C. J., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1960).
10. Smith, R. E., E. T. Friess, and M. F. Morales, *J. Phys. Chem.*, **59**, 382 (1955).
11. Tammann, G., and V. Jessen, *Z. Anorg. Allgem. Chem.*, **179**, 125 (1929).
12. Vivian, J. E., and C. J. King, *A.I.Ch.E. Journal*, **10**, p. 221 (1964).

The Mechanism of Liquid-Phase Resistance to Gas Absorption in a Packed Column

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The desorption of five sparingly soluble gases from water into air in a packed tower was studied at five different flow conditions. At 25°C. these systems represent a range of liquid-phase diffusivity from 1.4 $\times 10^{-5}$ to 6.3 $\times 10^{-5}$ sq. cm./sec. The mass transfer coefficient was found to vary as the 0.5 power of liquid-phase diffusivity in all cases. This result, obtained through the variation of diffusivity alone, is in agreement with the predictions of penetration theory and strongly suggests a penetration mechanism based on molecular processes and independent of eddy processes during a surface lifetime. A discussion of the nature of the diffusion and surface renewal process in flow over packing is included.

Packed columns for gas absorption and distillation systems continue to assume importance in chemical operations, and many investigations have been carried out to provide a basis for their design. In general these investigations have had to depend on empirical analyses in view of the complex geometries and flow patterns encountered in industrial-sized equipment and have resulted in useful correlations valid for the conditions investigated.

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This article is introduced by the communication to the editor on page 220.