partition coefficients of nonelectrolytes that have appreciable vapor pressures. With this study, the solubilities of benzene and its C_1- and C_2-substituted analogues have been determined by a single method in water and in aqueous NaCl solutions having ionic strengths μ = 0-5 mol dm^{-3}. These solubilities will be useful in estimating environmental impacts and in other industrial problems. When it is applicable, and in the absence of data needed by more sophisticated techniques, eq 2 offers a way to at least estimate the solubilities. Indeed for 1,2,3- and 1,2,4-trimethylbenzene, the solubilities estimated from eq 2 and Figure 4 are in better agreement with mean literature solubility values than are the values predicted from the extrapolation of either the molar volume, Figure 2, or molecular surface area, Figure 3, plots.

Literature Cited

(1) Keeley, D. F.; Meriwether, J. R. *J. Energy Resour. Technol.* **1988**, *110*, 177.
(2) Keeley, D. F.; Hoffpauir, M. A.; Meriwether, J. R. *J. Chem. Eng. Data* **1988**, *33*, 87.
(3) Keeley, D. F.; Meriwether, J. R. *Rev. Sci. Instrum.* **1986**, *57*, 1434.
(4) Massaldi, H. A.; King, C. J. *J. Chem. Eng. Data* **1973**, *18*, 393.
(5) Ben-Naim, A.; Wilf, J. *J. Phys. Chem.* **1980**, *84*, 583.
(6) Bohon, R. L.; Clausen, W. F. *J. Am. Chem. Soc.* **1951**, *73*, 1571.
(7) Owens, J. W.; Wasik, S. P.; Devoe, H. *J. Chem. Eng. Data* **1986**, *31*, 47.
(8) Polak, J.; Lu, B. C. Y. *Can. J. Chem.* **1973**, *51*, 4018.
(9) Sanemasa, I.; Araki, M.; Deguichi, T.; Nagai, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1054.
(10) McAuliffe, C. *J. Phys. Chem.* **1966**, *70*, 1267.
(11) Sutton, C.; Calder, J. A. *J. Chem. Eng. Data* **1975**, *20*, 320.
(12) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 5034.
(13) Price, L. C. *Am. Assoc. Pet. Geol. Bull.* **1976**, *60*, 213.
(14) Fuhner, H. *Chem. Ber.* **1924**, *57*, 510.
(15) Klevens, H. B. *J. Phys. Colloid Chem.* **1950**, *54*, 283.
(16) Morrison, T. J.; Billett, F. J. *J. Am. Chem. Soc.* **1952**, *74*, 3819.
(17) Hermann, R. B. *J. Phys. Chem.* **1972**, *76*, 2754.
(18) Tewari, Y. B.; Miller, M. M.; Wasik, S. P.; Martire, D. E. *J. Chem. Eng. Data* **1982**, *27*, 451.
(19) Langmuir, I. *Third Colloid Symposium Monograph*; Chemical Catalog Co.: New York, 1925; p 3.
(20) Amidon, G. L.; Anik, S. T. *J. Chem. Eng. Data* **1981**, *26*, 28.

Received for review April 11, 1991. Revised June 26, 1991. Accepted July 11, 1991. This work was supported by the United States Department of Energy under Contract No. DE-AS08-83NV10338.

Solubility and Diffusivity of Oxygen and Chlorine in Aqueous Hydrogen Peroxide Solutions

Gabriel Ruiz-Ibanez, Ali Bidarian, Richard A. Davis, and Orville C. Sandall*

Department of Chemical & Nuclear Engineering, University of California, Santa Barbara, California 93106

In this work the solubility and diffusion coefficients of oxygen in aqueous hydrogen peroxide solutions have been measured. The solubility of chlorine in 0.1 N HCl and 1 N KCl/0.1 N HCl solutions was measured along with the diffusivity of chlorine in aqueous hydrogen peroxide solutions. The measurements were conducted over the temperature range +20 to −10 °C. Methods are proposed to use the measurements of this work in order to predict the solubility and diffusivity of these gases in an aqueous solution of basic hydrogen peroxide.

Considerable interest has recently been shown in singlet delta oxygen [$O_2(^1\Delta_g)$], which is molecular oxygen in its lowest excited electronic state (*1*). This is mainly due to its use in the chemical oxygen-iodine laser (COIL) in which metastable $O_2(^1\Delta_g)$ pumps iodine to an electronically excited atomic state that lases as the iodine atoms release their energy (*2*). The performance of a COIL depends on the ability to produce $O_2(^1\Delta_g)$ generated from its singlet oxygen generator.

The chemical reaction between chlorine and basic hydrogen peroxide (BHP) is the most common reaction used for the production of singlet oxygen. The stoichiometry of this reaction is as follows:

$$2KOH + H_2O_2 + Cl_2 \rightarrow 2KCl + 2H_2O + O_2(^1\Delta_g) \quad (1)$$

In order to interpret kinetic studies of this reaction and for reactor design, it is necessary to have knowledge of the solubility and diffusivity of chlorine and oxygen in BHP solutions. It is the solubility of the unreacted gas in the case of Cl_2 and not the total solubility that is of interest here. It is not possible to directly measure these physicochemical properties in BHP solutions. This is due to the fact that Cl_2 reacts with fast kinetics in BHP and that these solutions are quite unstable, with H_2O_2 decomposing to H_2O and O_2. In the work reported here, we have measured O_2 and Cl_2 solubilities and diffusivities in aqueous hydrogen peroxide solutions over a range of temperatures and propose methods to extrapolate these measurements in order to predict these properties in BHP solutions.

A gas/liquid solubility apparatus which volumetrically measures the volume of gas dissolved in a known volume of liquid was used to measure the solubilities. A laminar liquid jet absorber was used to measure the diffusivity of Cl_2 and a wetted-sphere absorber was used to measure the diffusivity of O_2.

Experimental Equipment

Solubility Apparatus. This apparatus is used to measure the solubility of a gas in a liquid solution. The principle idea of the method used here is to bring a known volume of liquid into contact with a volume of gas in a closed system at constant temperature and pressure. Equilibrium is reached by agitating the liquid for some time until no change in the volume of the gas is observed. The amount of gas absorbed is measured volumetrically. This apparatus, shown in Figure 1, was modified from the original solubility apparatus described by Haimour and Sandall (*3*). The main modification for this work was the addition of a spherical volume in the mercury buret. The sphere, which has a volume of 48.2 mL, allows a larger volume of liquid sample to be injected into the equilibrium cell and thereby increases the volume of gas absorbed at equilibrium. This modification was necessary for the experiments with oxygen because of its relatively low solubility.

Figure 1 also shows a further modification of the solubility apparatus that was made for measurements using chlorine. The Cl_2 reacted with mercury and several substitute manometer fluids, such as butyl phthalate, silicon oil, Meriam red and blue oil (brominated aromatics), and aqueous hydrochloric acid solutions. The solution to this problem was to include two coils in the gas lines, as shown in Figure 1. One coil, labeled I, which initially contains air, delays the diffusion of chlorine to the

0021-9568/91/1736-0459$02.50/0 © 1991 American Chemical Society

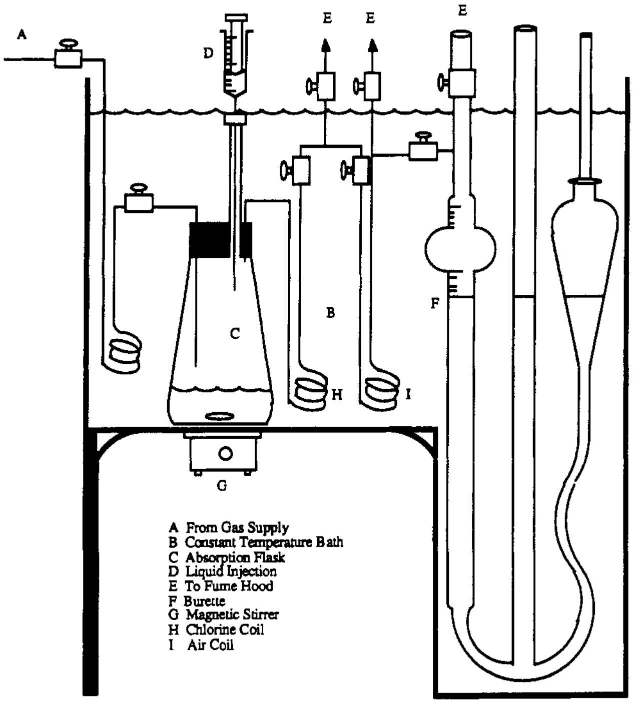

Figure 1. Modified solubility apparatus for use with chlorine.

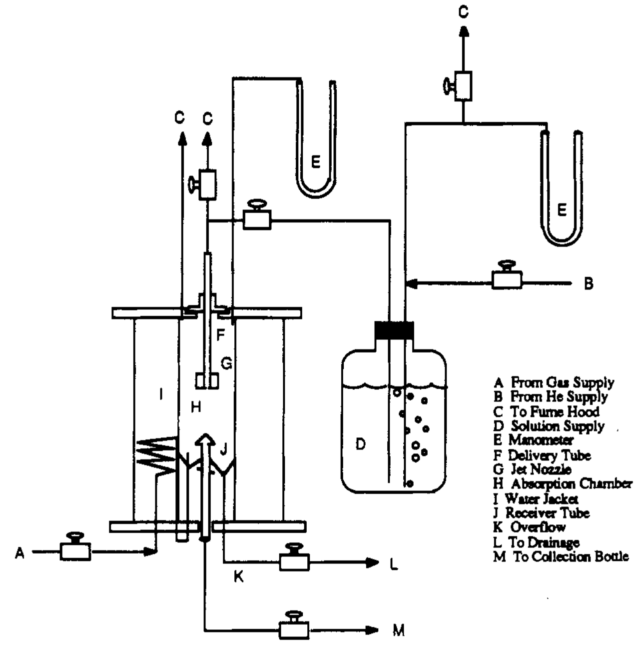

Figure 2. Laminar liquid jet absorber.

mercury in the gas buret. The other coil, labeled H, which initially contains chlorine, is to ensure that only Cl_2 is in contact with the liquid sample in the equilibrium cell.

The procedure for making a solubility measurement is as follows. A gas saturated with the vapors of the absorbing liquid is passed through the system at constant temperature long enough to completely purge the absorption flask. Then the inlet and outlet valves are closed. The heights of mercury in the three branches are leveled, ensuring that the pressure in the flask is atmospheric, and the position of the meniscus is recorded. An aliquot of degassed liquid which was kept at the same temperature as the experiment is weighed and then injected into the absorption flask. The liquid sample is continuously agitated via an external magnetic stirrer. The levels of mercury in the three branches are leveled every few minutes to make sure that the gas phase is at atmospheric pressure. Equilibrium is reached when the position of the meniscus in the buret (while the three branches are leveled) stops changing. The whole apparatus is kept at constant temperature inside a temperature-controlled bath. The bath temperature variation is usually less than 0.05 °C during any given run.

The concentration of gas dissolved in equilibrium with the liquid sample, $A^{\bullet}$, is calculated from the volume of absorbed gas, V_{ABS}, measured in this way by

$$A^{\bullet}/(\text{g-mol L}^{-1}) = \frac{(V_{ABS}/\text{cm}^3)(P_i/\text{atm})}{(V_l/\text{L})(R/(\text{atm cm}^3\ \text{g-mol}^{-1}\ \text{K}^{-1}))(T/\text{K})} \qquad (2)$$

where P_i is the total pressure inside the equilibrium flask (atmospheric minus the vapor pressure of the liquid), V_l is the volume of the liquid sample, R is the ideal gas constant, and T is the temperature of the experiment. Then the solubility of the gas is calculated in terms of Henry's law constant, H, as

$$H/(\text{atm L g-mol}^{-1}) = \frac{P_i/\text{atm}}{A^{\bullet}/(\text{g-mol L}^{-1})} \qquad (3)$$

where P_i is the partial pressure of the gas in the equilibrium cell.

The solubility of a gas in a liquid cannot be measured directly when the gas reacts with the solution as in the case of Cl_2 in BHP. However, for the case of electrolytic solutions, Danckwerts (*4*) gives a method of relating the gas solubility in the electrolyte solution to the solubility of the gas in the solvent at the same temperature. This solubility expression in terms of Henry's law constant is

$$\log (H/H^{\circ}) = (h/(\text{L g-mol}^{-1}))(I/(\text{g-mol L}^{-1})) \qquad (4)$$

where H is Henry's law constant for the gas in the electrolyte solution, H° is the value in the solvent, and I is the ionic strength of the solution defined by

$$I/(\text{g-mol L}^{-1}) = \tfrac{1}{2}\sum(c_i/(\text{g-mol L}^{-1}))z_i^2 \qquad (5)$$

with c_i being the concentration of the ions of valency z_i. The quantity h (with units of inverse ionic strength) is the sum of the contributions of the negative ions, the positive ions, and the gas itself.

$$h/(\text{L g-mol}^{-1}) = (h_-/(\text{L g-mol}^{-1})) + (h_+/(\text{L g-mol}^{-1})) + (h_G/(\text{L g-mol}^{-1})) \qquad (6)$$

In eq 6, h_+ and h_- are constants and h_G is a function of temperature. Values of the h parameter for some ions and gases are reported in the literature (*4*).

Laminar Liquid Jet Absorber. The laminar jet apparatus, shown in Figure 2, is a gas-liquid contacting device with a very small contact time between the gas and the liquid in the range of 10^{-3}–10^{-2} s. A detailed description of this apparatus and its operation has been given previously (*5*).

According to the penetration theory (*4*), when a gas is absorbed in a liquid jet without a chemical reaction (physical absorption), the rate of absorption is

$$q/(\text{g-mol s}^{-1}) = 4(A^{\bullet}/(\text{g-mol cm}^{-3}))[(D_A/(\text{cm}^2\ \text{s}^{-1}))(L/(\text{cm}^3\ \text{s}^{-1}))(x/\text{cm})]^{1/2} \qquad (7)$$

Thus by measuring the rate of absorption, q, liquid flow rate, L, and jet length, x, the diffusivity may be determined through knowledge of the solubility, $A^{\bullet}$.

Wetted-Sphere Absorber. The wetted-sphere absorber is another common device used in gas absorption studies. The apparatus used in this work, shown in Figure 3, has larger contact times than the laminar liquid jet absorber in the range of 0.1–1.0 s. Al-Ghawas et al. (*5*) give a detailed description of this apparatus.

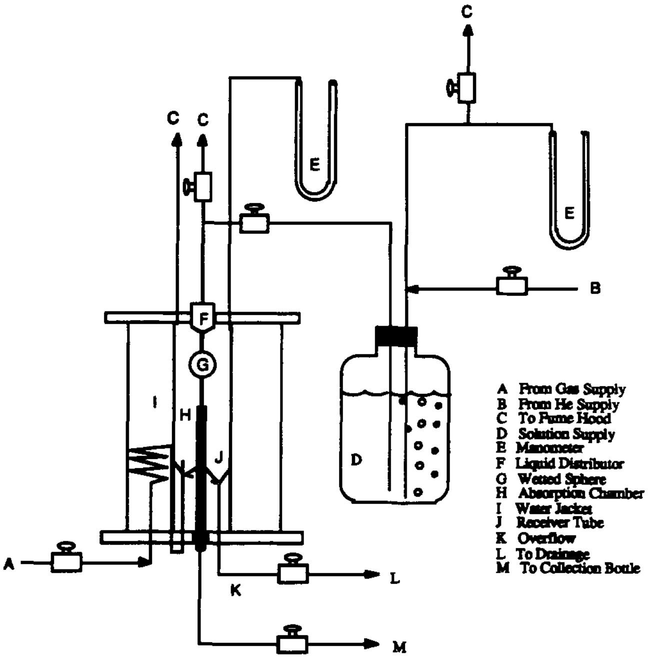

Figure 3. Wetted-sphere absorber.

The sphere is fixed at 0.3 cm from the liquid feed orifice. This distance was chosen because at longer distances the liquid tended to break away from the rod and produced uneven distribution over the sphere. This condition is undesirable since it would alter the contact time and surface area by unpredictable amounts. At shorter distances, the liquid tended to spray out over the ball even at moderate flow rates. The length of the rod between the sphere and the receiving tube was fixed at 2.0 cm, since it was found experimentally by Davidson and Cullen (*6*), Goettler (*7*), Wild and Potter (*8*), and Tomcej et al. (*9*) that for distances of less than 2.0 cm the rate of absorption drops appreciably because of a stagnant layer end effect. It was found in the work reported here that there was no significant difference in the absorption rate when the distance was varied between 2.0 and 2.5 cm. When the distance was greater than 2.5 cm, rippling effects became significant. The experimental apparatus and procedure were checked by comparing experimental results with literature values for the well-known diffusivity of carbon dioxide in water.

Freshly degassed liquid is initially fed to the distributor at high flow rates to ensure complete wetting of the sphere. When the liquid film has stabilized, the flow rate is reduced to the desired rate. After the liquid film is flowing satisfactorily, the gas is turned on for enough time to purge the absorption chamber and for all the tubing to fill with the gas. The gas is then turned off, and the rate of gas absorption is found by measuring the amount of time needed for a soap film to travel through a fixed volume.

All of the experiments were carried out under atmospheric pressure. The temperature of the system was monitored by thermometers in the constant-temperature jacket, in the absorption chamber, and in the liquid feed distributor. The temperature was controlled to within ±0.3 °C.

Davidson and Cullen (*6*) presented a solution for the problem of physical gas absorption by a laminar liquid film flowing over a sphere. For a small depth of penetration, the rate of absorption, q, can be predicted by a series expansion of the form

$$q/(\text{g-mol s}^{-1}) = (L/(\text{cm}^3\ \text{s}^{-1}))(A^* - A^\circ)/(\text{g-mol cm}^{-3})) \times [1.0 - \textstyle\sum(\beta_i \exp(-\gamma_i \alpha))] \quad (8)$$

where L is the liquid flow rate, A° is the initial concentration of the gas in the liquid before the absorption (equal to zero for our case of degassed liquid), β_i and γ_i are constants given by Davidson and Cullen (*6*), and α is defined as

$$\alpha = 3.36\pi\left[\frac{2\pi(g/(\text{cm s}^{-2}))}{3(\nu/(\text{cm}^2\ \text{s}^{-1}))}\right]^{1/3} (r/\text{cm})^{7/3} \times (L/(\text{cm}^3\ \text{s}^{-1}))^{-4/3}(D_A/(\text{cm}^2\ \text{s}^{-1})) \quad (9)$$

where g is the acceleration due to gravity, ν is the kinematic viscosity of the liquid, and r is the radius of the sphere. Olbrich and Wild (*10*) improved the general solution of Davidson and Cullen by adding more terms to the series. The diffusivity can be calculated from the measured absorption rate, q, with eq 8. An iterative calculation is required since D_A appears in the exponent.

Solubility of O_2 and Cl_2

The concentration of interest here is an aqueous solution of 4 M KOH and 8 M H_2O_2. Similar concentrations are used in the operation of singlet oxygen generators. The preparation of this solution has to be done under specific conditions to avoid catastrophic results because of their very unstable behavior. The reactants used in the preparation of the solution were 90 wt % aqueous hydrogen peroxide provided by the U.S. Air Force Weapons Laboratory, KOH pellets from Fisher with a purity of 85% KOH by weight (with the remainder consisting of water), and deionized and distilled water. For most BHP solutions, in the concentration range of interest, the components are not completely in ionic form. According to the equilibrium constant for the dissociation reaction

$$K^+(aq) + OH^-(aq) + H_2O_2(aq) \rightarrow K^+(aq) + OH^-(aq) + HOO^-(aq) + H_2O \quad (10)$$

given by Balej and Spalek (*11*), hydrogen peroxide is the main component in undissociated form.

Solubility of Oxygen in BHP. BHP solutions are very unstable under normal conditions, with H_2O_2 decomposing to O_2 and H_2O. The addition of a stabilizer (oxine) and the preparation of BHP using KOH treated with charcoal was attempted with unsuccessful results. Also, on the basis of similar systems, the solubility of O_2 in this solution is expected to be very small. These facts made it impossible to measure the oxygen solubility in BHP solutions by volumetric means. For this reason, it was attempted to carry out measurements so that eq 4 can be applied for the prediction of the physical solubility of oxygen in BHP solutions.

For this case in eq 4, H represents the Henry's law constant for the gas (oxygen) in the electrolyte solution (BHP) and H° represents Henry's law constant for the gas in the solvent (nonionic species). According to the equilibrium constant for the reaction in eq 10, the solvent corresponds to an aqueous solution of 35 wt % hydrogen peroxide.

(a) Validation of Equipment. As a check on the experimental apparatus and procedure, several measurements were carried out for O_2 solubility in water. Deionized, distilled water was degassed under vacuum, and the solubility of O_2 was measured in the apparatus. The vacuum pressure available at our lab was 0.342 atm. The solubility was calculated in terms of Henry's law constant by using eqs 2 and 3. Although the degasification of the liquid sample was done under a pressure of 0.342 atm, the concentration of oxygen in equilibrium with the liquid at that pressure cannot be neglected compared with the concentration of oxygen in the liquid at atmospheric pressure. Therefore, the partial pressure is corrected as

$$P_i = P_T - P_w^{vap} - [(0.21)(0.342) - 0.02]$$

$$P_i = P_T - P_w^{vap} - 0.052 \quad (11)$$

where P_w^{vap} is the water vapor pressure at the temperature of the experiment, 0.21 is the mole fraction of oxygen in the air,

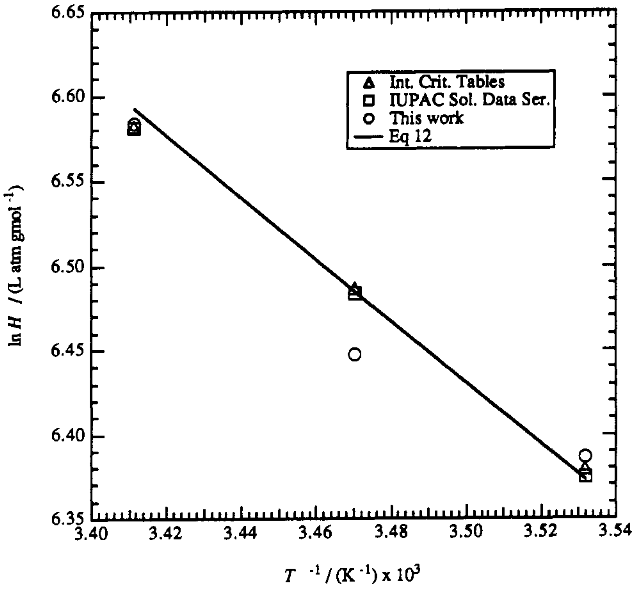

Figure 4. Solubility of oxygen in water.

Table I. Solubility of O_2 in Water

T/K	H/(atm L g-mol^{-1}) this work	IUPAC (*12*)	ICT (*13*)
283.15	593.8	587.0	589.3
288.15	631.2	654.3	656.1
293.15	723.3	721.6	722.1

0.02 atm is the water vapor pressure at the temperature of the degassing process, and the factor 0.052 is then the correction due to the partial pressure of oxygen in the air in equilibrium with the degassed solutions at the pressure of 0.342 atm. The results are shown in Table I and Figure 4 from which an average mean deviation of 2% is calculated when compared with values found in the *IUPAC Solubility Data Series* (*12*) and the *International Critical Tables* (ICT) (*13*). The values for the solubility of O_2 in water from the ICT can be correlated by

$$\ln\,[H/(\text{atm L}^{-1}\text{ g-mol}^{-1})] = 12.8067 - \frac{1821.75}{T/\text{K}} \qquad (12)$$

which predicts the solubility with an average mean deviation of 0.07%. This equation is valid in the temperature range of 0–20 °C.

(***b***) ***Solubility of O_2 in 35 wt % H_2O_2.*** A solution of 35 wt % H_2O_2 was prepared from deionized, distilled water and 90 wt % H_2O_2. Oxine was added to the solution as a stabilizer in the concentration of 1 mL/L of solution to avoid the decomposition reaction. It is believed that the small concentration of this chemical does not change the properties of the solution. The samples were kept under vacuum to degas them before injection into the equilibrium cell. A sample was weighed by using an analytical balance, and its volume (V_l) was determined from its density. The values of the density of H_2O_2 solutions were determined from Schumb et al. (*14*). The volume of the gas absorbed (V_{ABS}) was measured with the apparatus, and the concentration of O_2 absorbed by the liquid sample (A^*) was calculated according to eq 2. The solubility was then calculated by

$$H = \frac{P_T - 0.8P_w^{vap} - [(1)(0.342) - (0.8)(0.02) - (0.2)(0.02)]}{A^*}$$

or

$$H/(\text{atm L g-mol}^{-1}) = \frac{(P_T/\text{atm}) - 0.8(P_w^{vap}/\text{atm}) - 0.322}{A^*/(\text{g-mol L}^{-1})} \qquad (13)$$

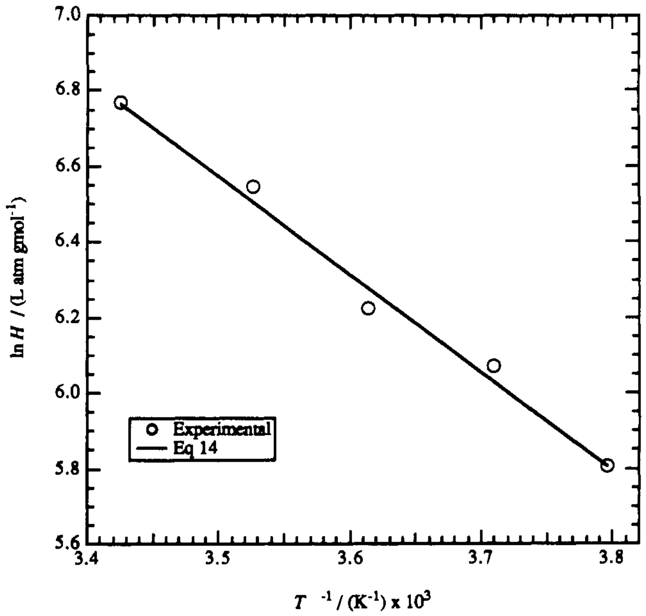

Figure 5. Solubility of oxygen in 35 wt % hydrogen peroxide.

Table II. Solubility of O_2 in 35 wt % H_2O_2

T/K	H/(atm L g-mol^{-1})	T/K	H/(atm L g-mol^{-1})
291.95	915.5	276.75	540.6
	990.9		506.0
	706.5		466.4
283.65	743.4		505.0
	793.1	269.55	445.7
	649.7		477.7
	604.9		374.4
		263.45	345.6
			318.3

The partial pressure of oxygen above the liquid sample was corrected for the vapor pressure of water by using Raoult's law and for the partial pressure of oxygen in equilibrium with the degassed liquid. In this case, due to the decomposition of the solution, the mole fraction of oxygen above the liquid during the degassification process was taken as 1 – (the mole fraction of water vapor). The results are shown in Figure 5, and the average of the values at every temperature are shown in Table II. The scatter in the experimental results is due to the decomposition of the aqueous hydrogen peroxide solution, which was reduced to a minimum but not completely eliminated. The solubility of O_2 in 35 wt % H_2O_2 can be correlated by

$$\ln\,[H/(\text{atm L g-mol}^{-1})] = 15.63 - \frac{2587}{T/\text{K}} \qquad (14)$$

which predicts the experimental values with an average mean deviation of 9.1%. This correlation is valid in the temperature range of −10 to +20 °C.

(***c***) ***h Parameters.*** The parameter h_{O_2} is reported by Danckwerts (*4*) at 15 and 25 °C. To extend the temperature range of h_{O_2}, data have been used from the ICT (*12*) for the solubility of O_2 in 1 M NaCl. Application of eq 4 to this system gives

$$\log\left[\frac{H/(\text{atm L g-mol}^{-1})}{H^\circ/(\text{atm L g-mol}^{-1})}\right] = ((h_{Na^+} + h_{Cl^-} + h_{O_2})/(\text{L g-mol}^{-1}))(I/(\text{g-mol}^{-1}\text{ L}^{-1})) \qquad (15)$$

Danckwerts gives $h_{Na^+} = 0.091$, and from the data for H from the ICT and with H° calculated from eq 12, h_{O_2} was calculated for the temperature range 0–20 °C. These values are plotted

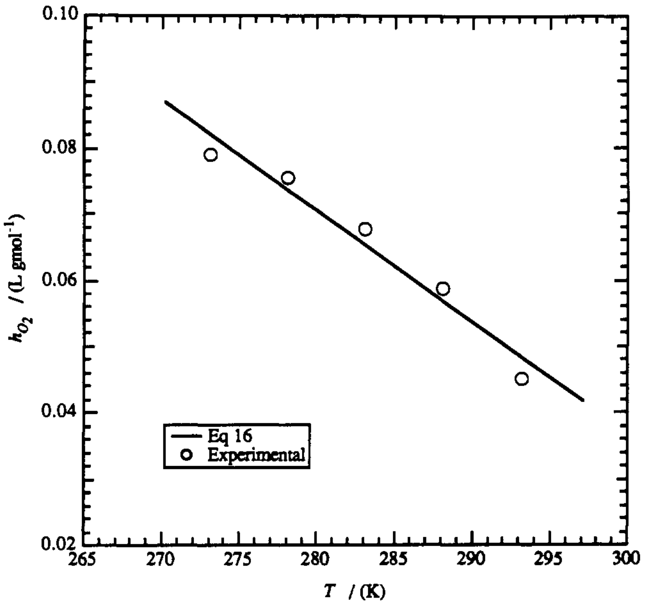

Figure 6. h_{O_2} as a function of temperature.

Table III. Parameter h_{O_2} as a Function of Temperature

T/K	h_{O_2}/(L g-mol^{-1})	T/K	h_{O_2}/(L g-mol^{-1})
273.15	0.0789	288.15	0.0587
278.15	0.0754	293.15	0.0451
283.15	0.0677		

in Figure 6 and tabulated in Table III. The values calculated in this work for h_{O_2} are correlated by

$$h_{O_2}/(\text{L g-mol}^{-1}) = 0.5426 - 1.6860 \times 10^{-3}(T/\text{K}) \quad (16)$$

Even though the values of h in Figure 6 seem to yield a parabolic behavior, there was not a theoretical basis to assume this. The purpose of the correlation was to obtain an approximation to the values in this range of temperature. The difference between the values and the correlation may be attributed to experimental error.

A value for h_{HOO^-} could not be determined in this work. However, Danckwerts suggests that when the value of the parameter h for an ion is not known, the value for a similar ion may be used. In this case it would be reasonable to assume that $h_{HOO^-} = h_{OH^-} = 0.066$ L g-mol^{-1}.

For a typical BHP solution prepared by mixing equal volumes of 6 M KOH and 90 wt % H_2O_2, the concentration of the ions can be calculated from the equilibrium constant (*11*), and it can be shown that eq 4, together with eqs 14 and 16 and the values of $h_{H^+} = 0.00$, $h_{OH^-} = 0.066$, $h_{OOH^-} = 0.066$, and $h_{K^+} = 0.074$, yields the expression for the solubility, in terms of the Henry's law constant, of O_2 in BHP as

$$\ln (H_{O_2-BHP}/(\text{atm L g-mol}^{-1})) = 24.545 - \frac{2586.66}{T/\text{K}} - 0.02329(T/\text{K}) \quad (17)$$

in which the third term has been included to show the contribution of the parameter h as a function of temperature. This expression is valid in the range of 0–20 °C.

Solubility of Chlorine in BHP. Since chlorine reacts with BHP, its solubility cannot be measured directly. Equation 4 could be used if the h parameters in eq 6 and the solubility of chlorine in 35 wt % hydrogen peroxide could be determined. But, chlorine also reacts with hydrogen peroxide solutions, and its solubility cannot be measured directly either. However, since it is found that, over the temperature range of this work, the Henry's law constant of O_2 in 35 wt % H_2O_2 is only 1–19% higher than in water by itself, a reasonable estimate for $H_{Cl_2-H_2O_2}$ would be

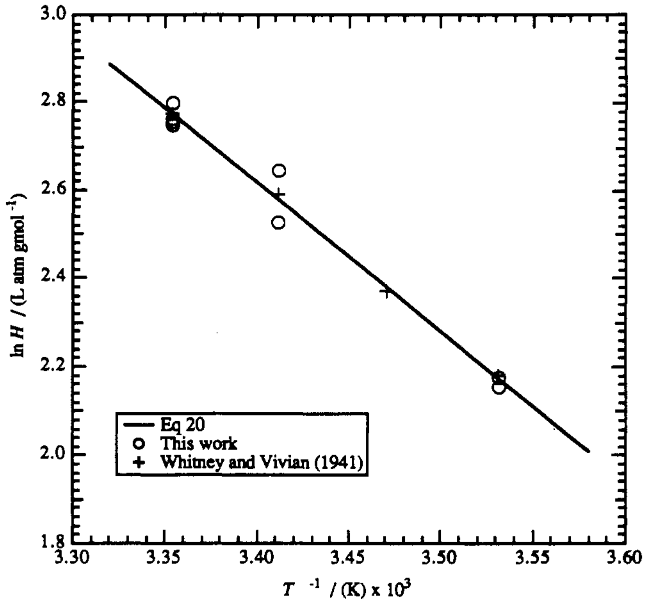

Figure 7. Solubility of chlorine in water.

Table IV. Solubility of Cl_2 in Water

T/K	H/(atm L g-mol^{-1})	ref
283.15	8.83	15
283.15	8.80	this work
283.15	8.62	this work
288.15	10.69	15
293.15	13.31	15
293.15	14.10	this work
293.15	12.50	this work
298.15	16.01	15
298.15	16.40	this work
298.15	15.76	this work
298.15	15.62	this work
298.15	15.82	this work

$$H_{Cl_2-H_2O_2}/(\text{atm L g-mol}^{-1}) = H_{Cl_2-H_2O}\frac{H_{O_2-H_2O_2}}{H_{O_2-H_2O}} \quad (18)$$

Thus, eqs 12 and 14 can be used together with the values of solubility of chlorine in water to estimate the solubility of chlorine in 35 wt % hydrogen peroxide. Then these values can be used to estimate the solubility of chlorine in BHP solutions by using eq 4. To implement this equation, it is necessary to have knowledge of the value of the h parameter for chlorine as a function of temperature.

The value of h_{Cl_2} can be determined by measuring the solubility of chlorine in an aqueous KCl solution and comparing this to the solubility of chlorine in water in a range of temperature by using eqs 4–6.

(*a*) ***Validation of Equipment.*** As a check on the modified solubility apparatus, several measurements were carried out for Cl_2 solubility in water. However, when chlorine is absorbed in water, the following hydrolysis reaction occurs

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \quad (19)$$

Whitney and Vivian (*15*) measured the equilibrium constant for this reaction and the physical solubility of chlorine in water. From equilibrium calculations it may be shown that by adding HCl to water, to give a concentration of 0.1 N HCl, the hydrolysis reaction will be suppressed and the physical solubility (the solubility of undissociated chlorine) can then be measured directly in the solubility apparatus. Equation 4 may be used to estimate the effect on the physical solubility of Cl_2 in water by

Table V. Solubility of Cl_2 in Aqueous KCl

T/K	H/(atm L g-mol^{-1})	T/K	H/(atm L g-mol^{-1})
283.15	10.73	293.15	13.97
288.15	11.91	298.15	17.92

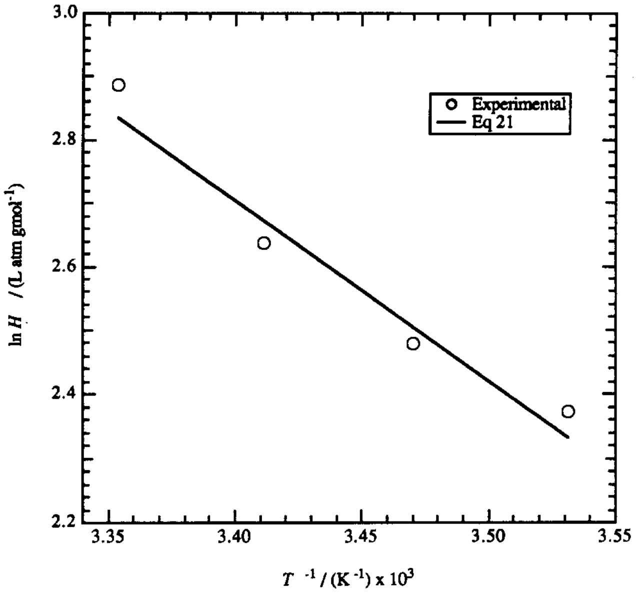

Figure 8. Solubility of chlorine in 1 N KCl.

adding this small amount of HCl. At 0 °C, eq 4 predicts that the solubility of Cl_2 is reduced by only 0.5% by the addition of 0.1 N HCl. Figure 7 and Table IV give the experimental results of this work. Figure 7 also shows the data of Whitney and Vivian plotted as H versus T^{-1}. The data of this work show very good agreement with the Whitney and Vivian data with an average mean deviation of 2.8%. These data can be correlated by

$$\ln\,(H/(\text{atm L g-mol}^{-1})) = 14.124 - \frac{3384.1}{T/\text{K}} \qquad (20)$$

(b) Solubility of Cl_2 in Aqueous KCl. Solubility measurements for Cl_2 in aqueous KCl were carried out to determine h_{Cl_2} as a function of temperature. Solutions of 1 N KCl were prepared with HCl added to give 0.1 N HCl. The HCl was added to limit the hydrolysis reaction. The solutions were degassed under vacuum, and the solubility of Cl_2 was measured as a function of temperature. The data are given in Table V and are shown plotted in Figure 8. This figure also shows the correlation line given by the equation

$$\ln\,(H/(\text{atm L g-mol}^{-1})) = 12.336 - \frac{2832.87}{T/\text{K}} \qquad (21)$$

Equations 4–6 can be used now, with H being the solubility of chlorine in the 1 M KCl/0.1 M HCl solution and $H°$ the solubility of chlorine in water, to determine h_{Cl_2} as a function of temperature.

Substituting eqs 20 and 21 into eq 4, together with the values of the h parameters (Danckwerts reports the value of 0.021 for h_{Cl^-}), h_{Cl_2} is obtained as

$$h_{Cl_2}/(\text{L g-mol}^{-1}) = 0.7449 - 2.72 \times 10^{-3}(T/\text{K}) \qquad (22)$$

This parameter has been determined by Hikita et al. (*16*) at other temperatures. Table VI compares their values with the values obtained in this work. Considerable differences exist between our values and those from Hikita. However, no explanation could be given to justify this difference.

Table VI. h_{Cl_2} as a Function of Temperature

T/K	h_{Cl_2}/(L g-mol^{-1})	ref
273.15	0.0024	this work
278.15	−0.0119	
283.15	−0.0258	
288.15	−0.0391	
293.15	−0.0520	
293.15	−0.0145	16
303.15	−0.0247	
315.15	−0.0296	
323.15	−0.0357	

Finally, with all the information required to use eq 4, the solubility of chlorine in a typical BHP solution can be obtained as

$$\ln\,(H_{Cl_2\text{-BHP}}/(\text{atm L g-mol}^{-1})) = 28.6389 - \frac{4149.01}{T/\text{K}} - 0.03758(T/\text{K}) \qquad (23)$$

in which the third term has been included to show the contribution of the h parameter. This equation is valid in the range of 0–20 °C.

Diffusivity of O_2 and Cl_2

The objective of this part of the work is to measure and correlate the diffusivity of oxygen and chlorine in aqueous and basic hydrogen peroxide solutions. No measurements were performed directly between the gas and the BHP solutions due to the high instability of these solutions. Theories for the diffusivity of liquids are incomplete. However, for small changes in temperature and composition, the diffusivity of the gas in BHP solutions can be estimated if we know the diffusivity of the gas in a similar solution according to the semiempirical equation for diffusivity given by Akgerman and Gainer (*17*) based on the absolute rate theory of viscosity

$$\frac{(D/(\text{cm}^2\ \text{s}^{-1}))(\mu/\text{cP})}{T/\text{K}} = (A/(\text{cm}^2\ \text{cP s}^{-1}\ \text{K}^{-1}))\exp\left(\frac{E/(\text{cal g-mol}^{-1})}{(R/(\text{cal g-mol}^{-1}\ \text{K}^{-1}))(T/\text{K})}\right) \qquad (24)$$

where E is a combination of the activation energy for diffusion and viscosity. A is determined by the geometric configuration of the diffusing solute gas in the liquid solvent and the partition functions for viscosity. Each of these parameters is determined from information about the molecular weights, molar volumes, and viscosities of the solute and solvent (*17*). Thus, a method of estimating the diffusivity at the same temperature but at another concentration would be

$$D_2 = D_1\frac{A_2\mu_1}{A_1\mu_2}\exp\left(\frac{E_2 - E_1}{RT}\right) \qquad (25)$$

In eq 25, D_1 is the known value of the diffusivity in a solvent with viscosity μ_1, and D_2 is the desired value of the diffusivity in a solvent with viscosity μ_2.

The laminar liquid jet absorber is used to measure the diffusion coefficient of chlorine gas in aqueous hydrogen peroxide solutions. These measurements can be used to estimate the diffusion coefficient of chlorine in alkaline hydrogen peroxide solutions. The technique involves the measurement of the gas absorption rate of Cl_2 gas into a flowing stream of liquid. The absorption data may be interpreted in terms of the penetration theory to give the liquid-phase diffusion coefficient. The effect of chemical reaction on the rate of absorption is suppressed by operating at short gas–liquid contact times.

Table VII. Absorption of Cl_2 in 35 wt % H_2O_2 in the Laminar Jet

T/K	x/cm	L/ (cm^3/s^{-1})	$(xL)^{1/2}$/ ($cm^2\ s^{-1/2}$)	10^7q/ (g-mol s^{-1})
293.15	1.353	0.835	1.063	5.62
		1.026	1.179	6.39
		1.242	1.296	7.12
	2.384	0.890	1.457	8.09
		1.138	1.647	9.04
		1.325	1.777	9.83
283.15	1.476	0.857	1.125	8.92
		0.977	1.201	9.87
		1.138	1.296	10.46
		1.363	1.419	11.51
	2.489	0.843	1.449	11.74
		1.055	1.621	12.93
		1.282	1.786	14.67
273.15	1.418	0.872	1.112	14.51
		1.092	1.244	16.82
		1.312	1.364	18.48
	2.344	0.857	1.417	18.83
		1.135	1.631	21.51
		1.353	1.781	23.95
263.15	1.502	0.908	1.168	21.90
		1.105	1.288	25.50
		1.325	1.411	26.30
	2.445	0.837	1.430	28.40
		1.172	1.693	32.20
		1.368	1.829	35.60

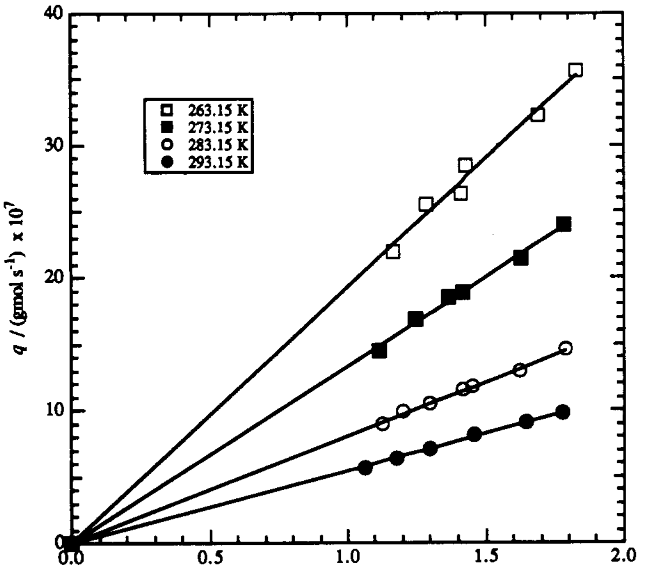

Figure 9. Absorption of chlorine in the laminar liquid jet.

Diffusivity of Cl_2 in Aqueous H_2O_2. In this study, the absorption rate of chlorine in 35 wt % aqueous hydrogen peroxide was measured over a temperature range of −10 to +20 °C. The contact time in the jet apparatus was varied between 2.5 × 10^{-3} and 6.9 × 10^{-3} s. The absorption rates were measured by analysis of the outlet liquid stream for chloride ion concentration using a Fisher Model 825 MP pH/mV/ion meter equipped with an Orion Model 96-17B combination chloride ion electrode. The Fisher ion analyzer was calibrated with standard chloride solutions. The experimental data are presented in Table VII. The contact time was varied by changing the jet length and the liquid flow rate. The data are plotted in accordance with eq 7 in Figure 9. As expected, a straight line passing through the origin is obtained for each temperature. The product $A^*D_l^{1/2}$ is obtained for each temperature from the slope of the straight lines. These values are reported in Table VIII, along with the values of the diffusivity. The value of 0.50 × 10^{-5} cm^2/s measured in this work for the diffusivity of Cl_2 in 35 wt % hydrogen peroxide at 20 °C may be compared to a value of 1.21 × 10^{-5} cm^2/s for the diffusivity of chlorine in water at 20 °C, as extrapolated from the measurements at 25 °C reported by Tang and Sandall (*18*).

Table VIII. Diffusivity of Cl_2 in 35 wt % H_2O_2

T/K	slope × 10^7/ (g-mol $cm^{-2}\ s^{-1/2}$)	$10^7A^*D_A^{1/2}$/ (g-mol $cm^{-2}\ s^{-1/2}$)	10^6D_A/ ($cm^2\ s^{-1}$)
293.15	5.47	1.37	4.99
283.15	8.05	2.01	3.94
273.15	13.00	3.25	3.53
263.15	19.08	4.77	2.40

Table IX. Diffusivity of O_2 in 35 wt % H_2O_2

T/K	$10^6D(cm^2/s^{-1})$	T/K	$10^6D(cm^2/s^{-1})$
285.15	8.83	269.55	4.49
277.95	6.70	265.35	4.02
271.15	5.04		

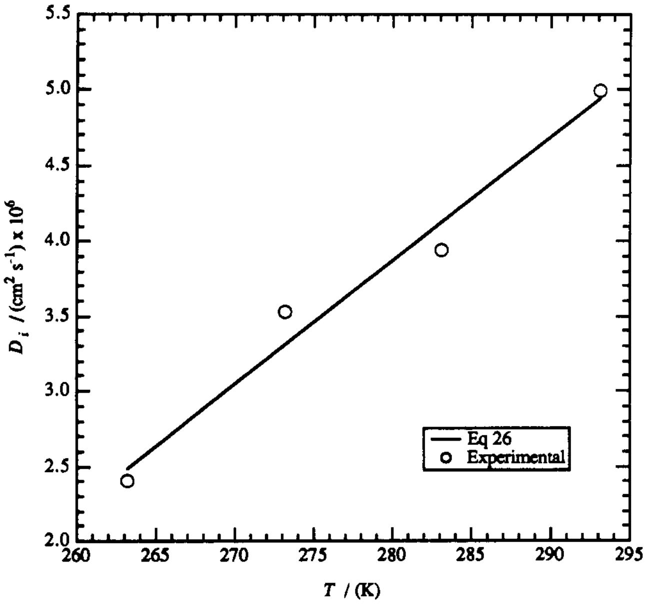

Figure 10. Diffusion coefficient of chlorine in aqueous hydrogen peroxide.

Calculation of the diffusion coefficient requires a knowledge of the solubility of chlorine in the liquid phase. A^* is calculated by using eq 18.

Figure 10 shows a plot of the diffusivity values for chlorine in aqueous hydrogen peroxide. The values are correlated by

$$D/(cm^2\ s^{-1}) = -1.904 \times 10^{-5} + 8.18 \times 10^{-8}(T/K) \qquad (26)$$

Diffusivity of O_2 in Aqueous H_2O_2. Several attempts were made to measure the diffusivity of O_2 in aqueous H_2O_2 by using the laminar liquid jet apparatus. The absorption rates could not be measured in this apparatus because of the low solubility of oxygen. A wetted-sphere device, as shown schematically in Figure 3, was used for these measurements. The wetted-sphere apparatus was modified from previous research (*5*) in that a pressure feed was used for the liquid rather than a pump. This modification was made to minimize any decomposition of the hydrogen peroxide.

After the gas absorption rate is measured, the diffusivity can be calculated with eq 8. An iterative calculation is required since D_A appears in the exponential series. The Newton iteration method was used in this work.

As a check on the operation of the apparatus, the diffusivity of oxygen in water at 12 °C was measured. A value of 1.41 × 10^5 cm^2/s was found. This may be compared to 1.45 × 10^5 cm^2/s determined by Baird and Davidson (*19*) using a sphere absorber and 1.40 × 10^5 cm^2/s determined by Baird and

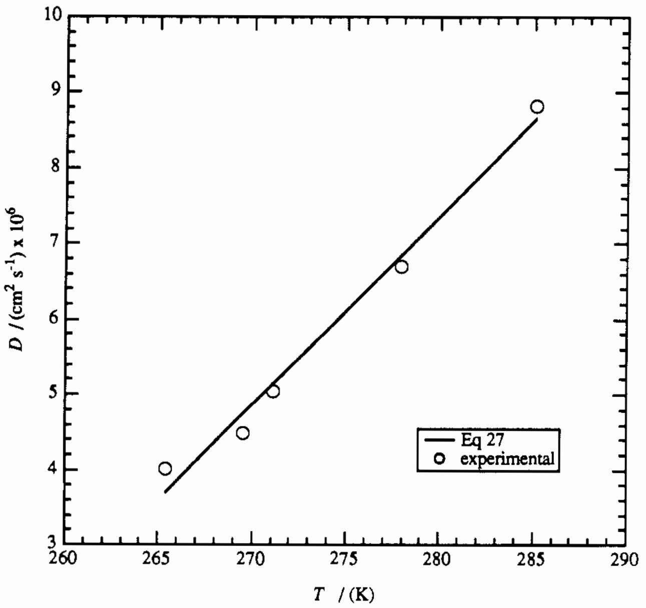

Figure 11. Diffusion coefficient of oxygen in aqueous hydrogen peroxide.

Davidson using a jet absorber.

Table IX gives the data obtained over the temperature range −8 to +12 °C for the diffusivity of oxygen in 35 wt % H_2O_2. The data are shown plotted in Figure 11. The experimental data are correlated by

$$D/(\mathrm{cm^2\ s^{-1}}) = -6.277 \times 10^{-5} + 2.5047 \times 10^{-7}(T/\mathrm{K}) \quad (27)$$

Again, the diffusivity at other concentrations or temperatures can be estimated by using eq 24 or eq 25.

Diffusivity of Cl_2 and O_2 in BHP. The diffusion coefficients of Cl_2 and O_2 in the typical BHP solution described in the section on solubility can be estimated from eq 25 as

$$D_2(\mathrm{Cl_2})/(\mathrm{cm^2\ s^{-1}}) = 1.006 D_1 \frac{\mu_1}{\mu_2} \exp\left(\frac{334.8}{RT}\right) \quad (28)$$

$$D_2(\mathrm{O_2})/(\mathrm{cm^2\ s^{-1}}) = 1.006 D_1 \frac{\mu_1}{\mu_2} \exp\left(\frac{337.8}{RT}\right) \quad (29)$$

where D_1 is the diffusivity of the gas in aqueous HP with viscosity μ_1 and D_2 is the diffusivity of the gas in a typical BHP solution with viscosity μ_2. The equations are similar due to the relatively small difference in size, geometry, and viscosity of Cl_2 and O_2.

Glossary

A	coefficient in eq 24, cm^2 cP/(sK)
A^*	concentration of gas A in the liquid at equilibrium, g-mol/L
c_i	concentration of ions, g-mol/L
D_A	diffusion coefficient of gas A into liquid solution, cm^2/s
E	activation energy for diffusion and viscosity, cal/g-mol
g	acceleration due to gravity, cm/s^2
h	parameter defined by eq 6, L/g-mol
h_-	parameter that accounts for negative ions, L/g-mol
h_+	parameter that accounts for positive ions, L/g-mol
h_G	parameter that accounts for the gas, L/g-mol
H	Henry's law constant, atm L/g-mol
H°	Henry's law constant for gas in solvent, atm L/g-mol
I	ionic strength of the solution, g-mol/L
L	volumetric flow rate, cm^3/s
P_i	partial pressure of gas i, atm
P_w^{vap}	vapor pressure of water, atm
P_T	total pressure, atm
q	total rate of gas absorption, g-mol/s
r	radius of sphere, cm
R	ideal gas law constant, 0.08205 atm L/(g-mol K)
T	temperature, K
V_{ABS}	volume of gas absorbed by liquid sample, cm^3
V_l	volume of liquid sample, cm^3
x	length of the liquid jet, cm
z_i	valency of ions

Greek Symbols

α	parameter defined by eq 9
β_i	constant in eq 8
γ_i	constant in eq 8
μ	dynamic viscosity, cP
ν	kinematic viscosity, cm^2/s

Registry No. O_2, 7782-44-7; Cl_2, 7782-50-5; H_2O_2, 7722-84-1.

Literature Cited

(1) Kumar, A.; McCluskey, R. J. *Ind. Eng. Chem. Res.* **1987**, *26*, 1323–1329.
(2) Demyanovich, R. J.; Lynn, S. *Fusion Technol.* **1987**, *12*, 488–501.
(3) Haimour, N.; Sandall, O. C. *Chem. Eng. Sci.* **1984**, *39*, 1791.
(4) Danckwerts, P. V. *Gas-Liquid Reactions*; McGraw-Hill: New York, 1970.
(5) Al-Ghawas, H. A.; Hagewiesche, D. P.; Ruiz-Ibanez, G.; Sandall, O. C. *J. Chem. Eng. Data* **1989**, *34*, 385.
(6) Davidson, J. F.; Cullen, E. J. *Trans. Inst. Chem. Eng.* **1957**, *35*, 51.
(7) Goetler, L. A. Ph.D. Thesis, University of Delaware, Newark, DE, 1967.
(8) Wild, J. D.; Potter, O. E. *Chem. Eng. J.* **1972**, *4*, 69.
(9) Tomcej, R. A.; Lal, D.; Ranwala, H. A.; Otto, F. D. Presented at the AIChE Meeting, Miami, FL, Nov 2–7, 1986.
(10) Olbrich, W. E.; Wild, J. D. *Chem. Eng. Sci.* **1969**, *24*, 25.
(11) Balej, J.; Spalek, O. *Collect. Czech. Chem. Commun.* **1979**, *44*, 488–494.
(12) *IUPAC Solubility Data Series*; Pergamon Press: New York, 1981; Vol. 7, p 2.
(13) *International Critical Tables of Numerical Data: Physics, Chemistry and Technology*; National Research Council, McGraw-Hill: New York, 1928; Vol. III.
(14) Schumb, W. C.; Satterfield, C. N.; Wentworth, R. L. *Hydrogen Peroxide*; Reinhold: London, 1955.
(15) Whitney, R. P.; Vivian, J. E. *Ind. Eng. Chem.* **1941**, *33*, 741.
(16) Hikita, H.; Asai, S.; Himikashi, Y.; Takatsuka, T. *Chem. Eng. J.* **1973**, *5*, 77.
(17) Akgerman, A.; Gainer, J. L. *Chem. Eng. Data* **1972**, *17*, 372.
(18) Tang, A.; Sandall, O. C. *Chem. Eng. Data* **1985**, *30*, 189.
(19) Baird, M. H.; Davidson, J. F. *Chem. Eng. Sci.* **1962**, *17*, 473.

Received for review April 14, 1990. Revised May 23, 1991. Accepted June 14, 1991.