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Solubility and Rate of Hydrolysis of Chlorine in Aqueous Sodium Hydroxide at 273 K

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Absorption of chlorine into aqueous media has been of interest because of its reaction to form hypochlorite which is used in industrial processes as a bleach or disinfectant. More recently, Cl_2 has been found to react in aqueous alkaline hydrogen peroxide to generate oxygen chemically in its lowest excited state, $O_2\ (a^1\Delta_g)$, along with some in the ground state $O_2\ (X^3\Sigma_g^-)$ (Held et al., 1978; McDermott et al., 1978). A possible mechanism for this reaction is given by Eqs. 1 to 3 (Held et al., 1978).

$$Cl_2 + OH^- \xrightarrow{k_1} Cl^- + HOCl \quad (1)$$

$$HOCl + OH^- \xrightarrow{\text{fast}} H_2O + ClO^- \quad (2)$$

$$ClO^- + H_2O_2 \xrightarrow{k_3} H_2O + Cl^- + O_2(^3\Sigma_g \text{ or } ^1\Delta_g) \quad (3)$$

The first step of the reaction involves the absorption of Cl_2 followed by hydrolysis by OH^- to give hypochlorous acid. In alkaline media, the HOCl is dissociated into hypochlorite, which then reacts with H_2O_2 to form oxygen. In concentrated peroxide, a similar mechanism may be postulated with HO_2^-, HOOCl, and $ClOO^-$ substituted for OH^-, HOCl, and ClO^-, respectively. Under usual operating conditions of low pressures and relatively long contact times the rate limiting step in this sequence appears to be the absorption of chlorine.

To model the rate of absorption of chlorine it is necessary to be able to predict both the solubility of chlorine in the liquid phase and the kinetic rate constant for the reaction described by Eq. 1. This note presents the results of a study carried out to measure these two parameters at 273°K.

EXPERIMENTAL APPARATUS AND PROCEDURE

The gas-liquid contacting device utilized in these studies was a roller-drum reactor shown schematically in Figure 1.

Aqueous sodium hydroxide solution entered the vacuum reactor through a Teflon nozzle and wetted roller 2 which was directly geared to the large roller 1 such that their surface speeds were matched. The wetted surfaces of both rollers were high density aluminum oxide. The gap between the rollers was variable and kept at approximately 5.1×10^{-4} m (0.020 in.). By controlling the aqueous hydroxide flowrate, roller speed, and the roller gap, a layer of base of even thickness and width could be applied to the large roller. Roller 1 had a diameter of 0.101 m and was actively cooled to 273°K with a methanol/water mixture which was circulated beneath the aluminum oxide sleeve. Thermocouples at the inlet and outlet of the roller indicated the temperature of the coolant. Typically they were not more than 1/4 to 1/2 °K apart during an experiment. Additionally, a thermocouple was located in the reaction zone to monitor the reacting liquid temperature. The roller speed was variable from 0 to 10 rpm, however, most data were accumulated at a roller speed of 5 rpm. The width of the wetted reaction zone (axial distance across the alumina surface) was variable but was maintained at 0.0254 m for these experiments. The unwetted portion of roller 1 was sleeved in Teflon and the reaction zone was an annular channel having rectangular cross section 0.0254 by 0.0066 m. The 0.0254 m wide surfaces were the wetted alumina surface and a coaxial Teflon baffle spaced 0.0066 m from roller 1. This baffle was held in place in grooves machined in annular Teflon baffles which were stationary and extended radially from the wetted surface to the reactor housing, which was 6 inch (0.1524 m) ID commercial Pyrex pipe.

An alumina scraper was located above a cold trap for removing the reaction by-products and unused base-solution from the roller. This waste slurry fell from the scraper into the cold trap below. The external casing of the roller drum reactor and trap were constructed of Pyrex thus allowing visual observation of the base application, reaction zone and scraping process throughout each run.

Flowrates of the reactants were carefully monitored. The aqueous base solution was delivered to the roller drum at ambient temperature from a burette and liquid volume versus time elapsed was recorded.

Chlorine was delivered into the reactor through an all Teflon slit nozzle. The slit width was 0.025 m and thus provided a homogeneous flux of Cl_2 gas across the reaction zone width. The slit height could be varied to control the exit gas velocity and the nozzle was designed to provide gas flow tangential to the surface of roller 1. The height of the nozzle above the alumina drum was adjustable such that the wetted surface of the drum could be made to pass beneath the nozzle with minimal clearance.

The chlorine gas flowrate was monitored with a rotameter and the pressure upstream of the rotameter was controlled to 101,000 Pa (14.7 psia). Figure 2 shows the vacuum system employed. Traps 1, 2 and 3 were maintained at 195°K using dry ice-trichlorethylene slurry and trap 4 was maintained at 77°K using liquid nitrogen.

A calibration of P_1 vs. chlorine flow was obtained with all traps cooled and with the reactor dry. This calibration was then used to determine the Cl_2 absorbed during a run. Typically, a fixed liquid concentration, liquid flowrate and roller speed, the Cl_2 flow was varied over the range from 0 to 0.7×10^{-6} kg · mol/s. Additional runs were made at different liquid flowrates and roller speeds. In the series of runs the concentration of base was increased sequentially. Figure 3 shows some typical data in the form of a plot of molar flow of Cl_2 out vs. Cl_2 in.

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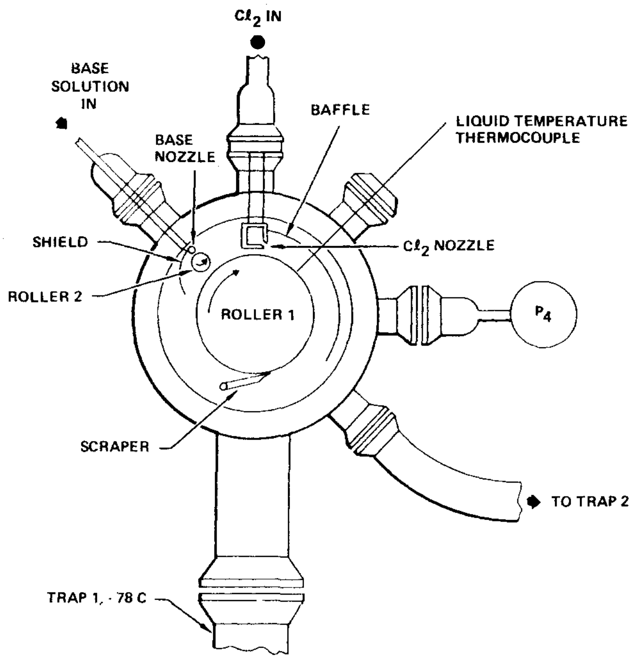

Figure 1. Reactor configuration.

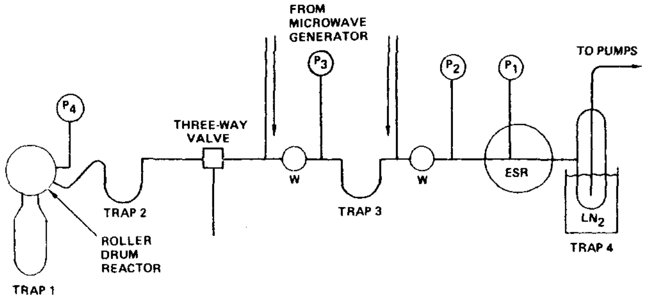

Figure 2. Vacuum system configuration.

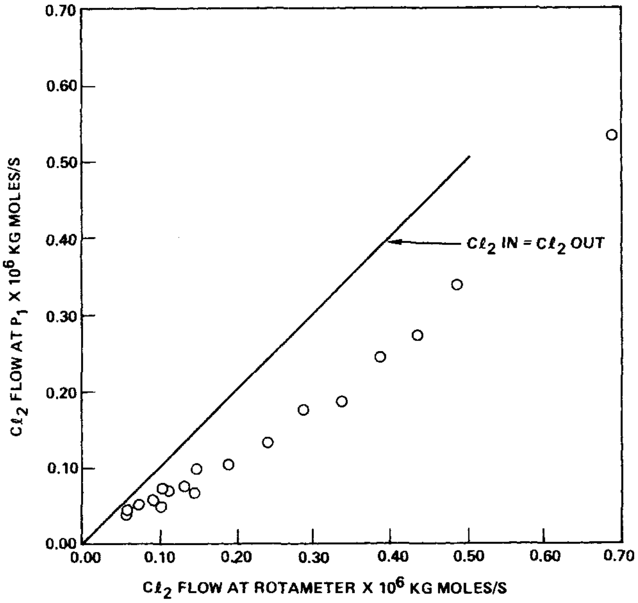

Figure 3. Chlorine out vs. chlorine in.

ANALYSIS OF EXPERIMENTAL RESULTS

The solubility of a gas in a liquid can normally be described by Henry's law,

$$P_i = HC_i^* \tag{4}$$

When electrolytes are present in solution, the solubility of the gas will be affected. The Henry's law constant in the electrolyte solution can then be related to that in pure water at the same temperature by the expression (Danckwerts, 1970):

$$\log_{10}(H/H^o) = hI \tag{5}$$

where I is the ionic strength of the solution and is defined by

$$I = \frac{1}{2} \sum_i C_i Z_i^2 \tag{6}$$

and the parameter h is considered to be made up of contributions due to the positive ion, the negative ion and the particular gas.

$$h = h_+ + h_- + h_G \tag{7}$$

Generally, h_+ and h_- contributions are considered to be temperature independent whereas h_G is usually temperature dependent.

The second-order reaction represented by Eq. 1 was considered to be pseudo-first order with respect to chlorine, since the concentration of hydroxide was always much greater than the free chlorine concentration. For absorption accompanied by a fast first-order reaction in the liquid phase, Astarita (1967) gives an expression for the average mass transfer coefficient based on the Danckwerts' surface renewal model. For the conditions of our work this expression reduces to

$$k_c = \sqrt{D(s + k)} \tag{8}$$

where s is the surface renewal rate and k is the first-order rate constant. For the case of the very fast reaction considered in our work, $s << k$ and Eq. 8 simplifies to

$$k_c = \sqrt{Dk} \tag{9}$$

The rate of absorption of Cl_2 is given by $k_c C_{Cl_2}^* A$. Using Eq. 9 for the mass transfer coefficient then gives

$$R = \sqrt{Dk} \cdot C_{Cl_2}^* \cdot A \tag{10}$$

Substitution of Henry's law (Eq. 4) into Eq. 10 gives

$$R = \sqrt{Dk} \cdot \frac{A}{H} \cdot (P - p_{H_2O}) \tag{11}$$

Since the total pressure, P, was measured rather than the partial pressure of chlorine, the substitution, $P_{Cl_2} = P - p_{H_2O}$, was made in deriving Eq. 11. Equation 11 is the basic relationship used to interpret the experimental data.

For a given concentration of hydroxide in water, the total pressure in the roller drum reactor increases with increasing chlorine flowrate whereas the partial pressure of water above the solution is expected to remain constant. The liquid composition changes from liquid inlet to outlet since when two OH^- ions react, a ClO^- ion, a Cl^- ion and an H_2O molecule are formed. However, because of the large excess of liquid phase reactant used, only a negligible change in liquid phase ionic concentration results. Thus, a plot of the rate of absorption (R), versus the total pressure (P), should yield a straight line with a slope equal to $\sqrt{Dk}\ A/H$ and an intercept on the pressure axis equal to p_{H_2O}. Figure 4 shows such a plot for a sodium hydroxide concentration of 6.1 kg · mol/m^3. It is seen that within the experimental uncertainty, the data fall on a straight line as expected. Also it should be noted that data for two different roller speeds can not be distinguished from each other on this plot. This confirms our assumption that the mass transfer coefficient is independent of the rate of surface renewal at these drum rotation rates.

Data for six solutions with sodium hydroxide concentrations varying from 2.211 to 14.005 kg · mol/m^3 were plotted as in

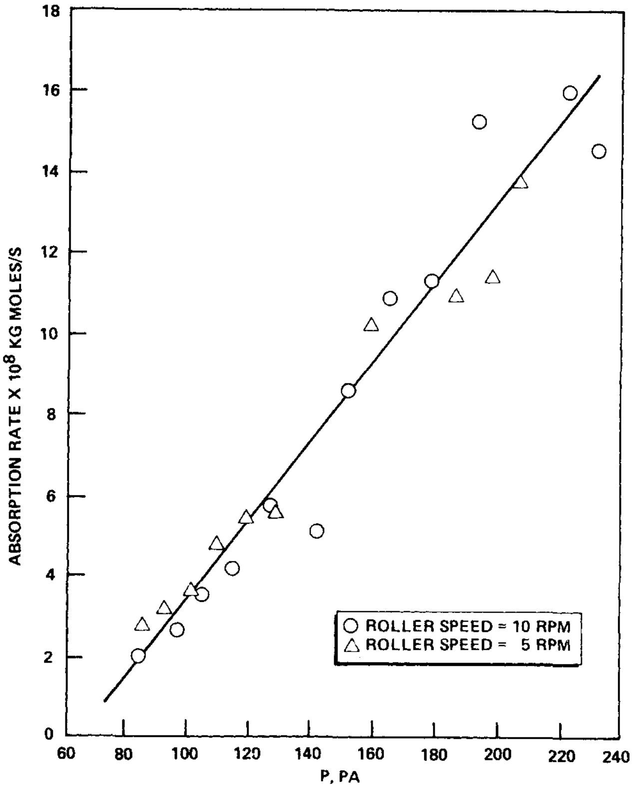

Figure 4. Chlorine absorption rate vs. pressure: $[OH^-] = 6.104N$.

Figure 4, and it was found that a straight line described the data in all cases. Since the first-order rate constant may be written as $k = k_1C_{OH^-}$ and $H = H^o \cdot 10^{hC_{OH^-}}$, then the slope of the plot of the absorption rate vs. pressure (Figure 4) is given by α in Eq. 12.

$$\alpha = \frac{\sqrt{Dk_1C_{OH^-}}A}{H^o} \cdot 10^{-hC_{OH^-}} \tag{12}$$

Rearranging and taking the logarithms gives

$$\log\{\alpha/\sqrt{C_{OH^-}}\} = \log\left\{\sqrt{Dk_1}\,\frac{A}{H^o} - hC_{OH^-}\right\} \tag{13}$$

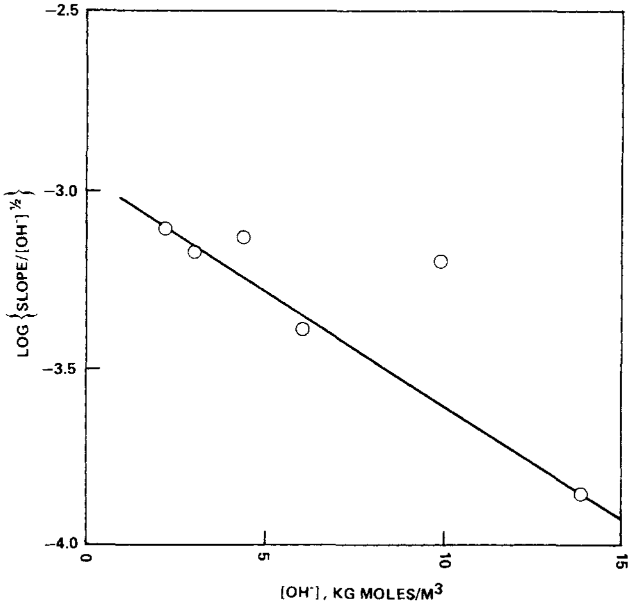

Figure 5. Plot to determine h and k_2.

Thus a plot of $\log\{\alpha/\sqrt{C_{OH^-}}\}$ vs. C_{OH^-} should give a straight line with a slope equal to $-h$.

Figure 5 shows the data plotted according to Eq. 13. With the exception of the data point for the hydroxide concentration of 10.006 kg · mol/m³, the data fall on a straight line. A least squares fit of this data, excluding the one anomalous point, gives

$$h = 0.066 \pm 0.014 \text{ m}^3/\text{kg} \cdot \text{mol} \tag{14}$$

Using the known values for the contribution to h of the sodium ion ($h_+ = 0.091$) and the hydroxide ion ($h_- = 0.066$) as given by Danckwerts (1970), gives

$$h_{Cl_2} = -0.091 \text{ L/g mol at } 273°\text{K} \tag{15}$$

This value may be compared to the value of $h_{Cl_2} = -0.0145$ m³/kg · mol at 293°K reported by Hikita et al. (1973), as determined from the earlier data of Olivera-Mandala (1920), and $h_{Cl_2} = -0.042$ m³/kg mol at 298°K calculated from the data in Spalding (1961).

The intercept on Figure 5 allows the calculation of the second-order rate constant at 273°K as

$$k_1 = 2.7 \times 10^7 \text{ m}^3/\text{kg} \cdot \text{mol} \cdot \text{s} \tag{16}$$

The value for chlorine solubility, H^o, needed for this estimation was determined from the data of Whitney and Vivian as given in Perry (1950) ($H^o = 573{,}300$ Pa · m³/kg · mol). The diffusivity for chlorine in water (D) at 298°K was obtained from Spalding (1962) and was corrected to the value of 273°K by assuming the group $D\mu/T$ constant. This gives $D = 6.80 \times 10^{-10}$ m²/s at 273°K. The contact area A, for the roller drum was taken to be 4.75×10^{-3} m². The value for k_1 found in this work may be compared to the order of magnitude estimate for k_1 of 10^6 m³/kg · mol · s found by Spalding (1962).

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NOTATION

A = contact area, m²
C_i = ion concentration, kg · mol/m³
C_i^* = equilibrium gas concentration in liquid, kg · mol/m³
D = diffusion coefficient, m²/s
h = parameter defined by Eq. 5, m³/kg · mol
h_+ = contribution to h due to positive ion, m³/kg · mol
h_- = contribution to h due to negative ion, m³/kg · mol
h_G = contribution to h due to gas, m³/kg · mol
H = Henry's law coefficient, Pa · m³/kg · mol
H^o = Henry's law coefficient for pure water, Pa · m³/kg · mol
I = ionic strength as defined by Eq. 6, kg · mol/m³
k = first order rate constant, $s^{-1} = k_1C_{OH^-}$
k_1 = second order rate constant, m³/kg · mol · s
k_c = mass transfer coefficient, m/s
p_i = partial pressure of i, Pa
P = total pressure, Pa
R = rate of absorption, kg · mol/s
s = surface renewal rate, s⁻¹
Z_i = valence of ion
μ = viscosity, Pa · s

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On the Short-Residence Time Hydropyrolysis of Single Coal Particles: The Effect of Unequal Diffusivities

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A relatively simple single-particle model recently developed by Russel, Saville, and Greene (1979) apparently explains the pressure and particle-size dependence of the weight loss in the rapid hydropyrolysis of coal. As in the kinetic model of Anthony, et al. (1976) the volatile products are divided into stable and reactive fractions, the latter of which can react further by depositing within the particle or combining with hydrogen to form a stable product. The predicted pressure and particle size effects reflect the competition between the kinetic rates and the diffusion of hydrogen into the particle against the outward flow of volatiles. The hypotheses of the model were supported by order of magnitude estimates based on experimental data or established theories with the exception of the equal binary diffusivities assumed for the gas phase components. These actually can differ significantly, so we have tested the sensitivity of the results by analyzing the alternative limiting case with at least one relatively small, and hence "controlling," binary diffusivity. Only the rapid devolatilization step is considered because the slower hydrogenation of the solid coal is relatively insensitive to diffusion.

The mathematical analysis parallels that in the original paper; only the differences will be discussed in detail here. Conservation equations for the gaseous constituents are integrated and the instantaneous yield η calculated as a function of the dimensionless particle size α^2, pressure π, the fraction of reaction volatiles ν, and the mole fraction of hydrogen in the bulk gas $x^o_{H_2}$.

The actual range of diffusivities can be estimated by characterizing the reactive volatiles with benzene, the stable volatiles with methane and the inert gas with helium so that (Reid and Sherwood 1958)

	pD_{ij}
H_2-He	16.6 N/s
H_2-CH_4	6.4
He-CH_4	6.9
He-C_6H_6	3.8
C_6H_6-CH_4	1.0

In slow devolatilization reactive volatiles are stabilized instantaneously throughout the particle leaving a ternary mixture in which the binary diffusivity for He-H_2 exceeds those for H_2-CH_4 and He-CH_4 by a factor of two and a half. Thus we assume that $D_{V,H_2} = D_{V,I} << D_{I,H_2}$. During rapid devolatilization the ternary mixture in the hydrogen-depleted core has the benzene-methane diffusivity controlling or $D_{V,V*} << D_{V,I}$, $D_{V*,I}$. Clearly the numerical differences fall short of the mathematical idealization and the chemical characterization of the components could be questioned, but this limiting case should accurately measure the influence of the original assumption of equal diffusivities on the predictions of the model.

GENERAL FORMULATION

The ternary mixtures within the particle during devolatilization require three conservation equations and three independent flux relations to determine the two independent mole fractions, the three fluxes, and the pressure. Our earlier order of magnitude estimates indicated that rapid equilibration of the pressure and concentration profiles should sustain a pseudo-steady state. Consequently, the flux of inerts (component 3) must be zero leaving five unknowns and five independent dimensionless equations:

$$\frac{1}{r^2}\frac{d}{dr}r^2N_i = R_i \quad i = 1, 2 \tag{1}$$

$$\alpha^{-2}\frac{dx_1}{dr} = \gamma_1(x_1N_2 - x_2N_1) - x_3N_1 \tag{2}$$

$$\alpha^{-2}\frac{dx_2}{dr} = \gamma_1(x_2N_1 - x_1N_2) - x_3\gamma_2N_2 \tag{3}$$

$$\alpha^{-2}\frac{dx_3}{dr} = x_3(N_1 + \gamma_2N_2) \tag{4}$$

with $x_3 = 1 - x_1 - x_2$. The fluxes are scaled on the instantaneous devolatilization rate and the radial position on the particle radius. The additional dimensionless groups are

$$\gamma_1 = \frac{D^e_{13}}{D^e_{12}} \quad \text{and} \quad \gamma_2 = \frac{D^e_{13}}{D^e_{23}}.$$

Only two of the three flux relations are independent; the final equation relating the pressure gradient to the total flux has been omitted because an explicit solution for the pressure is unnecessary.

SLOW DEVOLATILIZATION

When the hydrogen flux permits instantaneous stabilization of the reactive volatiles throughout the particle the remaining

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