(a) and (b), that is, by varying the value of $\alpha_0$ from zero to infinity, the shift of the enhancement factor between those accompanied by the simple reaction was given.

Nomenclature

- $C$: concentration in liquid phase [mol/cm$^3$]
- $D$: diffusivity in liquid phase [cm$^2$/sec]
- $k_m$: $m$-th order reaction rate constant [(cm$^3$/mol)$m^{-1}$/V$_s$]
- $k_L$: liquid-phase mass transfer coefficient for component A [cm/sec]
- $M_m$: $k_m C_{A_m} D_A k_L_m$ [cm/sec]
- $m$, $m'$, $n$: order of reaction
- $\nu$: liquid volume per unit interfacial area [cm$^3$/cm$^2$]
- $x$: $z/L_L$ [cm$^2$/cm$^3$]
- $Y$: $C/C_A$ [-]
- $z$: distance into liquid phase from interface [cm]
- $z_L$: thickness of liquid film [cm]

Introduction

One of the important aims of the containment spray during a maximum accident in a boiling- or pressurized-water reactor is to restrain the leakage of the radioactive iodine vapor from reactor fuel to the atmosphere. Usually, sodium hydroxide solution is used as a containment spray liquor.

Authors have reported the dependency of partic-

â€œREACTIONS OF IODINE IN AQUEOUS SOLUTIONS CONTAINING SODIUM HYDROXIDEâ€

MOTONARI ADACHI, WATARU EGUCHI, FUKUZO TOHDO** AND MINORU YONEDA***
Institute of Atomic Energy, Kyoto University, Uji

Reactions of iodine in aqueous phase were studied by a concentration relaxation method. From the result of the present investigation, the mechanism of the absorption of iodine in air by aqueous sodium hydroxide solution is as follows:

(Step 1) Molecular iodine in air dissolves into the aqueous phase through the gas-liquid interface according to Henry's law.

(Step 2) Instantaneous reversible reactions take place in the aqueous phase and $\text{HIO}$, $\text{I}^-$ and $\text{I}_3^-$ form.

(Step 3) $\text{HIO}$ formed by the above reaction is consumed gradually and $\text{IO}^-$ forms, while the instantaneous reversible reactions of step 2 are in equilibrium at any instant.

Overall consumption rate of $\text{HIO}$ can be approximated by the rate equation of the second-order reaction with respect to $\text{HIO}$.

** Received on October 19, 1973
Presented at the 5th Autumn Meeting of The Soc. of Chem. Engrs., Japan, October 6, 1971
** Kawasaki Jukogyo Co., Ltd.
*** Showa Denko Co., Inc., Kawasaki

JOURNAL OF CHEMICAL ENGINEERING OF JAPAN
of absorption of iodine by alkaline solution, it is necessary to make clear the rate of reactions of iodine dissolved in aqueous solution. Unfortunately there is no reliable data about this matter available at present, especially for dilute alkaline solution.

**Experimental Procedure**

A concentration relaxation method was employed in the present experimental investigation. Two solutions, different in iodine concentration but kept at the same temperature, were suddenly mixed in a desired ratio by sucking them into an injection-syringe type reactor. During this operation, an effort was made to allow no gas phase to remain in the reactor. Then, the reactor was set in a constant-temperature chamber kept at the same temperature. Liquid samples were carried off from the reactor for analysis at a desired time interval.

The experiments were performed at 10, 25 and 40°C. The fluctuation of temperature was within ±0.5°C. The total iodine and sodium hydroxide concentrations used in the experiments were 1.39×10⁻³ to 1.89×10⁻³ g-atom/l and 1.00×10⁻³ g-mol/l, respectively. The preparation of reagents for experiments and the method of analysis are the same as those in the previous papers¹,²,³.

**Results and Discussion**

An illustration of the experimental results is shown in Fig. 1(a). In this run, a solution which has [NaOH]=10⁻³ g-mol/l and [ΣI]=3.60×10⁻³ g-atom/l was mixed at 40°C with an equal volume of solution which has [NaOH]=10⁻³ g-mol/l and [ΣI]=0, where [ΣI] is total g-atoms of iodine per liter of aqueous phase. Measurements of the concentrations of participating species were started 1 min after the beginning of the reaction and their values were plotted against time in Fig. 1. These points are somewhat scattered and do not give a good balance of both the material and the electric charge. So, taking the material balance and the electroneutrality into consideration, these points were smoothed by the dotted lines shown in Fig. 1(a).

Now, if all of the reactions in the aqueous phase are very rapid, concentrations of all species should be constant and independent of the lapse of time, because an equilibrium is reached as soon as the two solutions are mixed. However, the observed values in Fig. 1(a) show a definite change with the lapse of time.

On the other hand, if all of the reactions are very slow, the initial concentrations should be close to the values which are calculated from the assumption that no reaction takes place when two solutions are mixed. These calculated initial concentrations are shown by arrows in the figure. However, it is difficult to consider that the observed concentrations at the earliest time (1 min) may result from the initial concentrations shown by arrows. But the only exception is observed for IO₃⁻, whose earliest concentration coincides with the value pointed by the arrow.

Further, it is noteworthy that a large quantity of HIO exists in the early period of the reactions, even though the quantity of HIO is negligibly small at the equilibrium state.

From the observations mentioned above, it can be expected that only the reaction of formation of IO₃⁻ is a slow one and that the other reactions are relatively rapid.

From the facts mentioned above and also described in the previous reports¹,²,³, the important reactions of iodine in aqueous phase are considered to be the following three.

\[
\begin{align*}
\text{I}_2 + \text{H}_2\text{O} &\rightleftharpoons \text{HIO} + \text{I}^- + \text{H}^+ \quad K_1 = \frac{[\text{HIO}][\text{I}^-][\text{H}^+]}{[\text{I}_2]} \quad (1) \\
3\text{HIO} &\rightleftharpoons \text{IO}_3^- + 2\text{I}^- + 3\text{H}^+ \quad K_2 = \frac{[\text{IO}_3^-][\text{I}^-]^2[\text{H}^+]^3}{[\text{HIO}]^3} \quad (2) \\
\text{I}_2 + \text{I}^- &\rightleftharpoons 2\text{I}_3^- \quad K_3 = \frac{[\text{I}_3^-][\text{I}^-]}{[\text{I}_2]^{1.5}} \quad (3)
\end{align*}
\]

The dissociation reactions of water and sodium hydroxide have to be taken into account.

\[
\begin{align*}
\text{H}_2\text{O} &\rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_4 = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (4) \\
\text{NaOH} &\rightleftharpoons \text{Na}^+ + \text{OH}^- \quad K_5 = \frac{[\text{Na}^+][\text{OH}^-]}{[\text{NaOH}]} \quad (5)
\end{align*}
\]
It can be safely assumed that NaOH dissociates completely.

Although the concentrations measured at any instant appearing in Fig. 1(a) were at nonequilibrium conditions, the values of $K_1$, $K_2$ and $K_3$ were tentatively calculated by substituting the observed values of the concentrations into Eqs. (1), (2) and (3). The results are shown in Fig. 1(b), wherein the activity coefficients of ions were calculated in the same way described in the previous papers.5 The calculated values of $K_1$ and $K_3$ are almost constant and independent of time. Moreover, the values of $K_2$ are in good agreement with that obtained in the previous paper and the values of $K_1$ almost agree with those reported in the literature. The calculated values of $K_2$, however, make extensive changes with time.

Eigen et al.4 have reported that the reaction rate of HIO formation is expressed as $(2.1+10^{10} \times [\text{OH}^-]) \text{[L]} \text{g-mol/l-sec}$ at 20°C and that the rate of I$_2$ formation is much more rapid than that of HIO formation. Taking the result reported by Eigen et al. into consideration, the half-value period of HIO formation is shorter than 0.1 sec under the experimental conditions of the present work. On the other hand, the half-value period of the consumption rate of HIO is longer than a few minutes as observed in Fig. 1(a). Therefore, when two solutions which have different concentrations of iodine are mixed in the usual way employed in an investigation of a normal homogeneous liquid-phase reaction, it can safely be considered that the mixing time is short enough compared with reaction time. Consequently, in the present investigation, it is taken that reactions (1) and (3) are instantaneous and reaction (2) proceeds slowly. The plotted points at $t=0$ in Fig. 1(a) are the concentrations calculated on the assumption that the reactions (1), (3), (4) and (5) reach equilibrium instantaneously but the reaction (2) does not proceed at all. It is quite acceptable to consider that these values will give the initial concentrations to be observed, if possible, in the relaxation method. Therefore, it was concluded that the reactions (1), (3), (4) and (5) will take place instantaneously and soon these reactions will be followed by the slow reaction of I$_2^-$ formation.

Equation (2), however, is not an elementary reaction for the formation of I$_2^-$ . Although many investigators have studied the reaction of formation of I$_2^-$, BrO$_3^-$ or ClO$_3^-$ and several complicated mechanisms have been constructed with many elementary reactions in their investigations, there has been no generally acceptable conclusion about the mechanism. Further, none of the mechanisms proposed hitherto can explain the experimental results of the present work.

This investigation is a part of a series whose aim is the estimation of the decontamination effect of iodine by alkaline containment spray liquor during a maximum accident in a boiling- or pressurized-water reactor. It is most important, from this point of view, to estimate the contribution of the chemical reaction resistance in aqueous phase to the overall absorption rate of iodine and also its temperature dependency. It is favorable for the estimation of the overall absorption rate of iodine that the consumption rate of HIO can be expressed in a form as simple as possible.

Figure 2 shows the plots of the reciprocal of the concentration of HIO against time. The observed values are located along straight lines with different slopes for different temperatures.

As a first approximation, the overall consumption rate of HIO was considered to be expressed by the following equation.

$$-\frac{d[HIO]}{dt} = k[HIO]^2$$  \hspace{1cm} (6)

The consumption rate of HIO should be equal to three times the rate of I$_2^-$ formation to meet the mass balance. Reaction rate constants determined from the slopes of the straight lines in Fig. 2 are plotted against the reciprocal of temperature in Fig. 3. The following equation is obtained from the straight line appearing in Fig. 3.

$$k = 4.29 \times 10^{11} \exp(-12000/RT)$$  \hspace{1cm} (7)

The change of concentration of each chemical
species participating was calculated, assuming that reactions (1), (3), (4) and (5) maintain an equilibrium state at any instant and that reaction (2) proceeds at the rate expressed by equations (6) and (7). An illustration is shown by solid lines in Fig. 1 (a), where it can be seen that the observed values agree well with the calculated ones.

Reactions (1), (3), (4) and (5) can be treated as instantaneous reversible reactions under the experimental condition of this work. However, it may be observed in the experiments where a time period so short as the order of milliseconds comes into question that the rate of reaction (1) is slightly slower than those of reactions (3), (4) and (5), as reported by Eigen et al.\(^4\).

Conclusion

Reactions of iodine in aqueous phase were studied by a concentration relaxation method.

From the results of the present investigation and those previously reported\(^3\), it was concluded that the mechanism of the absorption of iodine in air by an aqueous sodium hydroxide solution is as follows: (Step 1) Molecular iodine in air dissolves into the aqueous phase through the gas-liquid interface according to Henry's law. (Step 2) Instantaneous reversible reactions (1), (3), (4) and (5) take place in the aqueous phase and HIO, I\(^-\) and I\(^2\)\(^-\) form. (Step 3) HIO formed by reaction (1) is consumed gradually by reaction (2) and IO\(^3\)\(^-\) forms, while reactions (1), (3), (4) and (5) are in equilibrium state at any instant.

Overall rate of reaction (2) can be approximated by the second order rate equation, that is, Eq. (6) whose reaction rate constant is given by Eq. (7).