TABLE I

OXIDATION OF IODIDE ION BY ATOMIC HYDROGEN

| KI, *M* | $H_2SO_4$, *N* → 0.64 | 0.4 | 0.2 | 0.13 | 0.056 | 0.032 |
|---|---|---|---|---|---|---|
| 0.6 | 1.75 ± 0.13 | 1.4 ± 0.09 | 0.71 ± 0.12 | 0.48 ± 0.07 | 0.21 ± 0.05 | 0.13 ± 0.04 |
| .3 | 1.6 ± .14 | 1.28 ± .11 | 0.68 ± .14 | .44 ± .05 | .22 ± .04 | .13 ± .04 |
| .15 | 1.2 ± .05 | 0.98 ± .10 | .52 ± .08 | .38 ± .05 | .18 ± .03 | .10 ± .02 |
| .06 | 0.78 ± .12 | .61 ± .08 | .41 ± .11 | .29 ± .04 | .12 ± .02 | .06 ± .01 |
| .03 | .48 ± .09 | .45 ± .08 | .24 ± .04 | .19 + .02 | .048 ± .015 | .032 ± .01 |
| .012 | .32 ± .05 | .31 ± .04 | .12 ± .03 | .05 ± .01 | .033 ± .013 | .025 ± .002 |
| .006 | .09 ± .03 | .09 ± .02 | — | .025 ± .006 | — | — |

reaction vessel, which was made of Pyrex glass, and light shields were placed between the two vessels. The outer face of the reaction vessel was blackened. The inner bubbler tube itself was made of glass opaque to light below 3000 Å. and there were bends of 90° along the bubbler tube to prevent reflected ultraviolet light from the discharge reaching the solution. Blank experiments were carried out with solutions of 0.6 *M* KI in 0.64 *N* $H_2SO_4$, with the discharge in operation but without the $H_2$ being pumped along. No oxidation could be detected. When the discharge was operated and the $H_2$ was pumped so that instead of passing through the solution it was passed over its surface only, the oxidation rate obtained was 1% of that obtained under full operating conditions. Thus we conclude that the oxidation observed in our normal experimental conditions is not caused by light. No oxidation was observed when $H_2$ was bubbled through the solution without the discharge being operated. For our regular experiments, with the solution in the reaction vessel, the system was evacuated and without discharge $H_2$ passed through the solution for 10 minutes. Traces of $I_2$ formed by thermal oxidation were thus carried off. Only then was the discharge switched on and the trap beyond the reaction vessel immersed in liquid air, to retain the $I_2$ formed in the reaction vessel. Control experiments using $I_2$–KI solution, containing up to $10^{-3}$ mole/l. $I_2$ in the reaction vessel showed, that sweeping in this manner, not less than 90% of the $I_2$ was retained in $T_3$. The concentration of $I_2$ remaining in the reaction vessel in our experiments did not exceed 5 × $10^{-7}$ mole/l. For each experiment 25 ml. of solution was used. The reaction vessel was always maintained at 5 ± 3°. The discharge was operated for 5 minutes. After this the iodine in the trap was dissolved in 25 ml. of 0.06 *M* KI, and appropriately diluted for analysis with KI solution.

**Analysis.**—Iodine was determined at 3500 Å. using 1 cm. cells in a Beckman Model B spectrophotometer. We found the absorption coefficient of $I_2$ in 0.06 *M* KI at 20°, $\epsilon$ 25000 l. mole$^{-1}$ cm.$^{-1}$.

**Materials.**—The KI used was C.P. The $H_2SO_4$ was B. D.H. Reagent Grade. The water used was triply distilled, ordinary distilled water being redistilled from alkaline permanganate and phosphoric acid in an all-glass still. The $H_2$ was Matheson's Electrolytic. It was further purified by passage over palladized asbestos at 400°.

**Reproducibility of Results.**—Every experimental value represents the average of 4–10 separate runs. Values are given with the appropriate standard deviations. The reproducibility is comparable with that obtained by Littman, *et al.*[13] and is now somewhat better than that obtained by Davis, *et al.*,[7] or by ourselves previously.[8]

## Experimental Results and Their Evaluation

Using constant pressure, discharge and flow conditions and thus a constant dose of H atoms, the concentration of iodide ions and hydrogen ions in the solution was varied. The experimental results are summarized in Table I.

The quantity of H atoms reaching the solution is low enough (∼ 2 × $10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$) to assume that practically all H atoms reaching the solution will react within it, and that there will be in this respect no solubility limitation which may be *p*H dependent. We tested for and could not detect any H atoms in the gas leaving the solution. We do not assume equilibrium with the gas phase, regarding H atoms.

Irrespective of its actual mechanism, the formation of $I_2$ may be represented by assuming I atom formation

$$I^- + H + H^+ \longrightarrow I + H_2$$

The I atoms yield $I_2$ and $I_3^-$ by [14]

$$I + I^- \rightleftarrows I_2^-$$
$$2I \longrightarrow I_2$$
$$I + I_2^- \longrightarrow I_3^-$$
$$2I_2^- \longrightarrow I_3^- + I^-$$

Under our experimental conditions the concentration of $I^-$ is much greater than of I, $I_2^-$, $I_3^-$ or of $I_2$, which is constantly swept out by the gas stream. We neglect any competitive back reactions and assume that every I atom formed yields finally $^1/_2 I_2$. We shall assume that we may treat our system on the basis of homogeneous kinetics and shall apply the steady-state assumption for transient species occurring in the system.

Our results show that H atoms oxidize iodide ions, the yield depending on $[H^+]$ and $[I^-]$. The quantitative dependence on these factors enables us to differentiate amongst several possible mechanisms.

Let us denote by *A* moles l.$^{-1}$sec.$^{-1}$ the rate of introduction of H atoms into the solution, and by $k_1$ the rate constant of the recombination process

$$2H \xrightarrow{k_1} H_2 \qquad (1)$$

Uri[15] considered the possibility of the oxidation of inorganic ions in aqueous solution by H atoms through H atom transfer from the hydration layer of the ion. This mechanism was applied by Lefort and Douzou[16] to interpret the photochemistry of ferrous ions. In this case the oxidation will proceed by what we denote as mechanism I.

$$I^-{\cdot}H_2O + H \xrightarrow{k_2} I + OH^- + H_2 \qquad (2)$$

Steady-state treatment for H atoms gives

$$d[H]/dt = A - k_1[H]^2 - k_2[H][I^-] = 0$$

and *Y* — the yield of iodine is

$$Y = d\left[\frac{1}{2}\ I_2\right]/dt = k_2[H][I^-] =$$
$$\{(k_2[I^-])^2/2k_1\}\left\{\left(1 + \frac{4k_1A}{(k_2[I^-])^2}\right)^{1/2} - 1\right\} \qquad (a)$$

According to this mechanism the yield is independent of *p*H and should increase with increasing

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(13) F. E. Littman, E. M. Carr and A. P. Brady, *Rad. Research*, **7**, 107 (1957).

(14) L. I. Grossweiner and M. S. Matheson, THIS JOURNAL, **61**, 1080 (1957).

(15) N. Uri, *Chem. Revs.*, **50**, 376 (1952).

(16) M. Lefort and P. Douzou, *J. chim. phys.*, **53**, 536 (1956).

$[I^-]$ to the same limiting value, which equals $A$, at all pH values. Neither of these conditions is fulfilled experimentally and so mechanism I is excluded.

The second mechanism proposed[17,7] postulates oxidation through a triple collision between H, $H^+$ and $I^-$

$$I^- + H + H^+ \xrightarrow{k_3} I + H_2 \qquad (3)$$

so that

$$d[H]/dt = A - k_1[H]^2 - k_3[H][H^+][I^-] = 0$$

and

$$Y = \{(k_3[H^+][I^-])^2/2k_1\}\left\{\left(1 + \frac{4k_1A}{(k_3[H^+][I^-])^2}\right)^{1/2} - 1\right\} \qquad \text{(b)}$$

In this case the yield does depend on both $[H^+]$ and $[I^-]$, being a function of the product $[H^+][I^-]$. However, it should be constant for a constant value of the product, and should tend to the asymptotic value of $A$ whether the value of the product is increased by increasing $[H^+]$ or $[I^-]$.

We have also considered the possibility of oxidation through the interaction of an H atom with some complex formed between $I^-$ and $H^+$.[15] The investigation of the absorption spectra of $I^-$ in acid solution[18] did not yield any evidence for the existence of such a species. The kinetic scheme would in this case be

$$H^+ + I^- \underset{k_4'}{\overset{k_4}{\rightleftarrows}} H^+ \ldots I^- \qquad (4)$$

$$H^+ \ldots I^+ + H \xrightarrow{k_5} H_2 + I \qquad (5)$$

When $k_4\,[H^+][I^-] >> k_5\,[H^+ \ldots I^-][H]$ the concentration of the complex will be determined by equilibrium 4, and the yield will be a function of the product $[H^+][I^-]$ once again. When the concentration of the complex is low

$$d[H]/dt = A - k_1[H]^2 - k_5[H][H^+ \ldots I^-] = 0$$

$$d[H^+..I^-]/dt = k_4[H^+][I^-] - (k_4' + k_5[H])[H^+..I^-] = 0$$

and this third mechanism leads to the same asymptotic trend as the second one, depending on the product $[H^+][I^-]$ alone.

The plot of our experimental results according to this test is presented in Fig. 1. A unified curve is not obtained except at the lowest $I^-$ and $H^+$ concentrations. At higher concentrations a large divergence is observed. Thus mechanism II and III are inadequate for the interpretation of the experimental results.

We shall show however that the results are consistent with mechanism IV, involving the intermediate formation of the $H_2{}^+{}_{aq}$ ion. This mechanism, proposed by Weiss[1] and applied in detail previously,[2] is based on a charge transfer reaction between $I^-$ and $H_2{}^+$.

$$H + H^+ \underset{k_6'}{\overset{k_6}{\rightleftarrows}} H_2{}^+ \qquad (6)$$

$$H_2{}^+ + I^- \xrightarrow{k_7} H_2 + I \qquad (7)$$

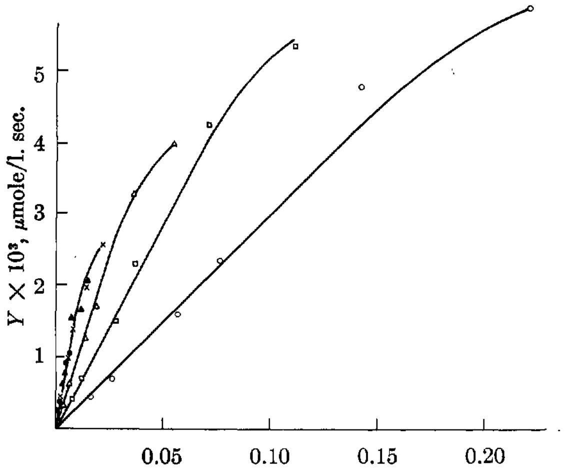

Fig. 1.—Dependence of the yield on the concentration product $[I^-][H^+]$. Experimental points: ○, 0.6; □, 0.3; △, 0.15; ×, 0.06; ▲, 0.03; ●, 0.012; ■, 0.006 $M$ $[I^-]$.

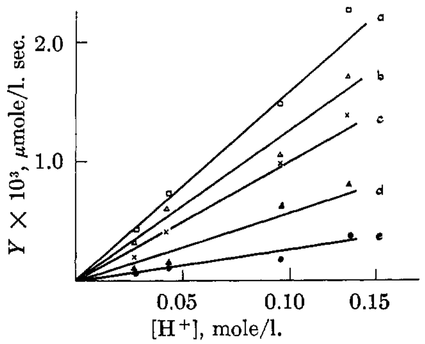

Fig. 2.—Dependence of the yield on $[H^+]$ at low and intermediate $[I^-]$ and $[H^+]$. Notation as in Fig. 1. (a) 0.3; (b) 0.15; (c) 0.06; (d) 0.03; (e) 0.012 $M$ $[I^-]$.

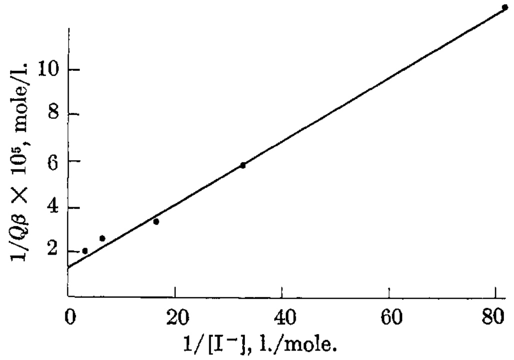

Fig. 3.—Graphical determination of $\beta$.

Steady-state treatment for H and $H_2{}^+$ leads to

$$d[H_2{}^+]/dt = k_6[H][H^+] - (k_6' + k_7[I^-])[H_2{}^+] = 0$$
$$d[H]/dt = A - k_1[H]^2 - k_6[H][H^+] + k_6'[H_2{}^+] = 0$$

thus

$$Y = \alpha\beta^2[H^+]^2 \left\{\left(1 + \frac{2A}{\alpha\beta^2[H^+]^2}\right)^{1/2} - 1\right\} \qquad \text{(c)}$$

where $\alpha = k_6{}^2/2k_1$ and $\beta = [I^-]/((k_6/k_7) + [I^-])$. This mechanism thus also predicts the dependence of the yield on both $[H^+]$ and $[I^-]$ but in a manner different to mechanisms II and III. Namely at constant $[H^+]$ the yield increases with increasing $[I^-]$ to the limiting value of

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(17) J. P. Ethier and F. Haber, *Naturwiss.*, **18**, 266 (1930).

(18) G. Stein and A. Treinin, to be published.

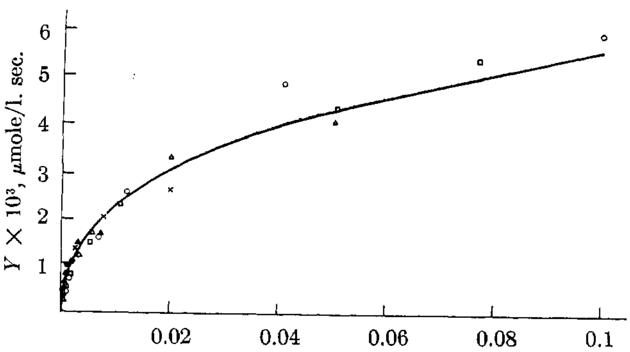

Fig. 4.—Dependence of the yield on $(\beta[H^+])^2$. Notation as in Fig. 1. Curve, calculated.

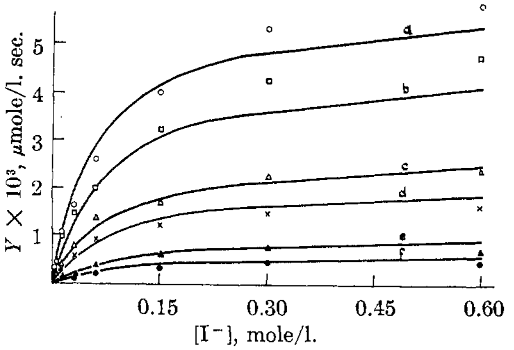

Fig. 5.—Dependence of the yield on $[I^-]$ at different $[H^+]$: (a) ○, 0.64; (b) □, 0.4; (c) △, 0.2; (d) ×, 0.13; (e) ▲, 0.056; (f) ●, 0.032 $N$ $H_2SO_4$. Curves, calculated.

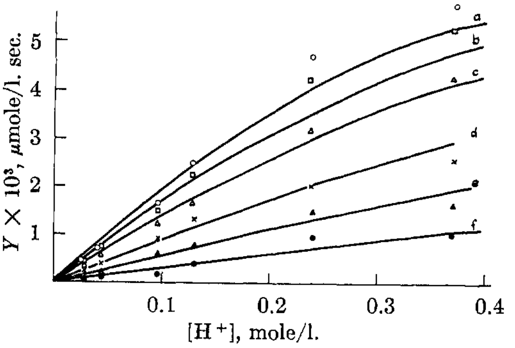

Fig. 6.—Dependence of the yield on $[H^+]$ at different $[I^-]$. Notation as in Fig. 1. Curves, calculated. (a) 0.6; (b) 0.3; (c) 0.5; (d) 0.06; (e) 0.03; (f) 0.012 $M$ $[I^-]$.

$$Y = \alpha[H^+]^2 \left\{\left(1 + \frac{2A}{\alpha[H^+]^2}\right)^{1/2} - 1\right\}$$

when $\beta \rightarrow 1$. Only at high $[H^+]$, where $2A/\alpha[H^+]^2 << 1$, does the limiting yield tend to the value of $A$. Thus in this case an asymptotic value of the yield achieved at constant $[H^+]$ by increasing $[I^-]$, does not necessarily mean the complete utilization for oxidation of all H atoms entering the solution. At low $[H^+]$ the limiting yield at high $[I^-]$ is determined by the rate of formation of $H_2^+$, while at low $[I^-]$ the rate-determining step is the oxidation by $H_2^+$.

In mechanism IV the yield depends on the product $([H^+]\beta)$ only. When both $[I^-]$ and $[H^+]$ are low, the yield approaches $Y = (k_7/k'_6)(2\alpha A)^{1/2} [H^+][I^-]$, in agreement with the results of Fig. 1.

We can now estimate the value of $(k'_6/k_7)$. At relatively low $[H^+]$, $Y = Q\beta[H^+]$, where $Q = (2\alpha A)^{1/2}$. Plotting $Y$ *versus* $[H^+]$ at constant $[I^-]$, at low $[H^+]$ we can obtain (Fig. 2) the value of $Q\beta$. Then plotting $1/Q\beta$ *versus* $1/[I^-]$ (Fig. 3) we obtain from the ratio of slope to intercept, $(k'_6/k_7) = 0.1 \pm 0.02$ mole l.$^{-1}$ and from the intercept $\alpha A = 3.1 \pm 0.3 \times 10^{-11}$ sec.$^{-2}$. Hence $\beta = [I^-]/(0.1 + [I^-])$.

To test the correctness of mechanism IV in Fig. 4 the yield is plotted as a function of the product $(\beta[H^+])^2$. It will be seen that within the entire experimental region a good fit with a single curve is obtained, and no dependence on $[H^+]$ or $[I^-]$ alone is observed. The best agreement with the experimental results was obtained by setting $\alpha = 1.2 \times 10^{-5}$ l. mole$^{-1}$ sec.$^{-1}$ and $A = 2.6 \times 10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$.

Using these values, we could now calculate theoretical curves to represent the dependence of the yield on $[H^+]$ and on $[I^-]$. In Fig. 5 and Fig. 6 our experimental results are plotted and the calculated theoretical curves drawn. Good agreement (within about 10% difference at most) is obtained.

From the value of $\alpha$ obtained from Fig. 4 the rate constant of the formation of $H_2^+$, $k_6$, can be calculated. $k_1$, the rate constant of the H atom recombination, is[10] of the order of $10^{10}$ l. mole$^{-1}$-sec.$^{-1}$. In aqueous solution at $p$H 2 Friedman and Zeltman found a value of only $10^8$ liter mole$^{-1}$-sec.$^{-1}$ for "$k_1$". We proposed[8] an explanation for this, according to which "$k_1$" of Friedman and Zeltman is a composite constant. Taking this uncertainty into account $k_6$ has a value of 50–500 l. mole$^{-1}$sec.$^{-1}$. This value is in agreement with the value of about 200 l. mole$^{-1}$ sec.$^{-1}$ which can be derived from the work of Friedman and Zeltman,[10] as will be discussed later.

## Discussion

Our experimental results are thus consistent only with the mechanism of oxidation involving the intermediate formation of $H_{2aq}^+$, which is the actual oxidizing species. It remains to be seen whether other experimental results in systems where reactions of H atoms in solution are postulated, support or contradict this conclusion.

**(a) $p$H Dependence of the Oxidation by H Atoms.**—It was shown[8] that the oxidation of $Fe^{2+}$ by H atoms proceeds by a $p$H dependent mechanism. The yield was nearly constant in the $p$H region of 0.4–1.3, whilst above $p$H 1.7 a sharp drop in yield occurred. The careful reinvestigation of the radiation induced oxidation in air-free ferrous sulfate solutions in which $H_2^+$ was assumed as an intermediate, indicates[3] that up to $p$H 2.1 the $p$H dependence of the yield can be adequately explained by assuming that it is due to the $p$H dependence of the primary yield of H atoms. Rigg and Weiss[19] found the photochemical oxidation of ferrous sulfate in air-free solution to be $p$H dependent, and assumed a mechanism involving $H_2^+$. Photochemical experiments carried out in our laboratories[20] confirm these results, rather than

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(19) T. Rigg and J. Weiss, *J. Chem. Phys.*, **20**, 1194 (1952).

(20) J. Jortner and G. Stein, to be published.

those of Lefort and Douzou.[16] However, we found that the $p$H dependence of the quantum yield is largely due to the effect of $p$H on the primary formation of H atoms.

Similarly, the photochemical oxidation of $I^-$ was found by Rigg and Weiss[5] to be $p$H dependent in the absence of $O_2$. They attributed this $p$H dependence to be due to $H_2^+$, formed in competition with the efficient back reaction between H and I. The primary photochemical formation of H they considered to be $p$H independent, according to the Franck–Haber mechanism. However, Farkas and Farkas[21] and Platzman and Franck[22] indicated that the primary photochemical formation of H may also be $p$H dependent.

If so, the different region of $p$H dependence due to $H_2^+$ observed by us in our work using H atoms externally generated and by, *e.g.*, Allen and Rothschild, who also assume $H_2^+$ as the active intermediate is determined by the steady-state concentration of the H atoms. The higher this concentration, the lower the $p$H at which pronounced competition between oxidation and recombination will be observed. In the experiments with radiation chemistry[3] the rate of formation of H atoms is $\sim 3 \times 10^{-8}$ mole $l.^{-1}sec.^{-1}$; in our experiments it is about 100-fold higher. In our work on the oxidation of $Fe^{2+}$ $p$H dependence is observed some one $p$H unit lower than in the radiation chemistry. Thus experiments performed under different conditions are self-consistent in this respect.

(b) **Competitive Reactions.**—Evidence derived from the investigation of competition between $Fe^{2+}$ and scavengers such as $O_2$ methanol for H atoms[3,9] showed that the ratio of the rate constants is not $p$H dependent. These results can be explained by assuming that $H_2^+$ ions react with these scavengers.

(c) **Investigations Using Isotope Exchange.**—The evidence obtained from work on the radiation induced hydrogen–deuterium exchange in aqueous solution[10,23] indicated the absence of chain propagated exchange reactions in acid solution. This was held to exclude the possibility of $H_2^+$ being present in significant concentrations,[7] Friedman and Zeltman[10] came to the conclusion that this absence of fast exchange could be explained on the basis of an acid prompted reaction only if the rate of formation of $H_2^+$ is as slow as about 200 l. $mole^{-1}sec.^{-1}$. We have shown that this value is in agreement with the rate constant obtained by us by a completely different method. Thus the existence of $H_2^+$ does not necessarily contradict the results of the isotopic exchange reactions. The slowness of its formation prevents it being a path for a fast and efficient isotopic exchange.

Thus the experimental results of this paper show that oxidation by H atoms in acid solution may proceed by a mechanism involving $H_2^+$; this is consistent with the available experimental evidence from other fields.

One of our conclusions is that $H_2{}^+{}_{aq}$ is not in rapid equilibrium with H and $H^+{}_{aq}$; $k_6$ is relatively slow. No reliable estimation of $k'_6$ or of the $pK$ of $H_2^+$ is possible at present.

The proof of the role of $H_2{}^+{}_{aq}$ as the actual oxidizing species in acid solutions where H atoms occur would account for a number of phenomena, which are difficult to explain otherwise. Thus Ives[24] very recently summarized the evidence to show that a number of reactions where H atoms are formed at an electrode receive their best explanation by assuming that in this case too it is the $H_2{}^+{}_{aq}$ ion as such that is the actual reactive species formed from H atoms.

**Acknowledgment.**—This work was partly supported by grant from the Israel Atomic Energy Commission.

## Appendix

**The Application of the Steady-state Treatment to a Kinetic System where an Active Reactant is Generated at a Constant Rate.**—The adequacy of the application of the steady-state approximation to our system where hydrogen atoms are formed at a constant rate and homogeneously distributed in the solution is shown. In the absence of a scavenger for the hydrogen atoms the kinetic equation will be presented by

$$\frac{d[H]}{dt} = A - k_1[H]^2 \qquad (A1)$$

The exact solution of this equation is

$$[H] = \left(\frac{A}{k_1}\right)^{1/2} \frac{\exp\{2(k_1A)^{1/2}t\} - 1}{\exp\{2(k_1A)^{1/2}t\} + 1} \qquad (A2)$$

Hence the concentration of the hydrogen atoms will tend to a stationary value

$$[H]_s = (Ak_1^{-1})^{1/2} \qquad (A3)$$

Under our experimental conditions $A \sim 2 \times 10^{-6}$ mole $l.^{-1}sec.^{-1}$, $k_1 = 10^{10}$ $mole^{-1}$ $l.^{-1}$ $sec.^{-1}$ and thus $[H]_s \sim 10^{-8}$ mole $l.^{-1}$. This steady state concentration will be reached after a time given by the condition

$$t_c >> (4k_1A)^{-1/2}\, 10^{-2} \text{ sec.} \qquad (A4)$$

which is much smaller than the duration of our experiments (~10 min.).

In the presence of a scavenger S for hydrogen both the steady-state concentration and $t_c$ are lower than in the former case. The kinetic equation is

$$\frac{d[H]}{dt} = A - k_1[H]^2 - k_s[S][H] \qquad (A5)$$

This differential equation can be integrated leading to the final result

$$[H] = \frac{(4Ak_1 + k_s^2[S]^{1/2}[F + 1) - k_s[S](F - 1)}{2k_1(F - 1)} \qquad (A6)$$

where

$$F = \frac{k_s[S] + (4Ak_1 + k_s^2[S]^2)^{1/2}}{k_s[S] - (4Ak_1 + k_s^2[S]^2)^{1/2}} \exp(4Ak_1 + k_s{}^2[S]^2)^{1/2}t$$

The stationary concentration is

$$[H]_s = \left(\frac{A}{k_1} + \frac{k_s^2[S]^2}{4k_1^2}\right)^{1/2} - \frac{k_s[S]}{2K_1} \qquad (A7)$$

and will be obtained after a period when

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(21) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

(22) R. Platzman and J. Franck, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

(23) S. Gordon and E. J. Hart, *J. Am. Chem. Soc.*, **77**, 3981 (1955).

(24) D. J. G. Ives, *Can. J. Chem.*, **37**, 213 (1959).

$$F >> 1 \tag{A8}$$

which is equivalent to

$$t_e >> (4Ak_1 + k_s{}^2[S]^2)^{-1/2} \tag{A8'}$$

Hence the steady-state treatment to this system appears to be justified since the time taken here to reach it is even shorter than before.

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# PHASE EQUILIBRIA IN THE BINARY SYSTEMS $PuCl_3$–NaCl AND $PuCl_3$–LiCl[1,2]

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Equilibrium diagrams for the binary systems $PuCl_3$–LiCl and $PuCl_3$–NaCl were studied over the temperature range 100–825° by thermal and differential thermal analysis techniques. A single eutectic was observed in each system with no evidence of solid solution or compound formation. The eutectic occurred at 461° and 28 mole % $PuCl_3$ in the $PuCl_3$–LiCl system and at 453° and 36 mole % $PuCl_3$ in the $PuCl_3$–NaCl system. The melting points of LiCl, NaCl and $PuCl_3$ in equilibrium with an atmosphere of anhydrous HCl were 607 ± 2°, 802 ± 2° and 767 ± 2°, respectively. Within experimental error, the same values were obtained for the melting points of these salts under vacuum.

## Introduction

Information concerning the equilibrium diagrams for the binary systems $PuCl_3$–LiCl and $PuCl_3$–NaCl was required for a proposed study of fused salt methods for processing irradiated plutonium–alloy fuels. Since only the melting points of the three compounds have been reported, it was necessary to investigate the entire composition range in both systems. The techniques of thermal and differential thermal analysis were adopted for this work.

Although the terms melting point and freezing point are used synonymously in this paper, all data are based solely on freezing points obtained from cooling curves.

## Experimental

**Materials.**—LiCl was purified in the quartz apparatus shown in Fig. 1. The evacuation–hydrochlorination technique developed by Laitinen, Ferguson and Osteryoung[3] for the preparation of LiCl–KCl eutectic mixtures was adapted for this purpose. The purified salt was then cast in the form of rods 4–14 mm. in diameter and was stored in an atmosphere of dry argon. Since molten commercial LiCl invariably was discolored by a suspension of black particles,[4] it was necessary to filter the salt between the hydrochlorination and casting steps. The equipment was designed so that the entire purification procedure could be carried out without exposure of the LiCl to atmospheric moisture. In a typical procedure, LiCl (Mallinckrodt, analytical reagent grade) was dried by evacuation (0.05–0.1 mm.) at room temperature for a period of 48–72 hr. Evacuation was continued for a 12 hr. period during which the temperature was increased to 400° at 0.5°/min. Anhydrous HCl was then admitted at a flow rate of 3 l./hr. through the filter tube embedded in the powder as shown in Fig. 1, and the temperature was raised to 650° at 1°/min. The salt melted at ~607°. The flow of HCl was continued for 30 min., after which argon was bubbled through the melt for 5 min., and the system was evacuated. Argon pressure was then used to force part of the molten salt successively into the filter tube and into the casting tube. The filled casting tube was raised to the cooler upper region of the filter tube to permit the LiCl to solidify completely. Additional castings were made by exchanging casting tubes. To prevent the entry of air during this exchange, a positive pressure of argon was maintained in the filter tube. The system was then evacuated, and the procedure was repeated. After their removal, the filled casting tubes were sealed with a torch and were stored in an atmosphere of dry argon.

Two modifications of the LiCl purification procedure were also tested. In one modification, LiCl prepared by the procedure described above was distilled under vacuum at 750°; in the other, commercial analytical reagent grade LiCl was recrystallized from aqueous solution prior to the evacuation–hydrochlorination–filtration procedure. Qualitative spectrographic analyses were obtained for samples of each product. The results are given in Table I.

Table I

Qualitative Spectrographic Analyses of Purified LiCl Samples

| Element | Filtered LiCl, % | Filtered and distilled LiCl, % | Recrystallized and filtered LiCl, % |
|---|---|---|---|
| Na | ~0.1 | ~0.1 | 0.01–0.1 |
| Mg | ~ .01 | < .001 | ND[a] |
| Ca | ~ .01 | < .001 | .001– .01 |
| Si | < .001 | < .001 | < .001 |
| Fe | 0.001–0.01 | 0.001–0.01 | .001– .01 |
| K | ND | 0.001–0.01 | ND |

[a] ND = not detected. Other elements not detected: Ag, Al, B. Ba, Be, Bi, Cd, Co, Cu, Cr, In, Mn, Mo, Ni, P, Pb, Sb, Sn, Sr, Ti, V, Zn, Zr.

A significant result of the purification procedure, in addition to the removal of carbonaceous material, was the elimination of constituents which promoted etching of the quartz containers. Purified LiCl could be held in quartz vessels under dry HCl or argon for several days at 650° with no appreciable effect on the vessels. Molten LiCl which had been dried at room temperature but which had not been treated with HCl etched the quartz vessels severely within a few hours. Corrosion was most pronounced on surfaces immediately above the melt.

$PuCl_3$ was prepared from plutonium hydride by reaction with anhydrous HCl at 450°. The hydride was obtained by reacting pure plutonium metal with hydrogen at about 200°. Since $PuCl_3$ prepared in this manner may still contain small amounts of oxide, hydride or unreacted metal, the $PuCl_3$ used in these experiments was subjected to further treatment. Anhydrous HCl was passed through the $PuCl_3$ powder in the quartz apparatus shown in Fig. 1 as the temperature was increased to 800° at 2–4°/min. The stream of HCl was bubbled through the molten salt at 800° for 45 min., after which the $PuCl_3$ was filtered and cast by the same procedure used in the LiCl preparation. Analytical data for

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[1] Presented at the 135th meeting of the American Chemical Society in Boston, April, 1959.

[2] This work was done under the auspices of the Atomic Energy Commission.

[3] H. A. Laitinen, W. S. Ferguson and R. A. Osteryoung, *J. Electrochem. Soc.*, **104**, 516 (1957).

[4] Some tiny black specks could also be observed in unopened bottles of analytical reagent grade LiCl. Suspensions of black particles observed in molten LiCl-KCl mixtures by C. T. Brown, H. J. Gardner, C. Solomons and G. J. Janz (NP-6483, Oct., 1957) were attributed to organic impurities which they suggested might decompose with heat in the same manner as sugar to give carbon and water.