was prepared within one hour of any run. That this precaution was adequate was shown by the complete absence of characteristic colors in all solutions except those containing *p*-anisidinium chloride. To estimate the effect of oxidation on K_A, one solution of *p*-toluidinium chloride in 82% dioxane was allowed to stand for one week. The K_A value for this solution was 20% greater than for the freshly prepared solution.

Additional details have been described in previous publications from this Laboratory.[6a,7]

K_A Values by the Differential Method.—We used a two-point method quite similar to that used by Gutbezahl for 95% ethanol.[22] However, our method of calculating K_A was different. We used the expression

$$c'_H/c''_H = Z'/Z'' \qquad (11)$$

where c'_H/c''_H is the potentiometrically determined ratio of lyonium ion concentrations at the two experimental points where the degrees of neutralization are ϵ' and ϵ'' and the formal amine concentrations are c' $(= c'_B + c'_{BH})$ and c'' $(= c''_B + c''_{BH})$. The function Z is equal to

$$(\epsilon - 1)c - K_A + [(\epsilon - 1)^2c^2 + 2K_Ac(1 + \epsilon) + (K_A)^2]^{1/2} \qquad (12)$$

and is evaluated at the two experimental points for various assumed values of K_A. The correct value of K_A is that for which $c'_H/c''_H = Z'/Z''$.

Equations 3 and 4 are derived from the more fundamental expression[9b]

$$c_H[c_H - (\epsilon - 1)c]/[\epsilon c - c_H] = K_Ay_{BH}/y_By_H = K'_A \qquad (13)$$

on the assumption that $y_{BH}/y_By_H = 1.00$. At the ionic strengths and concentrations used in our experiments (<0.012 *M*), this assumption seemed to be justified in view of the charge type of the acid and was corroborated by the absence of significant drifts in the calculated K_A values.

K_A Values by the Half-Neutralization Method.—The standard *p*H scale reading $E'_0 = E' + \log a_Ha_{Cl}$ was evaluated for each solvent by means of acids of known K_A value and was then used to calculate c_H values of solutions containing the acids to be studied. For best accuracy, $\epsilon \approx {}^1/_2$ and in our experiments ϵ was between ${}^1/_3$ and ${}^2/_3$. In the required calculations, the rigorous expression (13) was always used. The results were generally satisfactory except for ammonium and trimethylammonium ion in water. For these compounds the apparent pK_A values drifted downward by *ca.* 0.05 unit as sodium hydroxide was added to the cell and ϵ was varied from ${}^2/_3$ to ${}^1/_3$. Since calculation indicated that the amount of $Ag(NH_3)_2^+$ should be small and that silver chloride should be stable relative to silver oxide under the experimental conditions, the drifts could not be explained. Fortunately the drifts were small and disappeared, within the limit of experimental accuracy, in the high-dioxane media. In Table III we have listed the pK_A values obtained for these two compounds in the most acid solutions, at $\epsilon \approx {}^2/_3$, where possible errors due to the use of a glass electrode should be at a minimum. Our pK_A value for ammonium ion is in good agreement with the value 9.246, reported recently by Bates and Pinching.[23]

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[22] Reference 6a, pp. 560–561.

[23] R. G. Bates and G. D. Pinching, THIS JOURNAL, **72**, 1393 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKHAVEN NATIONAL LABORATORY]

Kinetics of Exchange and Disproportionation Reactions in Mercuric Cyanide Solutions[1]

BY RICHARD L. WOLFGANG AND RICHARD W. DODSON

RECEIVED NOVEMBER 13, 1953

The exchange of radioactive mercury between mercuric and mercuric monocyanide ions has been measured and found to be slow. This is in agreement with mechanisms postulated in an earlier study for the exchange reactions between mercurous and mercuric species. The mercuric–mercuric monocyanide exchange proceeds by two paths: (1) A route consistent with a direct bimolecular mechanism, according to the rate law $R_3 = 4 \times 10^7 e^{-11,800/RT}$ $(Hg^{++})(HgCN^+)$ mole-liter^{-1}-min.$^{-1}$; (2) The reactions involved in the disproportionation equilibrium $2HgCN^+ \rightleftarrows Hg^{++} + Hg(CN)_2$. The above disproportionation system has also been studied directly. The equilibrium constant has been determined, $K = (Hg^{++})\cdot(Hg(CN)_2)/(HgCN^+)^2 = 5 \times 10^{-2}$ at 25°. The approach to equilibrium has been followed spectrophotometrically and obeys the rate law $R_{12} = 6 \times 10^{11} e^{-17,000/RT} (Hg^{++})(Hg(CN)_2) - 3 \times 10^{10} e^{-17,000/RT} (HgCN^+)^2$ mole-liter^{-1}-min.$^{-1}$. The value obtained for K has been used to explain the zero-time exchange found in the study of the mercurous–mercuric cyanide exchange. An explanation is offered for the unusual and perhaps unique non-lability of the mercuric mono- and dicyanide complexes.

Introduction

An earlier study[2] of the mercurous–mercuric cyanide exchange showed that this reaction proceeds at a measurable rate which is first order with respect to the mercurous concentration and first order with respect to the mercuric concentration. The results obtained were incompatible with a rapid exchange between mercuric ion and the mercuric monocyanide complex. The latter conclusion was received with some surprise[3] on the basis that *a priori* it seemed unlikely that a species such as $HgCN^+$ should not be in rapid equilibrium with Hg^{++} and CN^- ions.

The present work is a further study of the mercury–cyanide systems and attempts to present a more unified picture of the kinetics of the several interdependent reactions involved. It is interesting that the species $HgCN^+$, referred to above, is not in rapid equilibrium with its constituent ions; and it seemed worthwhile to inquire into the kinetics of its reactions somewhat more closely. Accordingly, the exchange of $HgCN^+$ with Hg^{++} has been directly studied, using a chemical separation of these ions. The conclusion on the slow dissociation of $HgCN^+$ has been confirmed and a more detailed reaction mechanism obtained.

The rate data obtained for the Hg^{++}–$HgCN^+$ exchange indicate that this exchange proceeds not only by a direct bimolecular mechanism

$$Hg^{*++} + HgCN^+ \longrightarrow Hg^{++} + Hg^*CN^+ \qquad (1)$$

but also indirectly by the reactions involved in the disproportionation equilibrium

$$\begin{gathered} Hg^{*++} + Hg(CN)_2 \longrightarrow Hg^*CN^+ + HgCN^+ \qquad (2) \\ Hg^*CN^+ + HgCN^+ \longrightarrow Hg^{++} + Hg^*(CN)_2 \end{gathered}$$

It was therefore desirable to check the kinetics of these disproportionation reactions directly, and it was found possible to do this spectrophotometric-

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[1] Research carried out under the auspices of the Atomic Energy Commission.

[2] R. L. Wolfgang and R. W. Dodson, *J. Phys. Chem.*, **56**, 872 (1952).

[3] A. W. Adamson, *ibid.*, **56**, 876 (1952).

ally. The investigation gave the rate law involved in the above disproportionation equilibrium; and it was possible to use this result to complete the kinetic picture of the Hg^{++}–$HgCN^+$ exchange.

In the course of this work the equilibrium constant of the disproportionation of $HgCN^+$ to give Hg^{++} and $Hg(CN)_2$, as in equations 2, has been measured. The result serves as an explanation of the zero-time exchange found in the mercurous–mercuric cyanide exchange.

Experimental

Materials, Activity and Counting.—The sources, preparation and processing of most of the materials used in these experiments, including the radioactive mercury, Hg^{203}, have been described in a previous paper.[2] The procedures described in that paper for mounting and counting radioactive precipitates were again employed in these studies.

Mercuric dicyanide solution was prepared by mixing the requisite amounts of standardized $Hg(ClO_4)_2$ and NaCN solutions.

Separation of Cyanide-complexed and Uncomplexed Mercury.—A number of reagents were found to precipitate mercuric ion cleanly from solutions as dilute as 10^{-3} *f* while leaving cyanide complexed mercury in solution. These were: 8-hydroxyquinoline, phloroglucinol, anthranilic acid and iodate ion. Of these, the iodate ion separation induces exchange to the smallest extent, though even here the zero-time exchange runs to about 25%. In practice a two- to tenfold excess of 0.025 *f* KIO_3 was added to the system; then the precipitate was filtered, washed with 5×10^{-3} *f* $NaIO_3$, and counted as described previously. Under these conditions the precipitation of Hg^{++} is substantially complete; even at mercuric ion concentration of 5×10^{-4} *M* the separation was found to be greater than 90% effective. A carbon analysis carried out on a specimen precipitate showed that a negligible proportion of $HgCN^+$ was coprecipitated.[4]

Determination of $K = (Hg^{++})(Hg(CN)_2)/(HgCN^+)^2$.—In the determination of K by the precipitation of Hg^{++}, it is necessary to separate a small amount of mercuric iodate precipitate rapidly from a dilute solution, in order to prevent error caused by a shift of the equilibrium. Hg^{203} was used in these experiments so that the relative amounts of mercury in the small precipitates were readily determined by counting. To carry out a run, suitable proportions of $Hg(CN)_2$ and Hg^{*++} were mixed to give an approximately 10^{-2} *f* solution. This was adjusted to the desired ionic strength with $NaClO_4$. The mixture was allowed to equilibrate in a thermostat until, as calculated from the kinetic data, equilibrium had been reached. $Hg(IO_3)_2$ was precipitated from a suitable aliquot, filtered immediately and counted. As will be seen later, the disproportionation reaction of $HgCN^+$ is sufficiently slow to make post-precipitation of initially complexed mercury negligible as a source of error under the conditions used. The total activity of the mixture was determined by precipitating all the mercury in an aliquot with H_2S, filtering, and counting.

Kinetics of the Reaction $Hg(CN)_2 + Hg^{++} \rightarrow 2HgCN^+$.—The ultraviolet absorption spectrum of mercuric ion shows a strong absorption band starting at about 260 mμ and increasing with decreasing wave length. At 220 mμ the molar absorbency index is about 680 liters-mole^{-1}-cm.$^{-1}$. In contrast, the mercury cyanides show practically no absorption down to wave lengths shorter than 220 mμ. Hence, the reaction $Hg^{++} + Hg(CN)_2 \rightarrow 2HgCN^+$ can be followed by measuring the change of optical density of the reacting solution. Na^+ and ClO_4^- do not interfere.

To carry out a run, appropriate quantities of $Hg(ClO_4)_2$, $Hg(CN)_2$ and $NaClO_4$ solutions already at the desired temperature were mixed and poured into a quartz absorption cell. The change in optical density with time at 220 mμ was followed with a model DU Beckman spectrophotometer. During the measurement the absorption cell was thermostated to within ±0.2°.

Kinetics of the Exchange $HgCN^+$–Hg^{++}.—A measurement on the rate of exchange was initiated by adding to the experimental mixture, already containing the desired quantities of Hg^{++}, $HgCN^+$ and $Hg(CN)_2$ at equilibrium, a tracer quantity of Hg^{203} in the form of mercuric ion. The quantity thus added was small enough so that the shift in equilibrium according to the equation $Hg^{++} + Hg(CN)_2 \rightleftarrows 2HgCN^+$ was negligible. The solution also contained $NaClO_4$ and $HClO_4$ to establish the desired ionic strength and acid concentration, and was thermostated to ±0.1°. At suitable intervals aliquots were taken, including one when equilibrium had been attained; and the uncomplexed mercuric ion was separated as described above to give mercuric iodate precipitates which were then counted. The total activity in an aliquot was determined by precipitating the mercury with H_2S, filtering, and counting.

The concentrations of Hg^{++}, $HgCN^+$ and $Hg(CN)_2$ present were calculated on the basis of the experimentally determined disproportionation equilibrium constant K. These values were checked at the end of the experiment against the fraction of the total activity in the mercuric iodate precipitate from the final, equilibrium aliquot. Agreement was satisfactory in all cases.

Calculations and Results

Equilibrium Constant.—The counting data give the fraction of the total mercury in the equilibrium solution present in the form of Hg^{++}. In view of the fact[5] that all of the cyanide is complexed as $HgCN^+$ or $Hg(CN)_2$, the concentrations of these species, and thus the equilibrium constant, can be calculated directly from this figure. The result

$$K = \frac{(Hg^{++})(Hg(CN)_2)}{(HgCN^+)^2} = (5 \pm 1) \times 10^{-2}$$

is independent, within experimental error, of the temperature in the range 0° to 25°, and of the ionic strength in the range 0.01 to 1 *f*. The determinations were made at concentrations ranging from about 10^{-3} to 10^{-2} *M* and at a *p*H of 2.7 ± 0.1, this being the *p*H at which most of the experiments on the mercurous–mercuric cyanide exchange were made.

The Reaction $Hg^{++} + Hg(CN)_2 \rightleftarrows 2HgCN^+$.—Although the study of the reactions involved in the equilibrium

$$Hg^{++} + Hg(CN)_2 \rightleftharpoons 2HgCN^+ \qquad (3)$$

was carried out as a sequel to the investigation of the Hg^{*++}–$HgCN^+$ exchange we will, for the sake of continuity, discuss it first. Throughout this treatment R_1 and k_1 refer to the rate and specific rate constant of the forward reaction as written in 3, and R_2 and k_2 pertain to the back-reaction. The equilibrium constant K, as previously written, is equal to k_2/k_1.

For each experiment the optical density was plotted against the time, giving curves of the type shown in Fig. 1. Now, knowing the total change in optical density from the time of mixing ($t = 0$) to equilibration and also the initial and final concentrations (the latter calculated using K) we can relate a given change in optical density to a corresponding change in reactant concentrations. Thus the rate R_1 of the reaction at time t, can be calculated directly from the slope of the curve at time t.

It is simplest first to consider the initial rates of the reaction. These are obtained from the slopes at $t = 0$ of the curves extrapolated back to that

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[4] The authors are indebted to Dr. R. Christian Anderson and Miss Nancy Day for carrying out this analysis.

[5] M. S. Sherrill, *Z. physik. Chem.*, **43**, 705 (1903), gives $(Hg(CN)_4)^{=}/(Hg^{++})(CN^-)^4 = 2.5 \times 10^{41}$. We have established that no appreciable amounts of $Hg(CN)_3^-$ or $Hg(CN)_4^{=}$ are present in a solution where $CN^-/Hg(II) \leq 2$ since a solution of $Hg(CN)_2$ gives no test for Hg^{++}.

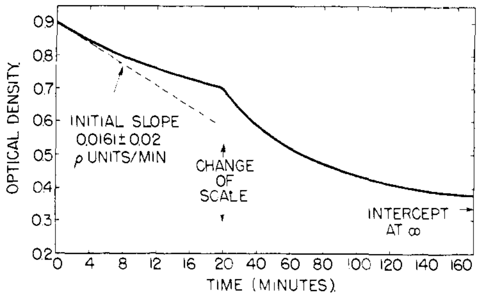

Fig. 1.—Change in optical density at 220 mμ of mixture of $Hg(CN)_2$ and Hg^{++}: $(Hg(CN)_2) = (Hg^{++}) = 1.28 \times 10^{-3} f$; 24.8°; 1 cm. quartz cell.

point. The relevant data are given in Table I. Assuming that $R = k(Hg^{++})^{\alpha}(Hg(CN)_2)^{\beta}$, we obtain α as the slope of a plot of log R *vs.* log (Hg^{++}) at constant $(Hg(CN)_2)$ and β is obtained similarly.

TABLE I

DATA FOR REACTION $Hg^{++} + Hg(CN)_2 \rightarrow 2HgCN^{+}$ AT *p*H 2.6

Init. (Hg^{++}) mole-l.$^{-1}$	Init. $(Hg(CN)_2)$ mole-l.$^{-1}$ $\times 10^3$	Temp., °C.	Ionic strength, mole-l.$^{-1}$	k_1,[a] mole^{-1}-l. min.$^{-1}$
1.28×10^{-3}	1.28	24.8	1.00	15.1, 12.3
1.28×10^{-3}	1.28	24.8	1.00	14.2, 12.8
1.28×10^{-3}	2.57	24.8	1.00	14.8
2.57×10^{-3}	1.28	24.8	1.00	12.6
2.57×10^{-3}	2.57	24.8	1.00	12.9, 12.4
6.42×10^{-4}	1.28	24.8	1.00	14.0
1.28×10^{-3}	1.28	24.8	0.12	15.4, 14.7
1.28×10^{-3}	1.28	24.8	0.01	15.7, 15.7
1.28×10^{-3}	1.28	14.7	1.00	4.93, 4.77
1.28×10^{-3}	1.28	36.4	1.00	38.8, 34.7

[a] The first value in this column was obtained by extrapolation of the rate to $t = 0$, the second value by the use of equation 5.

We find $\alpha = 0.98 \pm 0.1$ and $\beta = 0.90 \pm 0.1$. Thus the rate law for the forward reaction is

$$R_1 = k_1(Hg^{++})(Hg(CN)_2) \tag{4}$$

The bimolecular reaction rate constants, k_1, computed from R at $t = 0$ are given in Table I. The scatter of these values is of the same order as the uncertainty introduced by the extrapolation of the curves back to $t = 0$.

Although the analysis described above is sufficient to establish the rate law, it is of interest to investigate the reaction at $t \pm 0$, *i.e.*, when reaction products are present and a back-reaction must be considered. However, to avoid complex numerical calculation it is convenient to restrict such a treatment to the cases where $(Hg^{++}) = (Hg(CN)_2)$. Letting $(Hg^{++}) = (Hg(CN)_2) = a - p/2$ and $(HgCN^+) = p$ we have for the rate of the reversible second-order reaction 3

$$R_{12} = R_1 - R_2 = \frac{-d(Hg^{++})}{dt} = k_1(Hg^{++})(Hg(CN)_2) - k_2(HgCN^+)^2$$

$$\frac{dp}{2dt} = k_1\left(a - \frac{p}{2}\right)^2 - k_2p^2$$

$$= k_1\left(a - \frac{p}{2}\right)^2 - k_1Kp^2$$

Integrating, with the limit that $p = 0$ when $t = 0$ we get

$$k_1 = \frac{1}{t}\left(\frac{0.576}{a\sqrt{K}} \log \frac{(1 - 2\sqrt{K})p - 2a}{(1 + 2\sqrt{K})p - 2a}\right) \tag{5}$$

This equation is then applied using the K determined previously. On plotting log $(1 - 2\sqrt{K}) - 2a/(1 + 2\sqrt{K}) - 2a$ *vs.* t excellent linear relations are found (see Fig. 2). This confirms the validity of the rate law.

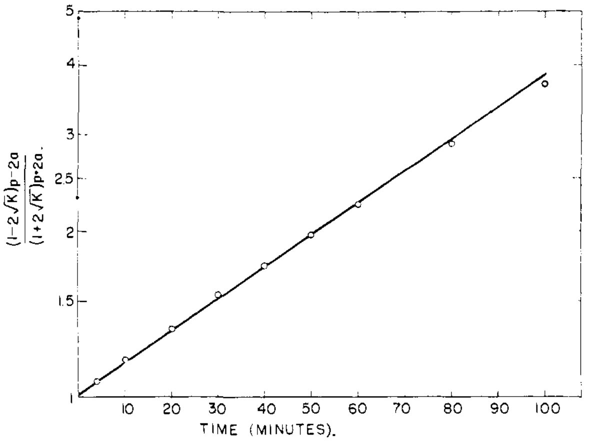

Fig. 2.—Adherence of data in Fig. 1 to rate law of reversible second-order reaction.

The temperature dependence of the rate of the forward reaction is given in Fig. 3. (The k_1's plotted are the weighted averages of the values given in Table I and the values determined using equation 5.) The energy of activation calculated from Fig. 3 by the usual method is 17.0 kcal.

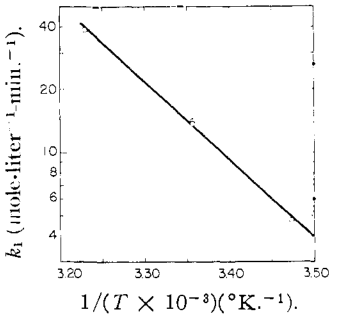

Fig. 3.—Temperature dependence of the specific rate constant of the reaction $Hg(CN)_2 + Hg^{++} \rightarrow 2HgCN^+$.

For the back-reaction ($2HgCN^+ \rightarrow$) the rate constant k_2 at 24.8° is calculated, using the relation $k_2 = k_1K$ to be 0.7 mole-liter^{-1}-min.$^{-1}$ while the energy of activation is the same within about 2 kcal. as that of the forward reaction. We have then for the over-all rate R_{12} of the approach to equilibrium at 24.8°

$$R_{12}\ (\text{mole-liter}^{-1}\text{-min.}^{-1}) = 13.8\ (Hg^{++})(Hg(CN)_2) - 0.7\ (HgCN^+)^2 \tag{6}$$

It is observed that on decreasing the ionic strength from 1.0 to 0.01 f the reaction rate R_1 increases by 15%, a change only about twice as great as the experimental error.

TABLE II

DATA ON EXCHANGE REACTION $Hg^{*++} + HgCN^+ \rightleftarrows Hg^{++} + Hg^*CN^+$

(Hg(II)) formal	(CN⁻) formal	Ionic strength mole-l.⁻¹	pH	Temp., T, °C.	(Hg⁺⁺) (calcd.), mole-l.⁻¹	(HgCN⁺) (calcd.), mole-l.⁻¹	(Hg(CN)₂) (calcd.), mole-l.⁻¹	$t_{1/2}$, min.	$k^M{}_3$, mole⁻¹-l.-min.⁻¹	k_3, mole⁻¹-l.-min.⁻¹
2.38×10^{-2}	2.38×10^{-2}	0.12	2.8	0.0	3.69×10^{-3}	1.64×10^{-2}	3.69×10^{-3}	27	1.28	1.05
4.28×10^{-2}	2.38×10^{-2}	.12	2.8	.0	2.01×10^{-2}	2.15×10^{-2}	1.15×10^{-3}	20	0.83	0.80
9.44×10^{-3}	9.44×10^{-3}	.12	2.6	.0	1.46×10^{-3}	6.52×10^{-3}	1.46×10^{-3}	87	1.00	.79
9.50×10^{-3}	9.50×10^{-3}	.12	2.6	.0	1.47×10^{-3}	6.60×10^{-3}	1.47×10^{-3}	88	0.97	.76
2.38×10^{-2}	3.44×10^{-2}	.12	2.5	.0	6.5×10^{-4}	1.19×10^{-2}	1.13×10^{-2}	39	1.44	~ .6
2.38×10^{-2}	1.46×10^{-2}	.12	2.5	.0	1.00×10^{-2}	1.30×10^{-2}	8.4×10^{-4}	35	0.86	.82
9.50×10^{-3}	9.50×10^{-3}	.12	2.6	13.0	1.47×10^{-3}	6.60×10^{-3}	1.47×10^{-3}	29	2.95	2.04
9.50×10^{-3}	9.50×10^{-3}	.12	2.6	20.7	1.47×10^{-3}	6.60×10^{-3}	1.47×10^{-3}	15.5	5.54	3.57
9.44×10^{-3}	9.44×10^{-3}	.12	1.5	0.0	1.46×10^{-3}	6.52×10^{-3}	1.46×10^{-3}	67	1.29	
4.9×10^{-2}	4.9×10^{-2}	.02	2.5	.0	7.6×10^{-3}	3.4×10^{-2}	7.6×10^{-3}	15.5	1.06	0.84

The Exchange Reaction of Mercuric and Mercuric Monocyanide Ions.—Considering the exchange of radioactive mercury between Hg^{++} and $HgCN^+$ as represented in equation 1 we define

$$a = (Hg^{++}) + (Hg^{*++}) \qquad b = (HgCN^+) + (Hg^*CN^+)$$
$$x = (Hg^{*++}) \qquad y = (Hg^*CN^+)$$

where x_0, y_0 and x_∞ and y_∞ are x and y when the time $t = 0$ or $t = \infty$, respectively.

On plotting data in the form log $(x - x_\infty)/(x_0 - x_\infty)$ *vs.* t a linear dependence is found (see Fig. 4). The rate of exchange can thus be expressed in terms of a half-time, $t_{1/2}$. Neglecting any effect of the $Hg(CN)_2$ present in the reaction mixture on the exchange we can apply the familiar McKay law[6]

$$R^M{}_3 = \frac{0.693ab}{t_{1/2}(a + b)} \qquad (7)$$

where $R^M{}_3$ is the rate of the exchange calculated on this basis. The data obtained and the $R^M{}_3$'s calculated are given in Table II. The rate law $R^M{}_3 = k^M{}_3 (Hg^{++}) (HgCN^+)$ gives a much better fit than any other simple relation and it thus appears that the chief mechanism of the exchange is represented by equation 1 as written.

It is noted from the $k^M{}_3$'s given in Table II that these show an unduly high scatter and that the higher values seem to be associated with higher relative concentrations of $Hg(CN)_2$. It appears to be necessary to apply a correction to the data before using it to calculate the rate of the direct reaction, as written in equation 1, of the exchange. This correction presumably corresponds to exchange *via* the indirect disproportionation reaction 2.

It is necessary to develop the mathematical equipment[7] treating exchange by a disproportionation mechanism as in equation 2.

Let $c = (Hg(CN)_2) + (Hg^*(CN)_2)$ and $z = (Hg^*(CN)_2)$. Then using the symbols previously defined, we can write from equation 2

$$\frac{dx}{dt} = R_1\left(\frac{y}{b} - \frac{x}{a}\right) \qquad (8)$$

$$\frac{dz}{dt} = R_1\left(\frac{y}{b} - \frac{z}{c}\right) \qquad (9)$$

$$x + y + z = A \qquad (10)$$

where A is the total activity and $R_1 = R_2$ is given in the previous section of this paper. With the use of 10, y is eliminated from equations 8 and 9, and they are combined to give two second-order differential equations, each in one variable only. On solving these we get

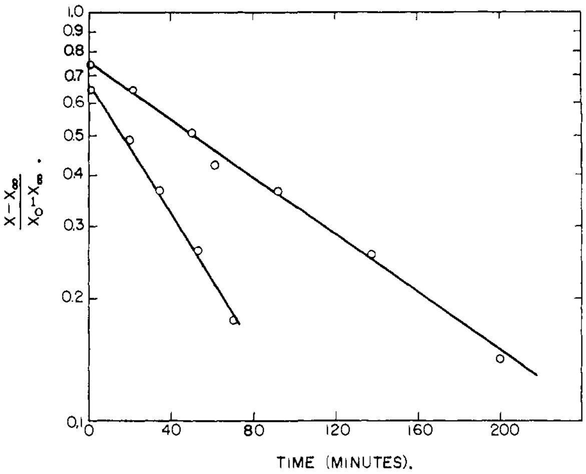

Fig. 4.—Representative curves of exchange data.

$$x = x_\infty + C_1e^{r_1t} + C_2e^{r_2t}$$
$$z = z_\infty + C_3e^{r_1t} + C_4e^{r_2t}$$

where $x_\infty = aA/(a + b + c)$ and $z_\infty = cA/(a + b + c)$ are the equilibrium activities, and r_1 and r_2 are roots. The constants of integration C_1, C_2, C_3 and C_4 (only two of which are independent) are evaluated by imposing the limit that when $t = 0$, $x = x_0$ and $z = 0$. We finally get

$$x = x_\infty + \frac{(x_\infty - x_0)(bc - ab - L) + 2acz_\infty}{2L}e^{r_1t} + \frac{(x_0 - x_\infty)(bc - ab + L) - 2acz_\infty}{2L}e^{r_2t} \qquad (11)$$

where

$$L = \sqrt{4a^2c^2 + (ab - bc)^2}$$
$$r_1 = \frac{R_1}{2abc}\left[-(ab + 2ac + bc) + L\right]$$
$$r_2 = \frac{R_1}{2abc}\left[-(ab + 2ac + bc) - L\right]$$

In the case where $c = a$ this expression can be simplified to

$$x = x_\infty + \frac{x_0}{2}e^{-\frac{R_1}{a}t} + \left(\frac{x_0}{2} - x_\infty\right)e^{-\frac{R_1}{ab}(2a + b)t} \qquad (12a)$$

or using result 4

$$x = x_\infty + \frac{x_0}{2}e^{-k_1ct} + \left(\frac{x_0}{2} - x_\infty\right)e^{-k_1\frac{c}{b}(2a + b)t} \qquad (12b)$$

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(6) H. A. C. McKay, *Nature*, **142**, 997 (1938); R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

(7) We are indebted to Dr. Arthur Kant for helpful discussions of the general problem of exchanges in complicated systems.

It is seen that equations 11 and 12 do not fit the form of the McKay law and should not give a linear dependence of the sort shown in Fig. 4. However, the fact that the data do follow the linear dependence within the experimental error cannot be taken to show that the disproportionation reaction 2 is not involved in the exchange. It is quite possible that the deviation from linearity even if mechanism 2 were dominant would be small over the range studied.

Since the function $(x - x_\infty)/(x_0 - x_\infty)$ for the case that only mechanism 1 prevails is a pure exponential of the form $e^{-\lambda_1 t}$ and since the data fit a pure exponential of the form $e^{-\lambda t}$, the correction to be sought must be an additive correction in λ. This suggests that the observed half-life $t_{1/2}$ be corrected as

$$\frac{1}{t_{1/2}(1)} = \frac{1}{t_{1/2}} - \frac{1}{t_{1/2}(2)} \qquad (13)$$

where $t_{1/2}(1)$ is the half-life which would be observed if only mechanism 1 prevailed, and $t_{1/2}(2)$ represents the contribution of the disproportionation mechanism. As an estimate of this contribution we take the length of time necessary for the exchange to be half completed by the disproportionation mechanism alone (equations 12). An exact solution can be found for the actual situation in which both reaction paths are operative, but the result is too cumbersome to be useful. The McKay law can now be applied to the corrected half-times, $t_{1/2}(1)$, and R_3 and k_3, the rates and bimolecular rate constant for the direct mechanism 1 are calculated. These corrected values of k_3 are given in the last column of Table II. A better fit of the data is now obtained. We have then for the rate at 0° of the exchange reaction by the direct mechanism of equation 1

$$R_3 = 0.80(\mathrm{Hg^{++}})(\mathrm{HgCN^+}) \qquad (14)$$

The energy of activation is calculated to be 11.8 kcal. from the temperature dependence of k_3 as shown in Fig. 5. The temperature dependence of k^{M}_3, the rate constant uncorrected for the disproportionation reaction indicated by the dotted line, is shown for comparison.

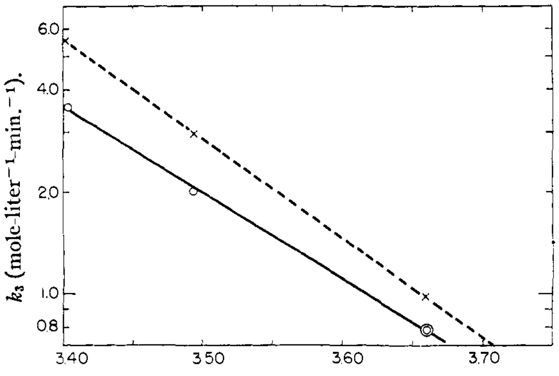

Fig. 5.—Temperature dependence of k_3 for exchange mechanism $\mathrm{Hg^{*++}} + \mathrm{HgCN^+} \rightleftarrows \mathrm{Hg^{++}} + \mathrm{Hg^*CN^+}$ (solid line). Dotted line shows temperature dependence of exchange rate uncorrected for disproportionation mechanism.

It is noted from Table II that change of pH from 2.8 to about 1.5 has no apparent effect on the rate of the reaction. A single experiment at ionic strength 0.02 *f* indicates that there is little, if any, dependence on the ionic strength in the range 0.02 to 0.12.

Exchange between Mercury Monocyanide and Dicyanide.—The exchange of radioactive mercury between the two lowest cyanide complexes

$$\mathrm{Hg^*CN^+} + \mathrm{Hg(CN)_2} \rightleftarrows \mathrm{HgCN^+} + \mathrm{Hg^*(CN)_2} \qquad (15)$$

can proceed by the reactions involved in the disproportionation equilibrium 2. Since the rates of these processes are known it is possible to calculate the minimum rate $\mathrm{d(Hg^*(CN)_2)}/\mathrm{d}t$ for this exchange using mathematics analogous to those employed above. If a good method of separation can be found (*e.g.*, by extraction of $\mathrm{Hg(CN)_2}$ into an organic solvent or by chromatography) this would be an interesting point to check.

Summary of Kinetics Results.—The complete expression for the rate of equation 3 representing the approach to chemical equilibrium of a system containing $\mathrm{Hg^{++}}$, $\mathrm{HgCN^+}$ and $\mathrm{Hg(CN)_2}$ is

$$R_{12} = 6 \times 10^{11}\, e^{-17,100/RT}(\mathrm{Hg^{++}})(\mathrm{Hg(CN)_2}) - 3 \times 10^{10}\, e^{-17,000/RT}(\mathrm{HgCN^+})^2$$

The rate of exchange between $\mathrm{Hg^{*++}}$ and $\mathrm{HgCN^+}$ (independent of the reactions of the disproportionation equilibrium 2) is

$$R_3 = 4 \times 10^7\, e^{-11,800/RT}\,(\mathrm{Hg^{++}})(\mathrm{HgCN^+})$$

and this exchange, as discussed, also proceeds by equation 2. (It may be noted that at higher temperatures the indirect mechanism 2 will become dominant.) These data are given for a pH of 2.6 and an ionic strength of 0.125 *f;* however, as mentioned before, there is little, if any, dependence on these factors in the ranges considered.

In the previous paper[1] the rate of the mercurous–mercuric cyanide exchange in a solution containing equivalent formal amounts of $\mathrm{Hg^{++}}$ and $\mathrm{CN^-}$ was given as

$$R = 0.34(\mathrm{Hg(I)})(\mathrm{Hg(II)})$$

Knowing K we can now write

$$R = 0.42\,(\mathrm{Hg(I)})(\mathrm{HgCN^+})$$
$$R = 1.4 \times 10^9\, e^{-14,000/RT}\,(\mathrm{Hg(I)})(\mathrm{HgCN^+})$$

In the latter two expressions the coefficient includes a small correction, about 15%, to allow for the contribution of the Hg(I) exchange with $\mathrm{Hg(CN)_2}$, which in the work cited was found to proceed with approximately the same specific rate constant as the exchange between Hg(I) and $\mathrm{Hg(CN)^+}$. The temperature coefficient given is that found in the previous work.[2]

The numerical results of the investigation are summarized in Table III. E_{exp}, $\Delta S^\ddagger$ and $\Delta F^\ddagger$, the experimental activation energy, entropy of activation and free energy of activation are defined and computed in the usual manner.[8] The errors indicated are estimates based simply on the apparent allowable range of slopes in log *k vs.* $1/T$ plots.

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[8] S. Glasstone, K. S. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 197.

TABLE III

SUMMARY OF KINETIC DATA IN THE MERCURY CYANIDE SYSTEM

pH 2.6, μ 0.12, 0°

Reaction (bimolecular mechanism as written)	k, 0° mole^{-1}-l.-min.$^{-1}$	$E_{\text{exp.}}$ kcal.	$\Delta S^{\ddagger}$, cal./°C.	$\Delta F^{\ddagger}$, kcal.
$Hg^*(I) + HgCN^+ \longrightarrow Hg(I) + Hg^*CN^+$	0.42 ± 0.04	14.0 ± 0.5	-18	19.0
$Hg^{*++} + HgCN^+ \longrightarrow Hg^{++} + Hg^*CN^+$	$0.80 \pm .1$	$11.8 \pm .5$	-26	18.8
$Hg^{++} + Hg(CN)_2 \longrightarrow 2HgCN^+$	$1.00 \pm .05$	$17.0 \pm .5$	-6	18.7
$2HgCN^+ \longrightarrow Hg^{++} + Hg(CN)_2$	$0.05 \pm .02$	17 ± 2	~ -12	20 ± 2

Discussion

Relevance of Results to Mercurous–Mercuric Cyanide Exchange.—The zero-time exchange observed in the study of the mercurous–mercuric cyanide exchange[1] varied from about 5% to 50% depending on the relative amounts of cyanide and Hg(II) present in the exchange solution. This zero-time exchange was presumed to be due to the rapid exchange of mercurous and uncomplexed mercuric ions, as postulated in that paper. Knowing K it is now possible to check whether this mechanism for the zero-time exchange is quantitatively correct.

We have then the two exchange reactions

$$\text{Rapid exchange: } Hg^{*++} + Hg(I) \rightleftarrows Hg^{++} + Hg^*(I) \quad (16)$$

$$\text{Slow exchange: } Hg^*CN + Hg(I) \rightleftarrows HgCN + Hg^*(I) \quad (17)$$

(where HgCN represents cyanide complexed Hg(II)) and assume that all zero-time exchange is due to reaction 16 going to equilibrium. It is readily shown that the zero-time exchange, E_0, of the mercurous–mercuric cyanide exchange by the above mechanism, is given by

$$E_0 = \frac{[(Hg(I) + (Hg^{++}) + (HgCN)]\,(Hg^{++})}{[(Hg(I) + (Hg^{++})][(Hg^{++}) + (HgCN)]} \quad (18)$$

The observed trend of the zero-time exchange follows[9] this dependence, within experimental error, thus supporting the mechanism postulated.

An important result of the present work relevant to the mercurous–mercuric cyanide exchange is the independent verification of the fact that the Hg^{++}–$HgCN^+$ exchange is slow. As stated in the introduction this was a necessary corollary of the mechanism postulated[1] for the mercurous–mercuric cyanide exchange. If the $HgCN^+$–Hg^{++} exchange were fast, then the mercurous–mercuric cyanide exchange could proceed by the mechanism

$$\begin{aligned} &Hg^*CN^+ + Hg^{++} \rightleftarrows HgCN^+ + Hg^{*++} \\ &Hg(I) + Hg^{*++} \rightleftarrows Hg^*(I) + Hg^{++} \quad \text{(rapid)} \end{aligned} \quad (19)$$

The half-time $t_{1/2}(3)$ for the mercurous–mercuric cyanide exchange by mechanism 19 can be shown to be (by a derivation analogous to, though more complex than, that in reference 5)

$$t_{1/2}(3) = \frac{0.693(HgCN^+)[(Hg^{++}) + (Hg(I))]}{R_3[(Hg(I) + (Hg^{++}) + (HgCN^+)]} \quad (20)$$

(The effect of the $Hg(CN)_2$ present can be safely neglected, thereby making it possible to write R_3 as defined in equation 14.) Using equation 14 it can be shown readily that, for mechanism 19 to be dominant over the bimolecular reaction path found, $(Hg(I)) \gtrsim (Hg^{++})$ which was not the case in our experiments. Although it would be desirable to verify this by carrying out the $Hg(I)$–$HgCN^+$ exchange when $(HgI) < (Hg^{++})$, this is unfortunately experimentally rather difficult since the zero-time exchange, E_0, (see equation 18) would be very large under these conditions.

Comments on the Non-lability of Mercuric Cyanide.—The data summarized in Table III suggest that the details of the bimolecular cyanide transfer process are similar for all the reactions discussed. However, the entropy of activation of the reaction $Hg(CN)_2 + Hg^{++} \rightarrow 2HgCN^+$ is considerably less negative than that of other processes. It might be surmised that this is due to the charge product of the reactants being zero, instead of one or two, but such an explanation cannot be accepted without having more definite knowledge of the hydration and possible perchlorate complex formation of the cyanide complexed species formally written as $HgCN^+$ and $Hg(CN)_2$. From the lack of pH dependence of the exchange reaction and from the data of Hietanen and Sillen[10] on the hydrolysis of Hg^{++} it is believed that the Hg^{++} species is present and reacts primarily as $Hg(H_2O)_n^{++}$ rather than as $HgOH^+$ or $Hg(OH)_2$.

These experiments have shown that the rates of dissociation of $HgCN^+$ and $Hg(CN)_2$ to give cyanide ion are very slow. The first-order rate constants of such reactions would be less than about 10^{-2} min.$^{-1}$.[11] Thus it is clear that these complexes are in Taube's nomenclature "inert" or "not labile."[12]

Taube in his review[12] finds that "inert" complexes fall into one of two classes: (1) "Inner Orbital Complexes" of the type in which none of the inner d orbitals are left unoccupied. In these complexes some of the bonding electrons occupy the same shell as is occupied by some of the atomic electrons. Unless a vacant orbital is left in that shell, substitution or dissociation of the ligand will require a relatively large activation energy, whether the complex is thermodynamically stable or not. (2) "Outer Orbital" complexes with a high (>3) charge on the central ion. Such complexes form such strong co-

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[9] The following are typical observed and calculated values of E_0, respectively: 0.59, 0.50; 0.31, 0.23; 0.30, 0.29; 0.22, 0.19; 0.51, 0.58; 0.11, 0.04.

[10] L. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **6**, **747** (1952).

[11] This conclusion may at first appear to be at variance with the statement of Adamson, Welker and Volpe (THIS JOURNAL, **72**, 4030 (1950)) that $Hg(CN)_2$ exchanges immeasurably rapidly with radiocyanide ion. These authors mixed approximately equivalent quantities of $Hg(CN)_2$ and C^*N^- and then precipitated silver cyanide (leaving $Hg(CN)_2$ in solution). However, since CN^- and $Hg(CN)_2$ combine to give $Hg(CN)_4^{=}$ or $Hg(CN)_3^-$ (from which Ag^+ will strip cyanides till $Hg(CN)_2$ is left), it is to be expected that complete exchange of activity will occur whether $Hg(CN)_2$ itself is labile or not.

[12] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

valent bonds, because of the high central charge, that a high activation energy is needed to break them.

$Hg(CN)_2$ and $HgCN^+$ fit into neither of these categories. The only orbitals available for bonding are *s* and *p* orbitals of quantum number higher than those occupied by the electrons of Hg^{++}. Thus, these complexes, though "inert," are evidently "outer orbital" complexes with low charge on the central ion. However, even though this case may be unique we do not believe it to be anomalous. Hg^{++} ion is a very strong polarizing agent and CN^- is exceptionally polarizable. Thus if there are only one or two cyanides per Hg^{++} very strong, largely covalent bonds, requiring a high activation energy to break, should be found even though the formal charge on the central ion is only two. This gives rise to the very great thermodynamic stability of aqueous $Hg(CN)_2$: $(Hg(CN)_2 \cdot)(Hg^{++})^{-1}(CN^-)^{-2} = 10^{32}$ [13] and by the same token to its non-lability. If the number of cyanides per Hg^{++} is increased to three or four the polarization interaction becomes saturated and the individual bonds become weaker. This is manifested in the relatively low association constant of $Hg(CN)_4^=$ with respect to $Hg(CN)_2$: $(Hg(CN)_4^=)(Hg(CN)_2)^{-1} \cdot (CN^=)^{-2} = 2 \times 10^9$.[14] Correspondingly $Hg(CN)_3^-$ and $Hg(CN)_4^=$ appear to be labile complexes; when Hg^{++} is added to them it is immediately cyanide complexed, as is evidenced by the disappearance of the Hg^{++} absorption at 220 mμ and the failure of the solution to give a precipitate with $NaIO_3$.

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(13) This constant approximately evaluated from data on Hg^{++}(aq)CN^-(aq) and $Hg(CN)_2$(crystalline) in Latimer ["Oxidation Potentials," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 176] and from the solubility of $Hg(CN)_2$.

(14) This constant approximately evaluated from data referred to in footnotes 4 and 12.

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The Decomposition of Hypobromite and Bromite Solutions

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RECEIVED AUGUST 26, 1953

The kinetics of the decomposition of hypobromite solutions were investigated in a limited range of *p*H and initial concentrations by measuring the change of concentration of both hypobromite and bromite. The results can be satisfactorily explained on the basis of two second-order consecutive reactions, the first involving the formation of bromite, and the second a comparatively fast reaction between bromite and hypobromite. The decomposition of the intermediate, bromite, was investigated separately and was found in the main to follow an analogous mechanism, hypobromite now taking the role of intermediate. In the *p*H range considered, the assumption that the reactions take place exclusively between an undissociated acid molecule and an anion does not give satisfactory agreement with experiment; much better agreement is obtained by assuming, in addition, reactions involving either free bromine or two uncharged molecules of acid.

Alkali hypobromite solutions are known to decompose to give a mixture of bromide and bromate. The kinetics and mechanism of this decomposition have been the object of several investigations.[2-7] However, the mechanism is still not fully understood.

Bromous acid and the bromite anion have been assumed by several authors as intermediates in the decomposition of hypobromite,[5,8,9] in the back reaction in acid solution, *i.e.*, the formation of bromine from bromate and bromide,[10] and in the acid reduction of bromate by hydrogen peroxide.[11] Some experiments have also been reported on the reaction between bromite and hypobromite.[5,8] However, the reactions involved in the formation of bromate from bromite have not yet been investigated in detail. An understanding of this reaction can be expected to throw some further light on the mechanism of the decomposition of hypobromite solutions.

The object of the present work was to clarify further, in a limited range of *p*H, the mechanism of the processes by isolating the single steps as far as possible.

Experimental

Hypobromite solutions were prepared by adding an appropriate amount of bromine to a cooled solution of sodium hydroxide. The solutions thus prepared were kept in a refrigerator for not more than 24 hours before use.

Bromite solutions were prepared by the method described by Chapin[5] and brought to the desired *p*H by adding solid boric acid and shaking vigorously. The bromide content of these solutions was regulated by the addition of either potassium bromide solution, or of silver nitrate solution, followed by rapid filtration.

The analyses of bromite, hypobromite and bromate were carried out by the methods used by Chapin,[5] the temperature being kept below 20° during the titration of bromite with iodine in the presence of phenol[12] and those of bromide by adding hydrogen peroxide to an alkaline solution in order to reduce the hypobromite and bromite to bromide, boiling off the excess of hydrogen peroxide, acidifying with acetic acid and titrating with silver nitrate. The difference between this titration and that of hypobromite and bromite gives the bromide concentration.[12]

The *p*H was ≥ 8.0. (At lower values of *p*H, free bromine appears in appreciable quantities and would complicate both the analytical methods and the experimental procedure.) The experiments were carried out in buffered solutions, using borax-boric acid mixtures, or sodium phosphate.

The *p*H was measured with a glass electrode, using a

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(1) To whom inquiries should be addressed.

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