The first crystals formed in any solution contain more radium than any of the later crystals.

The concentration of radium in the crystals increases with the time of crystallization for equal quantities of crystals from solutions of the same radium concentration.

In neutral or alkaline solutions radium-barium crystals form extremely slowly upon cooling, supersaturation being noticeable. Acid in the solutions seems to act as a catalyzer in forming crystals, supersaturation being less noticeable.

Summary.

Several systems of crystallizing a radium-barium solution are given with a modified form that is very efficient in crystallizing high grade radium.

The bromide system is more efficient than the chloride system.

Radium is much easier to separate from barium than formerly supposed.

Several important conditions of crystallization are noted.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

DETERMINATION OF THE EQUILIBRIUM BETWEEN CHLORINE, WATER, HYDROCHLORIC ACID AND CHLORIC ACID. THE FREE ENERGY OF THE CHLORATE ION.

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The object of this research was to determine the equilibrium constant, for which no direct measurements exist, of the following reaction:

$$3H_2O + 3Cl_2 = HClO_3 + 5HCl \qquad (1)$$

The kinetics of this reaction have been studied by various observers, in particular Sands,[1] Foerster,[2] Luther and MacDougall.[3] Sands attempted to calculate the equilibrium constant from reaction velocities. While this method of obtaining it is correct, it involves certain differential equations which must first be determined. Luther and MacDougall have shown that the differential equation expressing the velocity of the reverse reaction of (1) is not

$$dx/dt = K(ClO_3^-)\ (Cl^-)^2(H^+)^2$$

as assumed by Sands, but

$$dx/dt = K(ClO_3^-)^2\ (Cl^-)^2\ (H^+)^4.$$

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[1] Sands, *Z. physik. Chem.*, **50**, 465 (1904).

[2] Foerster, *J. prakt. Chem.*, **63**, 141 (1901).

[3] Luther and MacDougall, *Z. physik. Chem.*, **62**, 199 (1908).

Moreover, Sands' calculations are evidently not accepted by Skrabal, who has made a comprehensive study of halogen reactions. He succeeded in calculating the constants[1] from kinetic measurements for the analogous bromine and iodine reactions, but has not yet succeeded in calculating the constants for chlorine. The value of the constant, as calculated by Sands, differs from this experimental determination of it by a millionfold. This enormous discrepancy is explained by the previous considerations.

The reaction expressed by Equation 1 proceeds very slowly at ordinary temperatures. Luther and MacDougall found that chlorine dioxide also was invariably formed under these conditions. To accelerate the reaction the temperature may be raised. This, however, accelerates another slow reaction also, *i. e.*, the decomposition of chloric acid into hydrochloric acid and oxygen, according to the following equation; $2\ HClO_3 = 2\ HCl + 3\ O_2$. Since the equilibrium pressure of oxygen for this reaction is very high, a temperature must be selected which will permit the chlorine equilibrium to be attained within a reasonable time, and still not permit excessive oxygen pressure to develop. After several trials a temperature of about 90° was selected.

The method of procedure was to fill a set of glass tubes, usually 6, with a mixture of the reacting substances, seal the tubes and immerse them in a thermostat kept at 91°. Tubes were then taken out at intervals, analyzed and the concentration function calculated according to the equation

$$\frac{(H^+)^6\,(Cl^-)^5\,(ClO_3^-)}{(Cl_2)^3} = K'.$$

The tubes were made of Pyrex glass, and in the shape shown in Fig. 1. The function of the long, slender tip will become apparent when the analytical method is discussed. The solution for each series of tubes was made up in a flask similar to a wash-bottle. The liquid was then forced into the tubes by compressed air. In order to secure a high enough concentration of chlorine, and still keep the partial pressure of chlorine low, the solution was kept just above the temperature at which chlorine hydrate forms. Chemically pure hydrochloric acid and recrystallized potassium chlorate were used. All tubes were filled to such a height that, when they had been sealed off and heated to 91°, only a very small bubble of gas remained (approximately 0.1 cc.), and so the error made by assuming that all the chlorine was dissolved in the liquid was small. The filled tubes were then weighed, and all except one immersed in a thermostat kept at 91°. The remaining tube was analyzed in order to obtain the initial composition of the liquid for that set. The empty tube was weighed after analysis, and thus the mass of the solution in that tube determined.

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[1] Skrabal, *Monatsh.*, 32, 880 (1911); 33, 116 (1912); 36, 251 (1915).

When a tube was taken out of the thermostat to be analyzed, the long tip was inserted into one of the arms of a stopcock (see Fig. 1) which had been flared out at the end so as to fit the bulging tube. The tip of the tube was of such a length and thickness that it extended into the open stopcock proper. The other arm of the stopcock was ground to fit a U-tube, B, which in turn made a ground connection with a set of Liebig bulbs, L, in which was a neutral aqueous solution of potassium iodide. DeKhotinsky cement was used to make a gas-tight joint between the tube and the stopcock at K. A slight turn of the stopcock broke the tip of the tube and permitted the liquid to run into the U-tube. When the pressure had decreased a vacuum pump was attached to the open end of the Liebig bulb, the upper tip of the tube broken off, and to it a rubber tube from the wash-bottle W was attached. A slow stream of air saturated with water was drawn through the liquid in the U-tube, removing the chlorine, and then through the potassium iodide solution, where the chlorine immediately oxidized the iodide to iodine. All traces of chlorine were thus removed in a few hours. The potassium iodide showed no traces of iodine when pure air was drawn through it for a similar length of time. The iodine was then titrated with sodium thiosulfate solution. The hydrogen and chloride ions were determined by removing a sample of the liquid remaining in the U-tube with a pipet and titrating

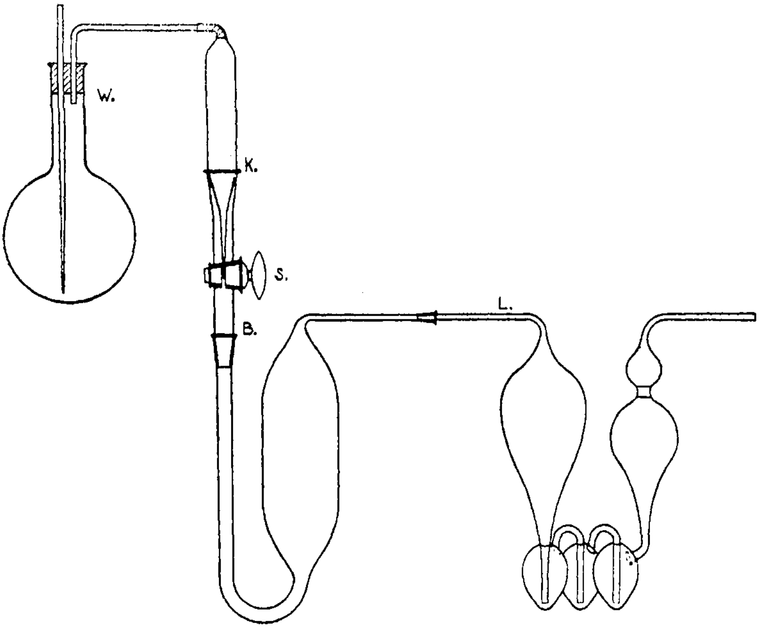

FIG. I.

it with sodium carbonate solution and then with silver nitrate solution, using methyl red and potassium dichromate, respectively, as indicators. Chlorate ion was determined by heating a known volume of the liquid (usually 10 cc.) from the U-tube with potassium iodide and hydrochloric acid in a sealed tube at 90° for ten minutes. Because of the small concentration of chlorate ion and the difficulty of obtaining potassium iodide, which gave a satisfactory blank test when so heated, potassium bromide was substituted for iodide in all later determinations. This gave a quantitative reduction of the chlorate and was not oxidized by perchloric acid which forms from chloric acid according to the reaction $4HClO_3 = 3HClO_4 + HCl$

The experimental data for the check on the chlorate ion determination by potassium bromide and hydrochloric acid is as follows: Several g. of potassium bromide, 10 cc. of 6 N hydrochloric acid, and 0.1577 g. of potassium chlorate were placed in a Pyrex glass tube. The tube was sealed and immersed in a thermostat kept at 91° for half an hour. It was then removed and cooled with tap water. The tip of the tube was broken under an aqueous solution of potassium iodide and the iodine titrated at once with sodium thiosulfate solution. It required 77.74 cc. of 0.09925 N sodium thiosulfate solution to reduce the iodine liberated, which corresponds to 0.1575 g. of potassium chlorate.

It has been mentioned above that Luther and MacDougall, working at 75°, found that chlorine dioxide was formed from hydrochloric and chloric acids, and, therefore, the chlorine was tested for chlorine dioxide, according to the method recommended by Bray,[1] but was found to be absent. This is doubtless due to the higher temperature and to heating in a closed tube.

Even at 90° Reaction 1 is very slow. Attempts were therefore made to find a homogeneous catalyzer for the reaction, the guiding factors being the following considerations: (1) the catalyzer must exist in at least 2 states of oxidation; (2) if R represents the lower state of oxidation and O the higher state, (a) R must reduce chlorate ion faster than chloride ion does, and (b) O must in turn be reduced by chloride ion fast enough to maintain an effective concentration of R; (3) neither O nor R must interfere with the scheme of analysis. $Fe^{++} \rightleftarrows Fe^{+++}$, for instance, would not catalyze this reaction, for in the presence of chloride the iron is almost completely in the form of ferric ion, and hence the concentration of ferrous ion which can react with the chlorate is negligibly small. A stronger oxidizing agent than ferric ion must therefore be employed, *i. e.*, one which rapidly reduced by chloride ion at the concentrations used in this reaction.

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[1] Bray, *Z. physik. Chem.*, **54**, 731 (1906).

The manganous-manganic equilibrium was finally selected as fulfilling the requirements. The salt used was manganous chloride, and the concentration was about 0.02 M. During analysis the manganese remained as dioxide in the U-tube, and was filtered off before analyzing for chloride, chlorate and hydrogen ions. The manganese which remained in solution did not interfere with the test of the chlorate ion determination mentioned above.

The effect of the catalyzer was well demonstrated in several instances. In Series I, Tube 6 was the only one into which manganous chloride was produced; in 3 days it had progressed almost as far toward equilibrium as Tube 5, which had practically the same concentration of all the constituents, had progressed in 35 days. The tubes of Series V did not contain enough manganous chloride to produce a precipitate of dioxide. In 248 days the K's corresponding to this series changed by only a factor of 10, whereas the K's corresponding to the tubes in Series IV, which contained a slightly larger amount of the catalyst, changed by a factor of 4000 in 13 days.

All concentrations are expressed in mols in 1000 g. of solution. The following tables show the values found for the first series of tubes, the initial composition being chlorine and water:

TABLE I.

Series I.

No. of tube.	Vol. of tube. Cc.	Time. Days.	(Cl_2.)	(H^+.)	(Cl^-.)	(ClO_3^-.)	K'.
1	44.81	8	0.10076	0.0342	0.0303	0.004161	1.66×10^{-16}
2	34.79	7	0.180	0.04218	0.04437	0.002733	3.16×10^{-16}
3	53.47	14	0.1203	0.07865	0.0708	0.01198	2.90×10^{-12}
4	Broken	..	....	....	....	....	....
5	59.54	35	0.0979	0.08899	0.0707	0.013525	1.26×10^{-9}
6	53.93	3	0.09938	0.08649	0.07355	0.01379	1.26×10^{-10}

In Tube 6, as well as in all later series, a catalyzer was used.

Another set of tubes, Series II, was then filled with an analyzed solution, the concentrations of the constituents of which were such that K' as calculated initially from them was further away from the true equilibrium constant than that calculated from the final concentration in the last tube of the preceding set. Thus, starting with chlorine and water (Series I), K' initially is 0, but in the last tube in that set to be opened, No. 5, it was 1.26×10^{-9}. The tubes of Series II therefore were filled with an aqueous solution of chlorine, hydrogen chloride and potassium chlorate in such concentrations that K' was initially less than 1.26×10^{-9}. In a similar manner Tube No. 1 of Series III shows that the initial concentration product of that set is less than the final concentration product of the last tube of Series II.

TABLE II.

Series II.

No.	Vol. Cc.	Time. Days.	(Cl_2).	(H^+).	(Cl^-).	(ClO^{3-}).	K'.
1	40.19	0	0.09826	0.09028	0.10905	0.006661	5.86×10^{-11}
2	35.71	23	0.08281	0.1635	0.1569	0.009262	2.92×10^{-8}
3	34.09	209	0.06365	0.2460	0.2445	0.00822	6.16×10^{-6}
4	38.90	212	0.0788	0.2599	0.2590	0.00842	6.25×10^{-6}
5	35.01	212	0.0594	0.2435	0.2444	0.00862	7.54×10^{-6}

TABLE III.

Series III.

No.	Vol. Cc.	Time. Days.	(Cl_2).	(H^+).	(Cl^-).	(ClO_3^-).	K'.
1	35.56	0	0.1049	0.1650	0.1824	0.00653	2.32×10^{-8}
2	34.10	29	0.1331	0.2317	0.2260	0.001998	7.85×10^{-8}
3	36.76	54	0.08908	0.2407	0.2320	0.006995	1.28×10^{-6}
4	33.24	69	0.08523	0.2478	0.2458	0.008579	2.87×10^{-6}
5	36.68	211	0.07025	0.2675	0.2750	0.00421	7.03×10^{-6}
6	42.71	212	0.0924	0.2881	0.2935	0.00473	7.57×10^{-6}

The equilibrium was approached from the other extreme as well. In Series IV the initial concentration of chlorine was zero, and, therefore, K' initially was infinite. When the last tube, No. 3, of this set was opened, K' had become 1.20×10^{-2}. The initial K' for the next series approaching from this side must now be larger than 1.2×10^{-2}, and the tubes of Series V fulfill this requirement.

TABLE IV.

Series IV.

No.	Vol. Cc.	Time. Days.	(Cl_2).	(H^+).	(Cl^-).	(ClO_3^-).	K'.
1	57.19	1	0.06053	0.8486	0.9377	0.03452	4.22×10
2	45.20	8	0.0952	0.5825	0.6770	0.004735	3.04×10^{-2}
3	46.98	13	0.08574	0.5950	0.6601	0.001371	1.20×10^{-2}
Series V.							
1	42.82	16	0.08441	0.7773	0.9973	0.0004498	1.62×10^{-1}
2	51.34	49	0.09168	0.8009	0.8426	0.0003331	6.09×10^{-2}
3	47.64	248	0.08750	0.8030	0.9125	0.0000766	1.49×10^{-2}

The tubes of Series V, because of an insufficient amount of catalyzing material, as has been explained, did not progress as far toward equilibrium as had been estimated, and so there is a slight gap in the K's between Series V and Series VI. That the constant cannot lie within this interval is shown by the regular trend of K' in Series VI and VII.

TABLE V.

Series VI.

No.	Vol. Cc.	Time. Days.	(Cl_2).	(H^+).	(Cl_2^-).	(ClO_3^-).	K'.
1	34.17	0	0.1089	0.5321	0.5372	0.006663	5.24×10^{-3}
2	36.70	31	0.1039	0.5120	0.5252	0.001166	7.50×10^{-4}
3	34.18	212	0.0965	0.542	0.564	0.0000766	1.23×10^{-4}
4	39.36	212	0.115	0.543	0.555	0.000086	9.18×10^{-5}
6	36.95	212	0.1054	0.540	0.574	0.0000383	5.01×10^{-5}

Series VII.

No.	Vol. Cc.	Time. Days.	(Cl_2).	(H^+).	(Cl_2^-).	(ClC_3^-).	K'.
1	37.00	0	0.1102	0.3954	0.4758	0.006667	4.63×10^{-4}
2	41.33	2	0.09044	0.4086	0.4163	0.00110	8.64×10^{-5}
3	41.20	30	0.1053	0.3741	0.3807	0.0030	5.63×10^{-5}
4	36.33	55	0.09560	0.4062	0.4143	0.000833	5.22×10^{-5}
5	38.13	71	0.08863	0.4053	0.4114	0.0006663	5.0×10^{-5}
6	34.54	211	0.1210	0.4230	0.4390	0.000335	1.80×10^{-5}

The whole possible range of values of the constant from 0 to 8 was thus thoroughly covered. Since K, the true equilibrium constant, must be greater than the largest K' for the forward reaction, and less than the smallest K' for the reverse reaction, we have

$$K = \lim K'$$

$$K'_f - K'_r \doteq 0.$$

The final limiting values of the constant as determined by the converging sets differ by a factor of 2.

The results from Series II, III, V, VI and VII have been plotted in Fig. 2. Not much weight can be attached to the value of K's in Series VI because of the exceedingly small concentration of chlorate ion. Tubes 3, 4 and 5 were analyzed the same day and yet the contents vary by a

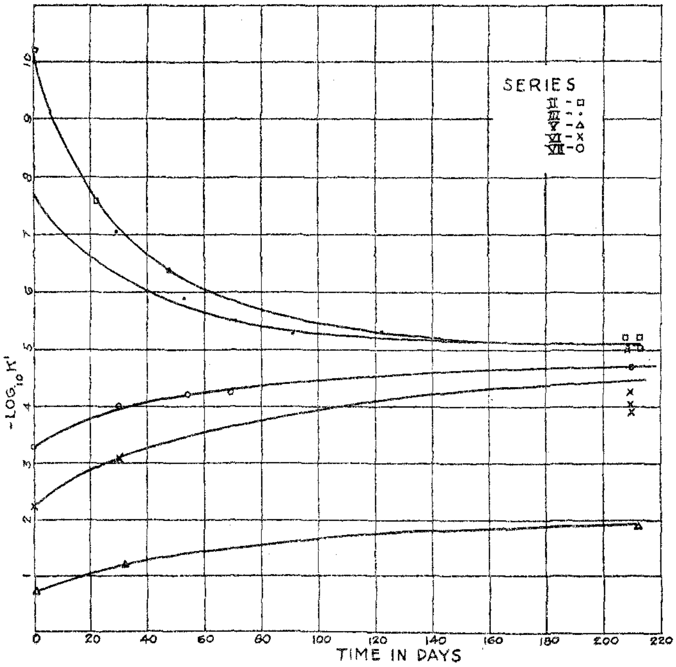

Fig. 2.

factor of 50. Series II and III approaching the equilibrium from one side are in close agreement, the final 3 measurements of the former giving an average K' of 6.65×10^{-6}, and the final 2 measurements of the latter giving an average K' of 7.30×10^{-6}. The only reliable measurement obtained by approaching the equilibrium from the other side is that of Series VII, where $K' = 18.0 \times 10^{-6}$. Thus the ratio of the values of K' from the 2 sides, which in the earlier experiments amounted to several powers of 10, has been reduced to a value between 2 and 3. Giving equal weight to Series II, III and VII, the final value becomes $K' = 10.0 = 10^{-6}$.

These values of K' have all been calculated for convenience on the assumption of complete dissociation of the 2 acids. This is justified by the fact that throughout the range of concentration of the experiments in the 3 series which have been employed the corrected degree of dissociation of hydrochloric acid is practically constant and equal to 0.77, as shown by a plot based upon the free energy measurements of Linhart[1] and of Ellis.[2] Assuming that the degree of dissociation of chloric acid is the same as that of hydrochloric acid, an assumption that can produce no serious error, since only one molecule of the former acid is involved, we find for the value of the true equilibrium constant

$$K = K' \times (0.77)^{12} = 4.3 \times 10^{-7} \text{ at } 364^\circ \text{ A.}$$

The free energy of the reaction can be calculated from the familiar equation, $\Delta F^\circ_{364} = -R'T \ln K_{364}$, whence

$$3Cl_2(aq) + 3H_2O(l) = 6H^+ + 5Cl^- + ClO_3^-;\ \Delta F^\circ_{364} = 10600 \text{ cal.}$$

In order to obtain the equilibrium constant or the free energy at the standard temperature of 250°, it would be desirable to repeat the equilibrium measurements over a wide interval of temperature. This seems hardly practicable with the catalyzer here employed. At lower temperatures the speed of the reaction would be altogether too low for the attainment of equilibrium. At higher temperatures, on the other hand, the decomposition of chloric acid to produce oxygen proceeds rapidly. For example a number of experiments were begun at 114°, but in a few weeks the pressure of oxygen had sufficed to break all the tubes employed.

It is, therefore, necessary to have recourse to thermal data. From the measurements of Berthelot and of Thomsen at about 18° the following figures are obtained:

$$\begin{array}{lll}
3Cl_2(g) & = 3Cl_2(aq.) & ;\quad \Delta H = -14600 \text{ cal.} \\
3H_2 + 1.5O_2 & = 3H_2O & ;\quad \Delta H = -204900 \text{ cal.} \\
2.5H_2 + 2.5Cl_2 & = 5H^+ + 5Cl^- & ;\quad \Delta H = -196500 \text{ cal.} \\
0.5H_2 + 0.5Cl_2 + 1.5O_2 & = H^+ + ClO_3 & ;\quad \Delta H = -23000 \text{ cal.}
\end{array}$$

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[1] Linhart, This Journal, **39**, 2601 (1917).

[2] Ellis, *ibid.*, **38**, 737 (1916).

Hence, for the reaction in question, $\Delta H_{291} = 0$. This, however, will not be true at other temperatures. The partial molal heat capacity of HCl(aq) has a high negative value, namely about —40.[1] For want of data we may assume that of $HClO_3$(aq) to be the same. The partial molal heat capacity of H_2O(l) is 18, that of Cl_2(aq), a non-electrolyte, is doubtless small. The change of heat capacity $\Delta\Gamma$ in the reaction has, therefore, the enormous values of about —300 cal. per degree. Using the 2 equations, $\Delta H = \Delta H_0 + \Delta\Gamma T$, and $\Delta F = \Delta H_0 - \Delta\Gamma T \ln T + IT$, the value of ΔH_0 is 87300, and for the above values of $\Delta F_{0\,364}$, $I = -1979.8$. This surprising value for I, which is greater than that for any other reaction studied, is doubtless due to the enormous value of $\Delta\Gamma$, which has just been mentioned above.

For the values of I the change of free energy in the reaction follows immediately:

$$3Cl_2(aq) + 3H_2O(l) = 6H^+ + 5Cl^- + ClO_3^-;\ \Delta F^\circ_{298} = 6640 \text{ cal.}$$

In order to get the free energy of formation of the chlorate ion we must add the free energies of all the substances entering into the above reaction, thus:

$$\begin{array}{lllll}
3Cl_2(aq) + 3H_2O & = 6H^+ + 5\,Cl^- + ClO_3^-; & & \Delta F^\circ_{298} = & 6640 \\
3Cl_3(g) & = 3Cl_2(aq) & ; & \Delta F^\circ_{298} = & 4950\text{[2]} \\
3\,H_2O + 1.5\,O_2 & = 3H_2O(l) & ; & \Delta F^\circ_{298} = & -169860\text{[3]} \\
6H^+ & = 3H_2 + 6\oplus & ; & \Delta F^\circ_{298} = & 0\text{[4]} \\
5\,Cl^- + 5\oplus & = 2.5Cl_2(g) & ; & \Delta F^\circ_{298} = & 156896\text{[5]}
\end{array}$$

From which

$$0.5Cl_2(g) + 1.5\,O_2 + \ominus = ClO_3^-;\ \Delta F^\circ_{298} = -1374.$$

In conclusion, I wish to acknowledge my indebtedness and to express my thanks to Professor G. N. Lewis and Professor W. C. Bray for their help and interest throughout this whole investigation, and to Professor Merle Randall for his help in checking the free energy calculations.

BERKELEY, CAL.

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[1] Lewis, THIS JOURNAL, **35**, 1 (1913).

[2] Lewis and Randall, unpublished work.

[3] Lewis and Randall, THIS JOURNAL, **36**, 1969 (1914).

[4] Lewis, *ibid.*, **35**, 1 (1913).

[5] Lewis and Randall, unpublished work.