

altered in position, while those of holmium and erbium are noticeably shifted toward the blue.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CHICAGO]

STUDIES ON COMPLEX IONS.
III.¹ THE RELATIVE STABILITIES OF THE
HALOGENOPLATINATES

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RECEIVED AUGUST 30, 1930

PUBLISHED NOVEMBER 5, 1930

As part of a study of the factors which determine the conditions under which complex ions are formed, a determination of the relative stabilities in solution of a series of complex ions of similar types has become desirable. Schlesinger and Tapley³ have shown that the halogenoplatinates are mutually and reversibly convertible into each other, and are therefore suitable for such an investigation.

The usual method of determining the "stability" or "instability" constants of such ions is inapplicable to this case, for aqueous solutions of the halogenoplatinates contain no detectable quantities of the free platonic ions. Relative values of the stabilities might, however, be obtained if the amount of transformation of one halogenoplatinate into the other could be determined in the presence of given quantities of halide ions. But even such measurements present difficulties, for the reactions involved probably proceed in many steps, leading through all of the theoretically possible mixed halogenoplatinates. No method available allows a determination of each of the seven possible components of such a system.

It nevertheless has become possible to obtain approximate relative values by the following procedure. When, for example, a chloroplatinate is mixed in aqueous solution with a bromide and a chloride in suitable proportions, a reaction occurs which leads to the formation of a mixture intermediate in color between that of the pure chloroplatinate and the pure bromoplatinate. An identical mixture, at least so far as the color is concerned, is obtained if the starting material is the bromoplatinate, a fact which demonstrates that a state of true equilibrium is attained. By comparing photometrically the color of such solutions with mixtures of chloro and bromoplatinates of known concentration, one could estimate the percentage of transformation of the one platinate into the other were no

¹ For the preceding papers of this series see *THIS JOURNAL*, 51, 3520, 3523 (1929).

² This paper is taken from a thesis presented by R. E. Palmateer to the Faculty of the Ogden Graduate School of Sciences of the University of Chicago, in part fulfillment of the requirements for the degree of Doctor of Philosophy.

³ Schlesinger and Tapley, *THIS JOURNAL*, 46, 276 (1924).

intermediate chloro-bromoplatinates formed. From this percentage transformation one could then calculate the ratio of the concentrations of the two complex ions. But, as will be demonstrated in the experimental part of this paper, intermediate complex ions are undoubtedly present, and the color of the solutions is, on that account, not a direct measure of the percentage transformation nor of the ratio of the concentrations of the complex ions. However, as the calculated ratios approach zero or infinity the fictitious values must approach the true ratio. That this assumption is warranted is shown by the fact that under these conditions the colors, as well as the absorption spectra, approach those of the pure complex ions. Hence, by plotting the values of these fictitious ratios⁴ against the ratios of the concentrations of the simple halide ions involved in the reaction, and extrapolating the curves to a point representing practically complete transformation, one can determine at what concentrations of the simple ions the transformation of the one complex ion into the other becomes complete. The extrapolation proved to be unexpectedly reliable because the curves proved to be straight lines.

Ratios of the simple ions found in this way to be necessary almost completely to transform one of the halogenoplatinates into the other are very striking. To convert 99% of bromoplatinate⁵ into chloroplatinate, the solution must contain approximately 660 times as much sodium chloride as sodium bromide, and to produce the corresponding result in the reaction between iodoplatinate and bromoplatinate, there must be present approximately 25,000 times as much sodium bromide as sodium iodide. From these data we have estimated, by a method to be described below, that to convert iodoplatinate ions almost completely into chloroplatinate ions, the solution must be approximately 16,600,000 times as concentrated

⁴ These fictitious ratios, calculated from the colorimetric data, will hereafter be called the "apparent ratios" and the corresponding percentage transformation will be called the "apparent % transformation" and will be designated by the letter *P*.

⁵ The choice of 99% for the calculation was based on the following reasons. Theoretically, 100% conversion cannot occur until the concentration of one of the simple halide ions reaches infinity. The data obtained could have been used to calculate the ratio of the simple ions required to produce any degree of transformation below 100%, but such calculations have a concrete meaning only for almost complete transformation, because only under that condition is the color a measure of the amount transformed. Another point of importance should be noted at this time. While it is undoubtedly true that the "apparent ratios" (see footnote 4) approach the true ratios, the two values might still be fairly widely different even at 99% transformation; but that is of no significance. In the transformation of bromoplatinate into chloroplatinate, for example, the color of the solutions is practically identical with that of the latter substance when the "apparent ratio" is 99:1. Hence practically all of the material is in the form of chloroplatinate. The remaining 1% may be largely an intermediate ion instead of bromoplatinate. Consequently the true ratio may be far from 99; but 99% of the material is nevertheless in the form of the chloroplatinate, and this is the quantity in which we are interested.

with respect to sodium chloride as to sodium iodide. An attempt was made to determine the corresponding quantities for the equilibrium between fluoroplatinate⁵ and iodoplatinate. The reaction requires months for completion at ordinary temperatures, and the solutions attack glass vessels and undergo decomposition. For these reasons no reliable data have been obtained, but the results indicate that the great difficulty of transforming fluoroplatinate into the other ions is possibly due in part to the sluggishness of reaction rather than entirely to inherent stability.

It is interesting to point out that the results here reported demonstrate how enormously greater is the tendency of iodide ion than of bromide ion, and of bromide ion than of chloride ion, to enter the coördination sphere in the case of the platinates. In the case of some of the solid ammines of chromium and certain other metals, according to the data obtained in this Laboratory and elsewhere,⁶ the reverse is true. Whether the difference is to be explained by the influence of changes in lattice energies in reactions between solid compounds as has been suggested,⁶ or is to be accounted for by specific influences of the central atoms, can be decided only when further data have been collected. The most likely cause for the difference, however, would seem to be that, in the platinates, the halogen ions are contained in a negative complex ion, while in the other compounds mentioned they are in a positive complex ion.

In the course of this investigation we have had occasion to review the evidence on which rests the idea that all possible intermediate halogenoplatinate complexes exist, and to contribute further data along these lines. We have made some interesting observations on the rates at which equilibria in such mixtures are established, as well as on some other properties of the halogenoplatinates. These observations as well as additional phases of the interpretation of our data will be taken up below.

Experimental

Preparation of Materials.—The platinum from which the salts were prepared was purified by recrystallizing sodium chloroplatinate from alcohol and further by the procedure of Mylius and Mazzucchelli.⁷ From the platinum thus purified sodium chloroplatinate was prepared according to the method of Precht.⁸

Potassium bromoplatinate was obtained according to the procedure of Biilmann and Andersen,⁹ and further purified by two recrystallizations, which yielded a product of constant absorption spectrum. The corresponding sodium salt was obtained by adding a dilute solution of sodium bicarbonate to bromoplatinic acid, an intermediate product in the preparation of the potassium salt. The solution was evaporated to a sirupy consistency on a water-bath and dried in a vacuum desiccator over phosphorus pentox-

⁵ See Ref. 1 and Biltz, *Z. anorg. allgem. Chem.*, **130**, 93 (1923); **166**, 351 (1927). Other references will be found in the articles cited.

⁷ Mylius and Mazzucchelli, *Z. anorg. Chem.*, **89**, 1 (1914).

⁸ Precht, *Z. anal. Chem.*, **18**, 509 (1879).

⁹ Biilmann and Andersen, *Ber.*, **36**, 1565 (1903).

ide. The resulting solid was dissolved in absolute alcohol, the solution filtered and treated with ether to precipitate the sodium bromoplatinate.¹⁰ Von Bonsdorff¹¹ claims to have prepared sodium bromoplatinate by the addition of sodium bromide to bromoplatinic acid; but sodium bromide is less soluble in water or in alcohol than is sodium bromoplatinate, and his method therefore leads to no results.

Datta's¹² method for the preparation of potassium iodoplatinate was used, and that of Schlesinger and Tapley³ for the potassium fluoroplatinate. In the latter case it was found preferable to heat the mixture of platinum and the double salt of lead tetrafluoride to just below the melting point of the latter, because under these conditions a better yield was obtained than that described in the earlier paper.

Sodium chloride and sodium iodide were purified by repeated recrystallization from commercial salts of good quality. The iodide was shown by the usual methods to be free from chloride. Sodium bromide was prepared from repeatedly redistilled hydrobromic acid and sodium bicarbonate. The final product contained too small a quantity of sodium chloride to be detected by the ordinary methods of titration. Sodium fluoride was prepared similarly from hydrofluoric acid. The usual drying of these salts by heating them to redness in platinum vessels was omitted, as it was shown spectroscopically that such a procedure introduced traces of the corresponding platينات.¹³

The measurement of the "apparent % transformation" could not be made by a direct comparison of the color of the unknown solutions with that of solutions containing known amounts of the halogenoplatinates in question, because synthetic mixtures cannot be prepared. Both bromo and iodoplatinates undergo moderately rapid decomposition in pure water. To stabilize the former a soluble bromide and for the latter an iodide must be added to the solutions. If these stabilizing salts were added to a mixture of these two platينات or to a mixture of either of them with a chloroplatinate, partial transformation to the more stable complex ion would occur.

It was, therefore, necessary to calculate from the color intensity of the separate halogenoplatinates what must be the color intensity of mixtures of the two salts. To do this we first proved both colorimetrically and spectrophotometrically that each of the salts obeyed Beer's law. Next it was found, for example, that a column of 0.0016 molar sodium chloroplatinate 50 mm. long matched the color of a 3-mm. column of 0.0016 molar sodium bromoplatinate¹⁴ in a Kober colorimeter. Consequently if $P\%$ of the chloroplatinate in the first solution were transformed to bromoplatinate, a column H mm. in length would have to be used to match a 10-mm. column of the 0.0016 molar standard bromoplatinate solution when

¹⁰ This salt is so hygroscopic that we did not weigh it out in making up the standard solutions, but determined the strength of the solution prepared by colorimetric comparison with a standard solution of the potassium salt.

¹¹ Von Bonsdorff, *Pogg. Ann.*, 19, 344 (1830); 33, 61 (1834).

¹² Datta, *THIS JOURNAL*, 35, 1186 (1913).

¹³ The amount of platinate was less than 0.00002 molar in the saturated solutions of the simple salts, but was easily discernible in the spectra.

¹⁴ The standard solutions of this salt always contained sufficient sodium bromide to prevent hydrolysis.

$$H = \frac{1000}{P + \frac{3}{50}(100 - P)}$$

The values of P in this equation are what have been called the "apparent % transformation" in the preceding discussion.⁴ For the reaction between bromo and iodoplatinates a similar procedure was used, except that the color of the mixtures was compared with that of a 0.0001 molar iodoplatinate solution stabilized by sodium iodide. The equation for calculating the percentage transformation, obtained as described for the preceding case, was

$$H = \frac{1000}{P + \frac{208}{50}(100 - P)}$$

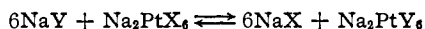
Although this method gives fairly satisfactory results, it suffers from the difficulty that, in spite of the fact that dilute solutions of these various platinum salts are similar in color, the shades are not exactly alike. For this reason colorimetric readings are difficult to duplicate for a given mixture more closely than to 1% in the most favorable case, that is, when the apparent transformation is about 50%, and to 7% in the least favorable cases, that is, when the reaction has gone nearly to completion toward the formation of the less intensely colored compound. Ten to fifteen readings were therefore made of each solution, and all the solutions were made up in several portions. Consequently each of the "apparent % transformations" tabulated below is really the average of from thirty to sixty readings. Since the errors are less marked in dilute than in concentrated solutions, the former were used exclusively. Finally, measurements were restricted to solutions of from three to five different concentrations of the platinum salts, because for each concentration the constants for the equations given above had to be redetermined.

It might be expected that provision would have to be made for keeping the mixtures at constant temperature both while equilibrium is being reached and during the measurement of the color, but this was found to be unnecessary for the degree of precision to which we were limited by the sources of error described. Thus we observed that even though the solutions were kept in the colorimeter for from ten to twenty minutes for measurement, there occurred no change in the reading greater than the reading error itself. Unquestionably this is in part due to the slowness of the transformation of bromoplatinate into chloroplatinate and *vice versa*, but the lack of disturbance caused by temperature changes must be largely due to a very small temperature coefficient for the equilibrium condition. This is shown by two facts. In the first place, the data obtained from solutions kept at 25° in a thermostat did not differ from data on solutions kept in the room. In the second place, the colors of the equilibrium mix-

tures for the transformation of iodoplatinate into bromoplatinate also remained constant in the colorimeter although in this case equilibrium is attained in a few minutes.

Rate of attainment of equilibrium is greatly affected by light. The reaction between a bromoplatinate and a chloride in a mixture exposed to the light of a north window came to completion in three days; another portion of the same solution was kept in a thermostat in a blackened flask, and did not reach equilibrium before the fiftieth day. Nevertheless, the final equilibrium reading was the same in the two cases. Consequently there is a great advantage in keeping the mixtures exposed to light instead of in a constant temperature bath, and the data presented below, therefore, refer to the reaction at room temperature, *i. e.*, from 20–25°.

In Table I are given the experimental results for the equilibrium between chloroplatinate and bromoplatinate ions. The first column gives the initial concentration of the platينات in moles per liter. The subscript B indicates that equilibrium was reached from the bromoplatinate, the subscript C that the equilibrium was reached from the chloroplatinate side of the reaction. The second and third columns give, respectively, the initial concentrations of the sodium chloride and the sodium bromide in moles per liter. The length of column of the equilibrium mixture required for a color match when read against a 10-mm. column of a solution of potassium bromoplatinate of the same concentration as that of the platinate in the original solution is given in the fourth column.¹⁵ The fifth column is the "apparent % transformation" of chloroplatinate into bromoplatinate, defined and obtained as has already been described. Obviously the transformation of the one halogenoplatinate into the other must be accompanied by decrease in the concentration of one of the simple halide ions and a corresponding increase in the other. Hence the equilibrium ratio of the simple halides differs from the ratio of the initial concentrations. To calculate the former we again proceeded as if no intermediate platinate ions were formed. Consequently these ratios are also fictitious, but they, too, must approach the real values as the "apparent % transformation" approaches 100. In fact, in most of the experiments the change in the ratio of the simple salts resulting from transformation of the platينات is very small, since a large excess of the simple ions was usually present. The calculation of the equilibrium ratios from the "apparent % transformations" is thus made on the basis of the chemical change represented by the equation



¹⁵ Potassium bromoplatinate was used as a standard because it can be weighed out accurately while the sodium salt is too hygroscopic; but in the equilibrium mixtures the sodium salts had to be used because potassium chloroplatinate would be precipitated from the solution and the equilibrium, therefore, disturbed.

in which X and Y represent halide ions. In Col. 6 are given the equilibrium ratios of the halide ions, and in Col. 7 the corresponding ratios for the platinate ions. As was pointed out above, when these ratios are plotted against each other, a straight line results. Hence, the product of the one set of ratios by the reciprocal of the other is a constant, the value of which is shown in Col. 8.

TABLE I
EXPERIMENTAL DATA

Halogeno- platinate	Sodium chloride	Sodium bromide	Reading, <i>H</i>	% Trans- formation, <i>P</i> ^a	Equilibrium ratios NaBr/NaCl	PtBr ₆ /PtCl ₆	Const.
0.0016 _C	1.3	0.034	54.4	13.37	0.02513	0.154	0.163
.0016 _C	1.1	.0325	50.18	15.25	.02814	.18	.156
.0016 _C	0.9	.027	48.8	16.00	.02817	.19	.148
.0016 _C	1.0	.033	46.3	17.12	.03125	.208	.155
.0016 _C	1.1	.039	45.87	17.25	.03387	.212	.159
.0016 _C	1.0	.0385	45.3	17.75	.03674	.214	.171
.0016 _C	1.3	.051	42.5	19.4	.03775	.24	.157
.0016 _C	0.85	.0374	40.83	20.4	.0416	.256	.162
.0016 _C	1.0	.044	36.98	23.08	.0417	.2975	.140
.0016 _C	1.0	.044	40.9	20.42	.04196	.256	.164
.0016 _C	0.65	.03575	34.87	24.4	.05109	.318	.161
.0016 _C	1.0	.055	32.52	26.42	.0522	.356	.146
.0016 _C	1.0	.055	34.7	24.5	.0525	.329	.159
.0016 _C	1.0	.055	34.8	24.4	.05254	.32	.161
.0020 _C	0.95	.055	25.97	26.0	.0544	.358	.152
.0017977 _B	1.0	.05	26.41	29.46	.0581	.418	.139
.0017977 _B	1.0	.055	25.82	30.29	.063	.433	.145
.0016 _C	0.55	.0385	30.63	28.12	.06477	.391	.165
.0016 _C	.7	.05	30.17	28.7	.0672	.404	.166
.0016 _B	.85	.05	30.19	28.7	.0674	.404	.167
.001387 _B	.7	.05	30.32	32.6	.080	.4849	.165
.0016 _C	1.0	.088	24.43	37.98	.084	.606	.138
.0020 _C	0.55	.055	19.7	36.75	.091	.588	.155
.0016 _C	.5	.05	22.55	41.4	.0915	.695	.133
.0016 _C	.55	.055	24.6	36.75	.09299	.586	.158
.0017977 _B	1.0	.088	19.36	33.75	.0949	.739	.128
.0017977 _B	1.0	.1	18.9	43.7	.1072	.777	.138
.0016 _C	0.55	.066	21.41	43.375	.1115	.77	.144
.00177 _B	.45	.05	18.21	46.6	.125	.872	.143
.0020 _C	.45	.0675	15.98	47.0	.1358	.877	.154
.0016 _C	.45	.0675	18.56	50.75	.1408	1.04	.136
.0016 _C	.45	.0675	18.71	50.5	.1410	1.01	.140
.0016 _C	.43	.07	19.42	48.5	.1505	0.942	.159
.0016 _C	.41	.0738	17.61	54.0	.1602	1.18	.140
.00177 _B	.43	.07	15.83	54.4	.176	1.18	.149
.0020 _C	.41	.082	13.85	55.00	.181	1.22	.141
.0016 _C	.41	.082	16.77	57.5	.18413	1.34	.137
.0016 _C	.41	.082	16.84	57.0	.18416	1.32	.140
.0016 _C	.33	.0762	16.3	59.0	.1993	1.44	.138
.00177 _B	.415	.085	14.64	59.4	.2175	1.485	.149

TABLE I (Concluded)

Halogeno- platinate	Sodium chloride	Sodium bromide	Reading, <i>H</i>	% Trans- formation, <i>P</i> ^a	Equilibrium ratios		Const.
					NaBr/NaCl	PtBr ₆ /PtCl ₆	
0.0016 _C	0.33	0.0825	15.76	61.2	0.228	1.58	0.144
.0016 _C	.4	.1	16.75	57.2	.233	1.345	.173
.00177 _B	.4	.1	13.55	64.2	.262	1.807	.145
.0020 _C	.25	.075	12.2	63.5	.2626	1.74	.151
.0016 _C	.25	.075	14.66	65.5	.2679	1.94	.138
.0016 _C	.23	.07	14.7	65.5	.269	1.91	.141
.0016 _C	.25	.0875	14.13	68.5	.3153	2.2	.141
.0016 _B	.16	.05	15.16	65.0	.341	1.85	.184
.001387 _B	.37	.13	15.4	71.9	.36	2.555	.141
.0016 _C	1.00	.375	13.44	72.95	.366	2.635	.138
.0016 _C	0.35	.15	13.36	73.0	.401	2.735	.146
.0016 _C	.2	.1	12.78	77.0	.446	3.35	.133
.0016 _C	.5	.25	12.9	76.47	.478	3.163	.151
.0016 _C	.32	.18	13.06	75.2	.527	3.2	.165
.0016 _C	.2	.15	12.32	80.0	.686	4.00	.171
.0017977 _B	.5	.375	10.46	85.08	.756	5.3	.142
.0017977 _B	.25	.25	10.21	86.39	1.01	6.4	.158

^a It must be borne in mind that the equations given above for calculating "*P*" from "*H*" merely show the principles employed. The solutions actually used as color standards did not always have exactly the same concentration as the experimental solutions, and the values of "*P*" in the table are corrected for this difference. Furthermore, "*P*" represents the fraction present as bromoplatinate irrespective of the side from which equilibrium was reached. Similar considerations apply to Table II.

It will be seen from the table that there are considerable deviations from the linear relationship between the "apparent % transformation" and the ratio of the concentrations of the simple halide ions. These deviations, however, show no trend, and can be fully accounted for by the unavoidable reading errors which have already been discussed. To show at a glance that the deviations are symmetrical throughout, we have reproduced the experimental results in Fig. 1. Instead of plotting the two ratios directly, we calculated from the constant what should be the curve for the plot of the "apparent" ratio of the concentration of complex ions against the logarithm of the "apparent" ratio of the concentrations of the simple ions. These curves are shown in solid lines; the circles representing the experimental data show no trend.

The data furthermore show that the equilibrium is determined by the ratio of the concentrations of the substances involved rather than by the values of the concentrations themselves. Thus, for example, there are two mixtures in which the apparent ratio of the concentrations of the sodium bromide to sodium chloride was 0.262 at equilibrium. Although one of these solutions contained 0.1038 mole of sodium bromide and 0.3962 mole of sodium chloride and the other 0.0674 mole of bromide and 0.2576 mole of the chloride, the constant for the first set of data is 0.145 and for the second set 0.151. The difference between the two values is accounted for by a

reading error of 1%, which is well within the limit attainable in the experiments. These two solutions illustrate also that the changes in the concentration of the platinate are without effect on the constant, for the first solution was 0.00177 molar with respect to this constituent and the second 0.0020. It should be stated, however, that the platinate concentrations were not varied between wide limits for reasons discussed previously. Numerous other cases showing that the constant is independent of the initial concentrations will be found in the table.

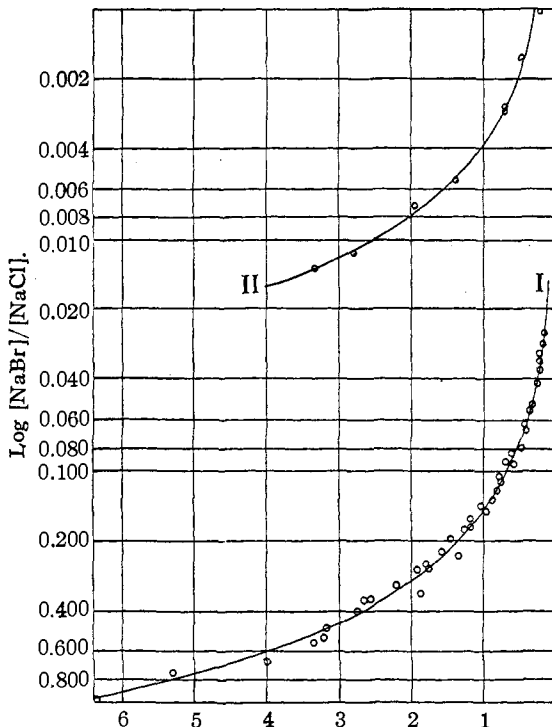


Fig. 1.—Curve I, $[\text{Na}_2\text{PtBr}_6]/[\text{Na}_2\text{PtCl}_6]$; Curve II, $[\text{K}_2\text{PtI}_6]/[\text{K}_2\text{PtBr}_6]$.

From the average value of this constant we may now calculate the conditions under which bromoplatinate is 99% transformed to chloroplatinate. For, as has already been said, as the "apparent % transformation" approaches 100% it also approaches the value of the real per cent. transformation. The equation by which the constants of Table I were calculated is

$$\frac{[\text{NaBr}]}{[\text{NaCl}]} \times \frac{[\text{Na}_2\text{PtCl}_6]}{[\text{Na}_2\text{PtBr}_6]} = 0.15$$

in which the bracketed symbols denote molar concentrations. If $[\text{NaBr}] = 1$, the ratio $[\text{Na}_2\text{PtCl}_6]/[\text{Na}_2\text{PtBr}_6]$ becomes 99 when $[\text{NaCl}] = 660$.

In Table II are given the corresponding data for the equilibrium between iodoplatinate and bromoplatinate ions. In addition to the difficulties of measurement mentioned above, another source of error proved troublesome in this case. Very small traces of alkali, even those dissolved from glass by the solutions, cause decomposition of the iodoplatinate. To prevent this, bromide ion was supplied in part in the form of hydrobromic acid. In these solutions, however, iodine is fairly rapidly liberated, probably on account of reduction of the platinum to the platinous condition since the reaction occurs in solutions free from oxygen. Fortunately the liberation of iodine is much slower than the attainment of the equilibrium under investigation, and causes no serious difficulty if the measurements are made rapidly. The great difference in speed of attainment of equilibrium in the reaction between chloro and bromoplatinate and in that between bromo and iodoplatinate is of considerable interest. For the present we can state, however, only that in the former case equilibrium was reached in about three days in daylight, while in the latter only thirty to eighty minutes are necessary.

TABLE II
EXPERIMENTAL DATA

Halogeno- platinate	Bromide concentration	Sodium iodide	Reading, % Trans- formation, P		Equilibrium ratio		Constant
			H	P	NaI/HBr	PtI ₆ /PtBr ₆	
0.0001 _I	0.8462	0.011	12.93	76.7	0.01318	3.29	0.00400
.0001 _B	1.6924	.02	13.5	73.5	.01155	2.777	.00416
.0001 _I	0.8462	.006	15.05	65.5	.00722	1.90	.0038
.0001 _B	0.8462	.005	16.82	57.6	.0055	1.358	.00405
.0001 _B	1.6924	.005	22.75	41.0	.00281	0.695	.00405
.0001 _I	0.8462	.002	24.00	39.0	.00279	.639	.00436
.0001 _I	.8462	.002	22.84	41.4	.00278	.707	.00393
.0001 _I	.8462	.002	23.02	41.0	.00278	.695	.0040
.0001 _I	.8462	.002	23.17	40.7	.00278	.686	.00405
.0001 _B	.8462	.0025	23.24	40.5	.00266	.68	.00391
.0001 _I	.8462	.001	29.82	30.6	.001643	.431	.00382
.0001 _B	1.6924	.001	60.3	12.7	.000545	1.455	.00374

Again the values in Col. 8 are constant to well within the range of experimental error. Hence, when transformation is almost complete

$$\frac{[\text{NaI}]}{[\text{NaBr}]} \times \frac{[\text{Na}_2\text{PtBr}_6]}{[\text{Na}_2\text{PtI}_6]} = 0.004$$

Substituting 1 for [NaI], 99 for [Na₂PtBr₆]/[Na₂PtI₆], [NaBr] becomes approximately 25,000.

If we multiply the equations [NaI]/[NaBr] × [Na₂PtBr₆]/[Na₂PtI₆] = 0.004¹⁶ and [NaBr]/[NaCl] × [Na₂PtCl₆]/[Na₂PtBr₆] = 0.15 by each

¹⁶ The actual measurements for this equation were carried out with solutions containing hydrobromic acid and sodium bromide for the reasons given above, but for the very rough calculations now to be discussed, substitution of the salt for the acid will make no difference. As a matter of fact, we showed experimentally that the same value for this constant would have been obtained had sodium bromide alone been used,

other we obtain

$$\frac{[\text{NaI}]}{[\text{NaCl}]} \times \frac{[\text{Na}_2\text{PtCl}_6]}{[\text{Na}_2\text{PtI}_6]} = 0.0006$$

This is admittedly a mathematical procedure of very uncertain justification. In obtaining the constant values 0.004 and 0.15, we substituted in the first two equations numerical values which in all probability represent concentrations only under the very definite conditions specified above. There was no well-established theoretical basis for expecting that the products of these ratios would be constants, and there is, therefore, no reason for anticipating that a similar relationship would prove true in the case of the equilibrium between iodoplatinate and chloroplatinate, but the last-named equilibrium cannot be studied in the same way as were the others, because the colors obtained, when attempts were made to cause partial transformation, are not intermediate in shade between those of the iodo and chloroplatinate. This is not surprising, for iodoplatinates differ very markedly in color from the chloroplatinates, and if intermediate compounds exist there should be a variety of shades in the equilibrium mixtures. For this reason it was necessary to find a way of estimating mathematically under what conditions almost complete transformation should occur, and then to corroborate this estimate approximately by experiment. The derived equation seemed the most rational approach to the solution of the problem.

According to this equation it would be impossible to transform more than a small fraction of iodoplatinate into chloroplatinate by the addition of chloride ion. A minimum of 0.001 molar potassium or sodium iodide is required to prevent decomposition of iodoplatinates into platinum tetraiodide. If this amount of potassium iodide is present in the solution, the equation requires that the concentration of the chloride ion constituent would have to be 16,000 normal for 99% transformation. In accordance with this prediction, it was found that iodoplatinates, stabilized with a minimum amount of potassium iodide and treated with a large excess of 6 molar hydrochloric acid, retain a much more intense color than they should, had the iodoplatinate been completely changed to chloroplatinate.¹⁷

Somewhat more definite information can be obtained by studying qualitatively the reverse reaction. According to the equation it is necessary to make the concentration of the chloride approximately 0.2 molar in order to prevent practically complete transformation of chloroplatinate to iodoplatinate when the former is dissolved in 0.001 molar potassium iodide. A solution thus prepared, using 0.0001 molar sodium chloroplatinate, does but since decomposition tended to occur under these conditions the data were not as reliable as those obtained with the acid.

¹⁷ If concentrated hydrochloric acid is used, the color of the solution gradually fades. The absorption spectrum of this solution shows, however, that the iodoplatinate has been transformed into compounds other than chloroplatinate. Also the addition of potassium iodide to these solutions does not completely reverse the reaction.

not quite attain the color of iodoplatinate of this concentration, but the experiment is only of qualitative character because decomposition to platinum tetraiodide cannot be entirely prevented. On the other hand, a solution molar with respect to hydrochloric acid, 0.001 molar with respect to potassium iodide and 0.0001 molar with respect to sodium chloroplatinate showed, when equilibrium was reached, the brown color characteristic of partial transformation instead of the violet shade of the iodoplatinate. Obviously, then, the data calculated from the derived equation do give results correct at least so far as the order of magnitude is concerned.

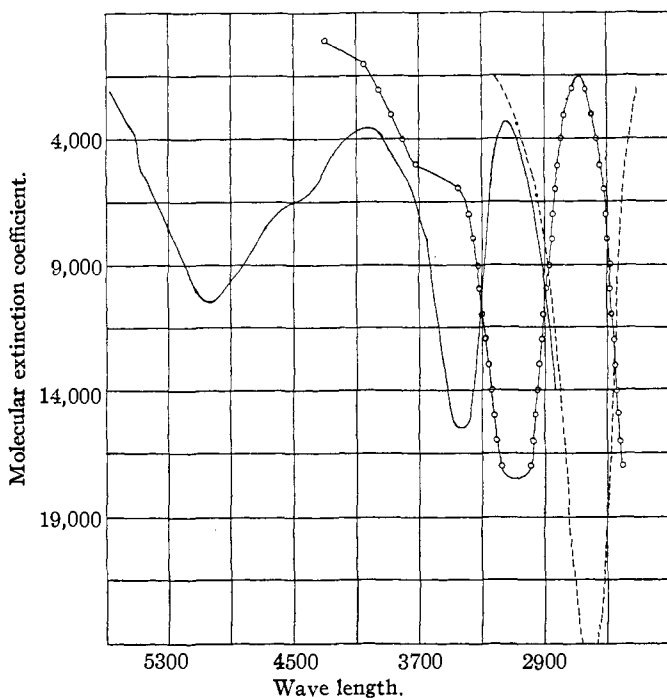


Fig. 2.— — — —, K_2PtCl_6 ; $\circ-\circ-\circ$, K_2PtBr_6 ; —, K_2PtI_6 .

There are several points of theoretical interest which should be indicated, although our data are as yet too limited to warrant extended discussion. One would expect that equilibrium conditions in the reactions investigated would be expressed by equations of the type $[PtX_6^-][Y^-]^6 / [PtY_6^-][X^-]^6 = K$; instead, an equation in which the apparent concentrations of the simple halogenide ions appear as the first power results from the data. The lack of agreement with the mass law is not surprising. We have neglected the activity coefficients; in dilute solutions these might cancel out because of the great similarity of the pairs of ions involved, but in the concentrations used this is hardly to be expected. But the most

probable reason for the enormous deviation from the mass law is the possibility that the apparent concentrations are in most instances not the real concentrations because of the formation of intermediate complex ions. Since the existence of such substances has repeatedly been denied, further investigation of this point was undertaken as described below.

While it is thus not difficult to explain the deviation from the mass law, no satisfactory explanation has as yet been found for the fact that the "apparent ratios" happen to vary with the first power of the ratio of the concentrations of the halogenide ions. A possible explanation is that the

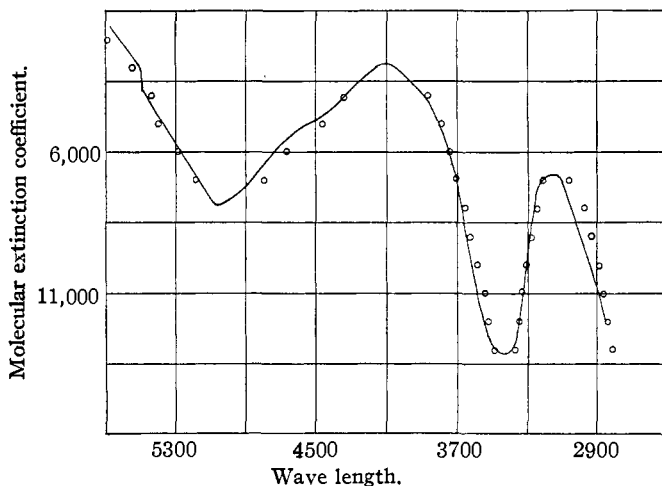


Fig. 3.—○ ○ ○, 0.000025 molar bromoplatinate + 0.000075 iodoplatinate; ———, calculated curve.

change in the absorption band, as one of the halogenoplatinates is transformed through a series of mixed platinates into the other, is divided into equal steps, and that the distribution of the concentrations of all of the complex ions is a symmetrical one. Since six such steps are involved in the "apparent % transformation," one might obtain the relationship

$$(\text{Apparent ratio of complex ions})^6 \times (\text{apparent ratio of simple ions})^6 = \text{constant}$$

This, of course, is what we have found. We believe, however, that too many assumptions are involved in this idea to warrant its acceptance on the basis of the one set of data thus far obtained; the first power relationship may, indeed, be purely accidental.¹⁸

¹⁸ It is also possible that the first power relationship means that the color change is complete in the first step of the series of reactions, for example, that the color of the hypothetical PtCl_4Br^- ion is identical with that of the PtBr_6^- ion. This explanation does not fit with the fact that the values for the constant are independent of the side from which equilibrium is attained nor with facts presented in the following section of this paper.

Existence of Mixed Halogenoplatinates

The existence of the mixed halogenoplatinates has been affirmed and denied. Pitkin¹⁹ and Pigeon,²⁰ by crystallization of mixtures of chloro- and bromoplatinates, claimed to have obtained mixed chlorobromoplatinates. The former also reported the preparation of the compound $K_2PtCl_4Br_2$ by the action of potassium bromide on platonic chloride. Herty²¹ demonstrated that none of these substances was a true compound, and Miolati,²² by conductivity methods applied to solutions, likewise concluded that there is no evidence for formation of mixed compounds.

The experimental work herein reported makes possible another method of attacking this problem. If the mixtures prepared by adding, for example, sodium bromide to sodium chloroplatinate contain no intermediate complex ions, the value of the "apparent % transformation" obtained colorimetrically is the real percentage transformation. From the latter we could then calculate the amount of the chloroplatinate and the bromoplatinate in the solutions. With this information and with photometrically determined absorption spectra of each of the platinates, the position of the absorption band of the solution should be calculable.²³ If the calculated and the observed spectra coincide, no intermediate complexes are present. The curves to be presented below show that this is not the case.

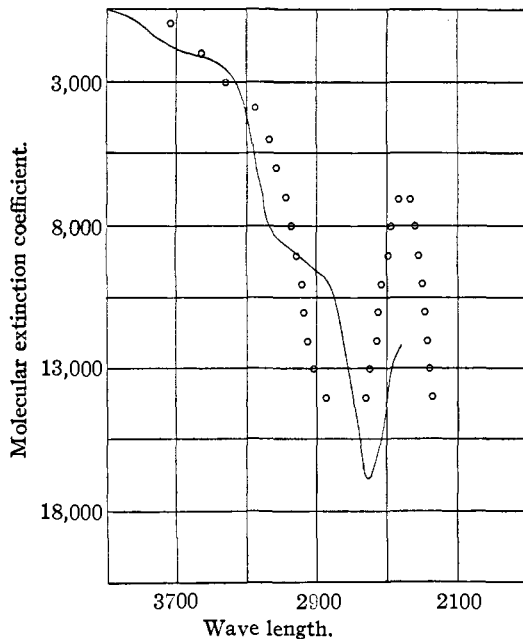


Fig. 4.—○ ○ ○, equilibrium mixture—colorimetrically 39.2% $PtBr_6$ and 61.8% $PtCl_6$; ———, calculated curve.

Before proceeding with these measurements, it seemed desirable to verify the method of calculating the spectra for the mixtures in question. As has

¹⁹ Pitkin, *THIS JOURNAL*, 1, 472 (1879); 2, 408 (1880).

²⁰ Pigeon, *Ann. chim.*, [7] 2, 488 (1894).

²¹ Herty, *THIS JOURNAL*, 18, 130 (1896).

²² Miolati, *Z. anorg. Chem.*, 14, 238 (1879).

²³ Kayser, "Handbuch der Spektroskopie," S. Hirzel, Leipzig, 1905, Vol. III, p. 92.

already been pointed out, mixtures of known quantities of the two halogenoplatinates cannot be prepared. Consequently we remodeled the Hilger sector photometer to permit us to insert two separate cells into each of the photometer tubes. This allowed us to have the light fall first through a solution of chloroplatinate and then through one of the bromoplatinate before entering the spectrograph.

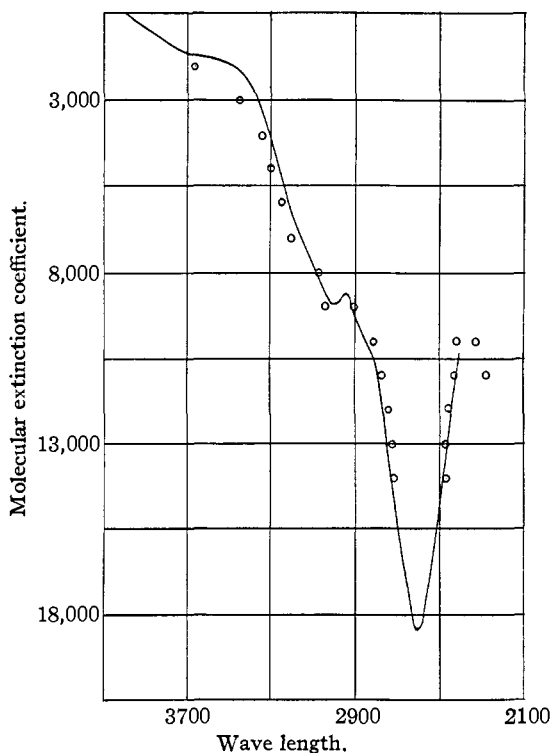


Fig. 5.—○ ○ ○, 0.0001 molar " $K_2PtCl_4Br_2$," ———, calculated curve.

In Fig. 3 the solid line represents the calculated molecular extinction coefficients for a mixture of chloroplatinate and bromoplatinate while the circles are values obtained in the way just described from the absorption spectra of the separate halogenoplatinates reproduced in Fig. 2. Similar curves for bromo and iodoplatinate were obtained but are not reproduced. The agreement is as good as can be expected, and proves that the usual method of calculating the extinction coefficient for solutions of mixtures is applicable to data obtained photographically in the region in which lie the absorption bands of the various halogenoplatinates.

In Fig. 4 the solid line represents the calculated absorption spectrum of a solution containing 39.2% of sodium bromoplatinate and 61.8% of sodium

chloroplatinate. The circles give the observed absorption spectrum of a solution of sodium bromoplatinate to which enough sodium chloride had been added to make the "apparent % transformation" 61.8%. Since the two curves are entirely different, the colorimetric data of such a mixture are not a measure of actual concentrations, and intermediate complex ions must be present. Similar curves have been obtained for solutions of different concentrations, and for mixtures of iodo and bromoplatinates; for them the original thesis² must be consulted as they have been omitted to save space.

In this connection Fig. 5 is of interest. In it the solid line represents the absorption spectrum calculated for a mixture of potassium chloroplatinate and potassium bromoplatinate in the proportion corresponding to the formula $K_2PtCl_4Br_2$. The circles represent the absorption spectrum of this "compound" prepared according to the method of Ptkin.¹⁹ It will be seen that the spectrum²⁴ is identical with that calculated for the mixture, and that Pigeon's conclusion that compounds can be prepared in this way is not borne out by the facts. In this we have corroborated the work of Herty.²¹

This research is one of a series of investigations carried out with the aid of a grant from the Bache Fund of the National Academy.

Summary

1. It has been shown that to cause the reaction $PtBr_6^- + 6Cl^- \rightarrow PtCl_6^- + 6Br^-$ to go 99% to completion there must be approximately 660 times as much chloride as bromide ion constituent in the solution. For the reaction between iodoplatinate and bromoplatinate ions there must be 25,000 times as much bromide as iodide ion constituent. From these data we have estimated that roughly 16,000,000 times as much chloride as iodide ion constituent must be present completely to convert PtI_6^- to $PtCl_6^-$, and have confirmed this order of magnitude experimentally.

2. A study of the absorption spectra of the various equilibrium mixtures indicates that in these reactions intermediate compounds are formed in solution.

3. We have also shown that the solid intermediate compounds which have at various times been reported in the literature are really mixtures. This confirms the conclusions of other workers in this field.

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²⁴ The absorption spectrum was measured as soon as possible after dissolving the solid to prevent possible transformation in solution to mixed halogenoplatinates.