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## THE EQUILIBRIUM RELATIONS OF CHROMATES IN SOLUTION.

BY MILES S. SHERRILL.
From experiments by F. M. Eaton, Alden Merrill and D. E. Russ.
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Introduction.

The constitution of chromates in aqueous solution has been the subject of a number of investigations. Walden[1] measured the conductance of solutions of normal chromates, of dichromates and of chromic acid. According to his measurements, solutions of chromic acid, CrO_3, and of hydrochloric acid at the same molal concentration have approximately the same conductance; moreover the equivalent conductance of chromic acid, also like that of the strong monobasic acids, varies but little with the concentration. These facts indicate that chromic acid exists in solution either as H_2CrO_4 dissociating thus,

$$H_2CrO_4 = \overset{+}{H} + \overset{-}{HCrO_4},$$
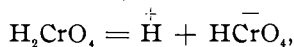
or, as Ostwald[2] has pointed out, as $H_2Cr_2O_7$ dissociating without the formation of any very large amount of an intermediate HCr_2O_7-ion directly into H-ion and Cr_2O_7-ion according to the reaction,

$$H_2Cr_2O_7 = 2\overset{+}{H} + \overset{=}{Cr_2O_7}.$$
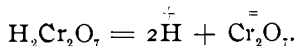
To test the correctness of this latter conception Ostwald determined the freezing-point of a solution containing 0.5-mol of CrO_3 per liter. The lowering of the freezing-point due to one mol of dichromic acid, $H_2Cr_2O_7$, for complete dissociation according to the second reaction, would be three times that produced by one mol of an undissociated substance. This factor, known as the van't Hoff factor, on the other hand, would be equal to four, for complete dissociation of the same amount of acid according to the first reaction. The value found experimentally by Ostwald was somewhat less than three, and after correcting for dissociation of the

[1] Z. physik. Chem., 2, 49 (1888).
[2] Ibid., 2, 78 (1888).

acid by means of the conductivity data of Walden, corresponded very closely to the existence of dichromic acid in solution.

This view of the constitution of chromic acid in solution has been very generally accepted by other investigators, and the possible existence of any appreciable amount of an $HCrO_4$-ion entirely overlooked.[1] If this is not neglected, both of the above reactions must be considered in determining how chromic acid exists in solution. The relative amounts of $HCrO_4$-ion and Cr_2O_7-ion present will depend on the concentration and on the value of the equilibrium constant of the reaction,

$$2H\overset{-}{C}rO_4 \quad H_2O + \overset{=}{C}r_2O_7.$$
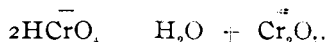
The same equilibrium equations must hold also in chromate and dichromate solutions. Thus potassium chromate in aqueous solutions shows an alkaline reaction due to the following hydrolysis,

$$\overset{=}{C}rO_4 + H_2O \quad H\overset{-}{C}rO_4 + \overset{-}{O}H.$$
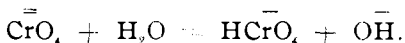
This hydrolysis goes on to a greater extent than it ordinarily would because the hydrochromate ion is removed from the solution by the above dehydration to form the dichromate ion.

On the other hand dichromates show an acid reaction because the dichromate ion becomes hydrated to a certain extent to form the hydrochromate ion, which in turn is slightly dissociated into the hydrogen ion and the chromate ion.

It was the purpose of this investigation to test the above conception of the equilibrium relations of chromates in solution, and to determine if possible, the values of the equilibrium constants involved. The work was started by F. M. Eaton in February, 1905, carried on further by A. Merrill in 1906, and completed by D. E. Russ in May, 1907. Their results will be presented in the order in which the experiments were carried out.

The Freezing-Point of Dilute Solutions of Chromic Acid and of Potassium Dichromate.

Experiments by F. Malcolm Eaton.

As already shown, a determination of the lowering of the freezing-point produced by chromic acid or by dichromates offers one means of studying their constitution in solution. Such measurements heretofore have always been made in rather strong solutions. If as above assumed, the dichromate ion becomes hydrated to form the hydrochromate ion, the conditions most favorable for its formation would be in the more dilute solutions, according to the mass-action law. Accordingly freezing-point determinations of dilute solutions of these two substances were made.

[1] In an article which appeared in the *Z. anorg. Chem.*, **54**, 265 (1907) since the completion of this investigation, Spitalsky does take this into consideration. His paper is discussed in the latter part of this article.

Before beginning these determinations the question arose as to whether the hydration of the dichromate might not be a time reaction, and hence the results obtained be dependent on the time taken to form the experiment. To answer this question the solubility method used by Hudson[1] in his work on the hydration of milk sugar was employed. When a salt in solution undergoes hydration the final equilibrium between the anhydrous salt and the solution will be reached only when the hydrated part is in equilibrium with the anhydrous part, which in turn is in equilibrium with the solid salt. If the hydration takes an inappreciable time, equilibrium will be reached quickly. If on the other hand hydration takes place slowly, the experimentally found solubility will vary with the time taken and with the way in which equilibrium is approached.

The following solubility experiments were made with potassium dichromate. Three excess portions of powdered salt were kept for thirty minutes in contact with water at 100°, 30°, and 20° respectively, then bottled separately and rotated in the thermostat at 20°. In this way equilibrium was being approached in the first two cases from supersaturation, and in the last case from undersaturation. From time to time 10 ccm. samples were pipetted off and analyzed by titration against ferrous ammonium sulphate. The results are given in Table 1, where the concentrations are expressed in gms. of potassium dichromate in 100 ccm. solution, and the time in minutes from the moment of entering the thermostat.

TABLE 1.

Time	Concentration		
	(1)	(2)	(3)
10	12.47	12.10	11.56
60	11.34	11.43	11.43
240	11.34	11.43	11.52

At the time the samples were first taken, equilibrium had not been reached, but after an hour's interval equilibrium seems to have been established, as no apparent increase is noted even after three hours longer rotation. It is therefore evident that the hydration of the dichromate-ion is complete in a short time.

This conclusion is verified by certain conductivity measurements of Costa[2] on chromic acid solutions. He found, namely, that the conductivity of a chromic acid solution at 0° remained unchanged by heating the solution to a considerably higher temperature and then cooling rapidly to the lower temperature.

The method employed in the determination of the freezing-points was a modification of that described by Richards[3]. The apparatus consisted

[1] This Journal, 26, 9, (1904).
[2] Gazz. chim. ital., 36, I, 535 (1906).
[3] Z. physik. Chem., 44, 563, (1898).

of a wide-mouthed bottle of about two liters capacity enclosed in a large glass battery jar, the intervening space being firmly packed with felt or cotton.   The battery jar was then placed in a pail and the space between the two filled with a mixture of finely crushed ice and water.   By these means conduction of heat to or from the inner bottle was reduced to a minimum.

The bottle was further provided with a stopper with three holes, through which extended a tube carrying a plug of glass wool at the lower end to act as a filter, a Beckmann thermometer, and an "up and down" stirrer made of a piece of thick glass rod the lower end of which was flattened and bent horizontally into an arc of about 180°.

In beginning a run with this apparatus the bottle was half filled with a mixture of pure ice (frozen distilled water) ground fine, and distilled water.   This mixture contained a large enough proportion of water to allow a thorough mixing by the stirrer.   The stopper was now placed in position with the sampling tube, the thermometer, and the stirrer.   By stirring at the rate of about one hundred strokes to one minute, and taking readings of the temperature every minute, equilibrium was found to be established in about five minutes so that the next five readings did not vary more than 0.001°.   This reading was taken as the freezing-point of the pure solvent.

About 10 ccm. of a strong solution of the substance under investigation was now added and the mixture stirred until readings taken after minute intervals remained constant for five minutes.   A pipette was then connected by a rubber connection to the upper end of the sampling tube, and two 10 ccm. portions withdrawn and discarded.   Then a sample of the liquid was withdrawn in the same manner, 20 ccm. in the case of the dilute solutions and 10 ccm. in the case of the concentrated, and set aside for subsequent analysis.   The mixture was then stirred quickly, the temperature taken, a duplicate sample withdrawn, and the temperature again read.   In these temperature readings before and after sampling there was a variation of not more than 0.002°, and the analysis of duplicate samples agreed within one per cent.

A new addition of strong salt solution was now made, enough water being added to make the volume up to the original amount, and the process continued.   By previously cooling the water and the solutions added, the amount of ice melted could be made very small and the series extended at small intervals over great ranges.

To ascertain the accuracy of the method two series of determinations of the freezing-points of potassium chloride solutions were made, the concentrations of the samples being determined by conductivity measurements at 25°, and the results compared with those of Hebb[1] in his most accurate work.

The results obtained are shown in Table 2, the corresponding lowerings as taken from Hebb's tables being also given.

TABLE 2.

|	Conc.	Obs. low.	Low. from Hebb
Series I	0.0252	0.089°	0.090
	0.0311	0.111	0.111
	0.0391	0.137	0.139
Series II	0.0136	0.048	0.049
	0.0332	0.117	0.116
	0.0453	0.159	0.160
	0.0550	0.194	0.194
	0.0686	0.242	0.241
	0.0900	0.317	0.315

From these results it will be seen that with only ordinary precaution, the readings can be depended on to 0.002°, and with special precautions it is probable that much finer work may be done.

In applying this method to potassium dichromate solutions the concentrations of the samples were determined by titration against standard ferrous ammonium sulphate. Four independent runs were made, the results being shown in Table 3. Concentrations are expressed as mols of potassium dichromate in one liter of solution.

TABLE 3.

Ccm. taken	Conc.	Lowering	i
10	0.01384	0.081°	3.16
10	0.02053	0.113	2.98
10	0.02889	0.154	2.88
10	0.03975	0.202	2.75
10	0.04850	0.244	2.71
10	0.05340	0.263	2.66
10	0.00510	0.035	3.70
10	0.01105	0.067	3.28
10	0.01525	0.090	3.19
10	0.01973	0.112	3.07
10	0.02760	0.150	2.94
10	0.03359	0.178	2.87
20	0.00639	0.038	3.22
20	0.01234	0.070	3.07
10	0.01807	0.098	2.93
10	0.02355	0.127	2.92
10	0.03004	0.158	2.84
10	0.03615	0.183	2.74
20	0.00764	0.047	3.33
20	0.01220	0.072	3.19
10	0.01743	0.098	3.04
10	0.02825	0.150	2.87
10	0.03680	0.190	2.79
10	0.04000	0.203	2.74

In the last column of the table are given values of the van't Hoff factor

i, that is the ratio of the observed lowering to that which would have been produced had the potassium dichromate remained as $K_2Cr_2O_7$ unionized in solution. It is evident that the maximum value of this factor corresponding to complete dissociation of the dichromate according to the reaction, $K_2Cr_2O_7 \rightleftharpoons 2\overset{+}{K} + \overset{=}{Cr_2O_7}$, is 3; while that for complete transformation into hydrochromate and complete dissociation thus, $2KHCrO_4 \rightleftharpoons 2\overset{+}{K} + 2\overset{-}{HCrO_4}$, is 4. The variation of i with dilution may be best observed by considering the accompanying curve, in which the concentrations are plotted as abscissae and values of i as ordinates. The fact that the values obtained in solutions less than 0.02-molal are actually greater than 3, indicates that not an inappreciable amount of the hydrochromate ion is present in these solutions. That the curve is concave upwards is conclusive evidence that the change of i is not simply due to an ordinary increase of dissociation.
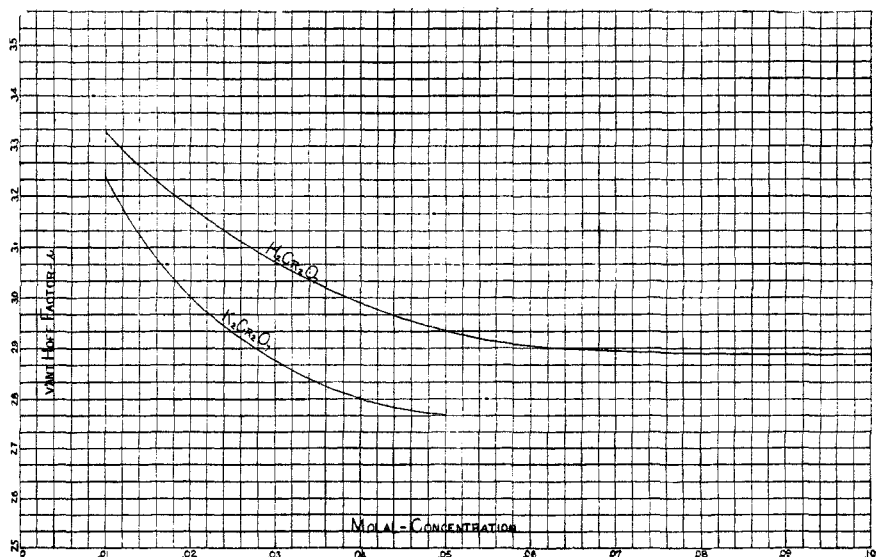
A similar line of investigation was carried out with chromic acid. Reasons for considering chromic acid in solution as analogous in constitution to a dichromate have already been mentioned. In Table 4 are shown the results of two independent series of freezing-point determinations. Concentrations are there expressed as mols $H_2Cr_2O_7$ in one liter of solution.

TABLE 4.

Ccm. taken	Conc.	Lowering	i
20	0.00958	0.059°	3.33
10	0.03340	0.189	3.06
10	0.04690	0.257	2.96
10	0.07180	0.387	2.92
10	0.10160	0.548	2.91
20	0.01370	0.083	3.26
20	0.02730	0.155	3.07
10	0.05880	0.305	2.90
10	9.06440	0.347	2.90
10	0.07670	0.408	2.89

The curve constructed from these data shows a close resemblance to that from the potassium dichromate. That the two are not identical is to be ascribed to a difference in the dissociation relations in the two solutions, and in order to make any quantitative interpretation of the results it is first necessary to make some assumption regarding these dissociation relations.

In the case of the potassium dichromate the solution may be considered as consisting of a mixture of $K_2Cr_2O_7$ and $KHCrO_4$, and hence the following principle shown by Noyes[1] is applicable. This principle states that in a mixture of salts having one ion in common, the degree of ionization of each salt is that which it would have if present alone at such an equivalent concentration that the concentration of either of its ions were equal to the sum of the equivalent concentrations of all the positive or negative ions in the mixture. The sum of the equivalent concentrations of all the positive or negative ions in the mixture may without any great error be considered equal to that ion concentration in a solution containing either salt alone at an equivalent concentration equal to the total equivalent salt concentration in the mixture. To obtain actual values for the degrees of ionization the further principle may be used that salts of the same type have at the same concentration the same degree of ionization.

Accordingly the assumptions as to dissociation relations made in the following considerations were that the ionization of the $K_2Cr_2O_7$ in the solution is the same as that of K_2SO_4, and the ionization of the $KHCrO_4$ like that of KCl at a concentration equal to the total equivalent concentration of salt present. The numerical values for the degrees of ionization were calculated from the conductivity measurements of Archibald[2] made at 0° with potassium sulphate and potassium chloride solutions. The further assumption is made that the ionization of the hydrochromate ion does not take place to an appreciable extent. This is justified by measurements made in another part of this investigation.

[1] Science, 20, 583 (1904); Z. phys. Chem., 52, 635 (1905).
[2] Proc. and Trans. Nova Scotia Inst. Sci., 10. 33 (1898).

If C represents the total concentration of salt present expressed as atomic in chromium, γ_1 the ionization of the $K_2Cr_2O_7$ in the solution, γ_2 that of the $KHCrO_4$, and i has the significance given in the previous tables, the four following condition equations may be formulated, in which the symbols correspond to molal concentrations.

$$\frac{\overset{=}{Cr_2O_7}}{K_2Cr_2O_7} = \frac{\gamma_1}{1-\gamma_1} \qquad (1)$$

$$\frac{\overset{-}{HCrO_4}}{KHCrO_4} = \frac{\gamma_2}{1-\gamma_2} \qquad (2)$$

$$C = \overset{-}{HCrO_4} + 2\overset{=}{Cr_2O_7} + 2K_2Cr_2O_7 + KHCrO_4 \qquad (3)$$

$$\frac{C}{2} \times i = 2\overset{-}{HCrO_4} + 3\overset{=}{Cr_2O_7} + K_2Cr_2O_7 + KHCrO_4 \qquad (4)$$

In the last equation $\dfrac{C}{2} \times i$ represents the total molal concentration of the solution as indicated by the freezing-point. Therefore

$$\frac{C}{2} \times i = \overset{+}{K} + \overset{-}{HCrO_4} + \overset{=}{Cr_2O_7} + K_2Cr_2O_7 + KHCrO_4$$

This equation can be put in the form of equation (4) by combining with it the additional condition equation,

$$\overset{+}{K} = \overset{-}{HCrO_4} + 2\overset{=}{Cr_2O_7}.$$

From the four above equations may be calculated for each case the concentrations of $KHCrO_4$, $K_2Cr_2O_7$, $\overset{-}{HCrO_4}$, and $\overset{=}{Cr_2O_7}$ respectively, and hence the equilibrium constant for the reaction, $\overset{=}{Cr_2O_7} + H_2O = 2\overset{-}{HCrO_4}$. This constant, $\overset{=}{Cr_2O_7}/(\overset{-}{HCrO_4})^2$. will hereafter be designated K_H, and spoken of as the hydration-constant for the dichromate ion.

The results of such calculations are given for a number of concentrations in Table 5. The values of i are taken from the plot, and therefore correspond to a mean of the several determinations.

TABLE 5.

Conc. Total Chromium C	van't Hoff Factor i	Ionization $K_2Cr_2O_7$ γ_1	Ionization $KHCrO_4$ γ_2	Conc. $K_2Cr_2O_7$	Conc. $KHCrO_4$	Conc. $\overset{=}{Cr_2O_7}$	Conc. $\overset{-}{HCrO_4}$	$K_H = \dfrac{\overset{=}{Cr_2O_7}}{(\overset{-}{HCrO_4})^2}$
0.02	3.24	0.83	0.943	0.00090	0.00054	0.00438	0.00891	55
0.04	3.00	0.785	0.925	0.00286	0.00101	0.01044	0.01241	68
0.06	2.88	0.755	0.913	0 00529	0.00147	0.01629	0.01539	69
0.08	2.80	0.728	0.905	0.00812	0.00193	0.02172	0.01840	64
0.10	2.77	0.712	0.896	0.01074	0.00266	0.02645	0.02278	51
							(Mean)	61

The dissociation relations in the chromic acid solutions differ from

those in the potassium dichromate solutions in virtue of the fact that there is a relatively large concentration of hydrogen ion present. This will have the effect of entirely preventing the ionization, $\overset{-}{H}CrO_4 = \overset{+}{H} + \overset{=}{C}rO_4$, which was considered negligibly small in the potassium dichromate, but on the other hand it will render the conditions most favorable for the formation of an HCr_2O_7-ion. As already pointed out, however, conductivity measurements on chromic acid show that this latter ion does not form to, at least, any great extent. Though the above considerations and the results indicate that it is not strictly correct, yet for want of a better assumption for a quantitative treatment of the results with chromic acid the same assumptions as to ionization relations were made with the chromic acid as were made with potassium dichromate, the $H_2Cr_2O_7$ corresponding to the $K_2Cr_2O_7$, and the H_2CrO_4 to the $KHCrO_4$. The results of the calculations are given in Table 6.

TABLE 6.

Conc. Total Chromium C	van't Hoff Factor i	Ioniza- tion $H_2Cr_2O_7$ γ_1	Ioniza- tion H_2CrO_4 γ_2	Conc. $H_2Cr_2O_7$	Conc. H_2CrO_4	Conc. $\overset{=}{C}r_2O_7$	Conc. $\overset{-}{H}CrO_4$	$K_H = \dfrac{\overset{=}{Cr_2O_7}}{(\overset{-}{HCrO_4})^2}$
0.02	3.33	0.830	0.943	0.00079	0.00062	0.00377	0.01029	36
0.04	3.18	0.785	0.925	0.00225	0.00143	0.00823	0.01762	26
0.06	3.07	0.755	0.913	0.00423	0.00223	0.01302	0.02330	24
0.07	3.03	0.740	0.908	0.00537	0.00264	0.01529	0.02603	23
							(Mean)	27

Considering the rather arbitrary assumptions made in these calculations the agreement of the values of the hydration-constant among themselves in the separate cases of the potassium dichromate and chromic acid solutions, and also of the mean values obtained from them is as good as could be expected. The calculation is very sensitive with respect to the ionizations assumed, and also with respect to the i value. For example, if in Table 5 at the concentration 0.02-normal, the ionizations assumed had been *0.82* and *0.93* instead of *0.83* and *0.94* respectively, the calculated value of K_H would have been 47 instead of 55. The effect of changing i from *3.24* to *3.33* may be seen by comparing the values obtained for the constant at this concentration in the dichromate and chromic acid solutions respectively. The calculated value changes from *55* to *36*.

This method of evaluation of the hydration-constant for the dichromate ion can be considered, therefore, as giving only the right order of magnitude. The results do indicate conclusively, however, the existence of the hydrochromate ion in no inappreciable amount.

It was thought that some idea of the amount of hydration could be obtained by measuring the absorption spectra of solutions of chromic acid, potassium dichromate, and potassium chromate. This was done with

solutions of different concentrations, being careful in each case to have
the same amounts of salts present in the two solutions in question, but
varying the amount of water in which the salt was dissolved.

The results showed that potassium dichromate and chromic acid give
identical absorption bands, cutting out all light beyond the bright green.
No change was noticed on dilution, although the amount of water was
increased ten-fold.   A solution of potassium chromate gave practically
no absorption in any part of the spectrum except the violet and extreme
blue.   It is therefore evident that the acid is very similar to the dichro-
mate as pointed out by Ostwald[1], and that the hydrochromate ion is not
very different in color from the dichromate ion.

The Hydrolysis of Ammonium Chromate by Means of Electrical Conductivity.

Experiments by Alden Merrill.

The hydrolysis of ammonium chromate may be represented by the re-
action,

$$\overset{+}{NH_4} + \overset{=}{CrO_4} + H_2O = \overset{-}{HCrO_4} + NH_4OH.$$
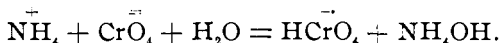
The subsequent formation of any dichromate in these experiments is
considered as negligibly small.

If ammonia be added to a solution of ammonium chromate, the hydrol-
ysis, according to the mass action law, must be driven back, thus in-
creasing the concentration of the NH_4-ion in the solution, and convert-
ing the $HCrO_4$-ion to the doubly charged CrO_4-ion.   This change would
have the effect of increasing the conductivity of the solution by an
amount which is a measure of the extent to which the salt had been hy-
drolyzed.

The exact relation between the change of conductance and the fraction
hydrolyzed is shown by the following considerations.

The equivalent conductance A_1 of an ammonium chromate solution, at
a given equivalent concentration C, assuming no hydrolysis to have taken
place, is given by the expression

$$A_1 = \gamma A_{NH_4} + \gamma A_{CrO_4}, \qquad (1).$$

where γ is the ionization of the ammonium chromate at the concentra-
tion in question.   If the salt now be considered as hydrolyzed by the
fractional amount h, then the solution will contain $(NH_4)_2CrO_4, NH_4HCrO_4$
and NH_4OH, at the equivalent concentration $(1-h)C, \dfrac{h}{2}C$, and $\dfrac{h}{2}C$ respect-
ively.   If further, γ_1 equal the ionization of $(NH_4)_2CrO_4$ and γ_2 that of
the NH_4HCrO_4 in the mixture, and the conductance of the NH_4OH be
neglected, then the expression for the equivalent conductance A_2 of the
ammonium chromate becomes

[1] Loc. cit.

$$A_2 = \gamma_1(1-h)A_{NH_4} + \gamma_1(1-h)A_{CrO_4} + \gamma_2\frac{h}{2}A_{NH_4} + \gamma_2\frac{h}{2}A_{HCrO_4} \qquad (2).$$

The ionization γ_1 of ammonium chromate in the mixture will not differ essentially from γ, the ionization of ammonium chromate assuming no hydrolysis. Furthermore the unionized fraction $(1-\gamma_1)$ of the ammonium chromate in the mixture may be estimated as twice the unionized fraction $(1-\gamma_2)$ of the ammonium hydrochromate.[1] That is

$$\gamma_1 = \gamma, \text{ and } (1-\gamma_1) = 2(1-\gamma_2)$$

Placing γ_1 and γ_2 in equation (2) in terms of γ with the help of these equations, and subtracting the resulting equation from equation (1) the following expression is obtained for the change of conductance ΔA produced by the hydrolysis.

$$\Delta A = \gamma h A_{NH_4} + \gamma h A_{CrO_4} - \frac{1+\gamma}{4}hA_{NH_4} - \frac{1-\gamma}{4}h A_{HCrO_4}.$$

This solved for h gives

$$h = \frac{4\Delta A}{\gamma(3A_{NH_4} + 4A_{CrO_4} - A_{HCrO_4}) - (A_{NH_4} + A_{HCrO_4})} \qquad (3).$$

The change in the equivalent conductances ΔA may be measured, as above indicated, by measuring the increase in the equivalent conductance of ammonium chromate produced by adding enough ammonia to completely drive back the hydrolysis. The conductance of the added ammonia may, of course, be corrected for. To calculate the hydrolysis from such a measurement it is evidently necessary to know all of the terms occurring in the denominator of the above equation. The equivalent conductance A_{NH_4} of the ammonium ion is given by Kohlrausch, that, A_{CrO_4}, of the chromate ion, as well as the value of γ, may be computed, as shown later, from the conductivity measurements made with ammonium chromate. In order to determine the equivalent conductance A_{HCrO_4} of the hydrochromate ion, the conductance of solutions of potassium dichromate and of chromic acid were measured at varying concentrations.

For these experiments, stock standard solutions of ammonium hydroxide, potassium dichromate and chromic acid were prepared, from which were made up the solutions whose conductance was to be measured.

The ammonia used was obtained from Baker and Adamson, and was marked strictly C. P., free from amines, carbonate and silicate, sp. gr. 0.90. Its conductance compared well with the values given by Kohlrausch. The solution was analyzed by direct titration against standard hydrochloric acid, methyl orange being used as the indicator. The stock solution was kept in a two-liter bottle fitted with a rubber stopper carry-

[1] See Noyes: Science 20, 584 (1904).

ing glass tubes as in a wash bottle. One tube served as a siphon for filling a 30 ccm. side arm burette, the other was connected with a series of potash bulbs to remove any carbon dioxide from the air, thus preventing any formation of ammonium carbonate.

The potassium dichromate was purified by repeated crystallizations from water, and was dried to constant weight at 110°. The stock solutions were prepared by dissolving a weighed amount of salt in water and diluting to the required volume by means of a graduated flask, conductivity water being used.

The chromic acid was purified by repeated crystallizations from water till free from sulphates. The stock solution was analyzed by standardizing against iron wire by the usual volumetric method. The value of this iron wire in terms of chromate was first determined by titration with a standard potassium dichromate solution. By this means any impurity of the iron wire, or inaccuracy in obtaining the absolute end point was eliminated. As the neutral ammonium chromate solutions later used were prepared by mixing exactly equivalent amounts of chromic acid and ammonium hydroxide, a very careful analysis was necessary. As a check on the above analysis the stock solution was also analyzed gravimetrically as follows. An excess of lead acetate was added to the solution, and the precipitate of lead chromate filtered through a Gooch crucible, washed thoroughly, and ignited to constant weight. The Gooch crucible during the ignition was supported in an asbestos ring inside of a large porcelain crucible, the latter being subjected to the full heat of a Tirrell burner. The two methods of analysis gave practically identical results.

All conductance measurements in this work were made in a thermostat kept constant at 18° within ±0.03°. At the time of measurement the exact temperature was noted and a corresponding correction of 2 per cent. per degree was applied. The specific conductance of the water used for the various dilutions varied from 1 to 2×10^{-6}. In each measurement a corresponding correction was made. The method used was the ordinary one of Kohlrausch. the slide wire and rheostat used being carefully calibrated.

For the measurements with potassium dichromate the usual form of Arrhenius cell with platinized electrodes quite close together was in general used. For one or two measurements, however, at the higher concentrations the pipette form of cell described below was employed. The cell constant was found by measuring in the cell, the conductance of 0.01 normal solutions of potassium chloride and sodium chloride, and a mean of the values thus obtained was used in the subsequent calculations.

The results of those measurements are given in Table 7.

TABLE 7.
POTASSIUM DICHROMATE.

Concentration ($\frac{1}{2}K_2Cr_2O_7$)	Specific Conductance κ	Equiv. Conductance Λ
0.04	0.004152	103.3
0.02	0.002132	106.6
0.01	0.001078	107.8
0.005	0.0005465	109.3
0.002	0.0002200	110.0
0.001	0.0001109	110.9

CHROMIC ACID.

Concentration ($\frac{1}{2}H_2Cr_2O_7$)	Specific Conductance κ	Equiv. Conductance Λ
0.02	0.006900	345
0.01	0.003482	348
0.0025	0.000875	350
0.001	0.000349	349
0.0005	0.0001742	348.4

The values given of the specific conductance are the mean of several readings with different resistances and with different fillings of the cell.

It is to be noted that in the case of the dichromate the increase in the equivalent conductance with the dilution is abnormally small even considering the chromate as a salt of the type of potassium chloride. This effect may be explained by the fact that on dilution the dichromate ion becomes hydrated to form the slower moving hydrochromate ion. Ionization of the latter would tend to have the opposite effect, that is to give an abnormally large increase in the conductance with the dilution. Some measurements of Whetham[1] on the conductance of potassium dichromate in very dilute solution are in accordance with this, and will be discussed more in detail later. On account of these complications no attempt was made to compute a value for the equivalent conductance for the hydrochromate ion from the measurements.

With the chromic acid solutions the case is somewhat better inasmuch as the ionization of the hydrochromate ion is prevented by the presence of the large concentration of the hydrogen ion. Assuming that in the solution 0.0025 atomic in chromium, chromic acid exists entirely as $H_2CrO_4 \rightleftharpoons \overset{+}{H} + \overset{-}{HCrO_4}$ ionized to the same extent as hydrochloric acid at this concentration, the equivalent conductance $\Lambda_{0(H_2CrO_4)}$ at zero concentration for chromic acid may be calculated from the proportion, $\Lambda_{0.0025(HCl)} : \Lambda_{0(HCl)} = \Lambda_{0.0025(H_2CrO_4)} : \Lambda_{0(H_2CrO_4)}$. Using the data of Kohlrausch for hydrochloric acid in the calculation, this value becomes *358*. By deducting from this the equivalent conductance Λ_H for the hydrogen ion *318*, a value is obtained for the equivalent conductance Λ_{HCrO_4} for the hydrochromate ion equal to *40*. For the reasons

[1] Pr. Roy. Soc., 71, 332 (1903).

above mentioned this can be considered as only an approximation to the true value, but an inspection of the expression given for the hydrolysis of ammonium chromate will show that it will suffice for that calculation.

In the measurements with the ammonium chromate solutions especial precautions had to be taken to prevent any formation of ammonium carbonate from the carbon dioxide of the air. The conductivity cell used was essentially a pipette with platinized vertical electrodes sealed on the inside. The requisite volumes of chromic acid and ammonium hydroxide solutions were drawn from burettes into a graduated glass-stoppered flask which had previously been filled with air-free from carbon dioxide. Dilution to the mark on the flask was made with conductivity water at 18°. By means of a wash bottle arrangement this solution was forced over with a blast of air free of carbon dioxide, into the pipette form of cell. The cell was always first rinsed with several portions of the solution, and finally several measurements made with independent fillings of the cell.

In the solutions to which an excess of ammonium hydroxide had been added it was necessary to make a correction for its conductance. This correction can be computed by making the following substitutions in the mass-action equation for the ionization-constant κ_B, for ammonium hydroxide, and solving for the specific conductance of the ammonium hydroxide. The concentration in equivalents per cubic centimeter of the ammonium ion in the solution is equal to $\kappa_S / \Lambda_{0(S)}$, the ratio of the specific conductance of the salt to its equivalent conductance at zero concentration; similarly that of the hydroxide ion is equal to $\kappa_B / \Lambda_{0(B)}$, the ratio of the specific conductance of the ammonium hydroxide to its equivalent conductance at zero concentration; and finally the concentration C_B of the unionized ammonium hydroxide is equal to that of the added ammonium hydroxide. The expression thus obtained for the specific conductance of the added ammonium hydroxide is

$$\kappa_B = \frac{\kappa_B \times C_B \times \Lambda_{0(B)} \times \Lambda_{0(S)}}{\kappa_S \times 10^6}$$

The value used in the calculations for κ_B, $\Lambda_{0(B)}$, and $\Lambda_{0(S)}$ were 17.1×10^{-6}, 237.6, and 141.3 (obtained from later measurements) respectively.

In Table 8 are placed all the results of the measurements and calculations. The values of the specific conductance always represents the mean of at least two fillings of the cell. Where duplicate values are given each value corresponds to a complete experiment including the making up of the solution from the stock solutions.

It is evident from the results that the addition of ammonium hydroxide, equivalent in amount to the salt present, is sufficient to completely drive back the hydrolysis. The equivalent conductance obtained in the presence of the added ammonium hydroxide is therefore the equivalent con-

TABLE 8.

0.005-Normal $(NH_4)_2CrO_4$.

Conc. of added NH$_4$OH	Spec. conductance of solution	Spec. conductance of NH$_4$OH κ_B	Equivalent conductance Λ	Mean equiv. cond. Λ	Increase in conductance $\Delta\Lambda$
0.0000	0.0006030	0.0000000	120.6		
0.0000	0.0006075	0.0000000	121.5		
0.0000	0.0006050	0.0000000	121.0	121.1	
0.0000	0.0006050	0.0000000	121.0		
0.0000	0.0006060	0.0000000	121.2		2.3
0.0025	0.0006195	0.0000022	123.5		
0.0050	0.0006229	0.0000044	123.7	123.4	
0.0050	0.0006199	0.0000044	123.1		
[0.0100	0.0006230	0.0000089	122.8]		

0.01-Normal $(NH_4)_2CrO_4$.

0.0000	0.001163	0.0000000	116.3		
0.0000	0.001166	0.0000000	116.6	116.4	
0.0000	0.001164	0.0000000	116.4		2.0
0.0100	0.001189	0.0000047	118.4	118.4	
0.0100	0.001189	0.0000047	118.4		

0.02-Normal $(NH_4)_2CrO_4$.

0.0000	0.002214	0.0000000	110.7	110.7	
0.0000	0.002214	0.0000000	110.7		1.8
0.0200	0.002255	0.0000049	112.5		
0.0200	0.002255	0.0000049	112.5	112.5	
0.0400	0.002260	0.0000100	112.5		
0.0700	0.002265	0.0000150	112.5		

0.04-Normal $(NH_4)_2CrO_4$.

0.0000	0.004152	0.0000000	103.8	103.8	
0.0000	0.004152	0.0000000	103.8		1.7
0.0400	0.004225	0.0000052	105.5	105.5	
0.0400	0.004225	0.0000052	105.5		

ductance of unhydrolyzed ammonium chromate. These values were plotted as ordinates, and the cube root of the corresponding concentrations as abscissae, and by extrapolation the value of the equivalent conductance Λ_0 at zero concentration was found to be *141.3* reciprocal ohms. Subtracting the value of the equivalent conductance Λ_{NH_4} of the ammonium ion from this gives as a value for the equivalent conductance Λ_{CrO_4} of the chromate ion *76.9* reciprocal ohms.

The expression on page 1651 for the hydrolysis of ammonium chromate can now be simplified by substituting in it the numerical values for the equivalent conductances of the respective ions to

$$h = \frac{4\Delta\Lambda}{460.8\ \gamma - 104.4},$$

in which $\Delta\Lambda$ is given in the preceding table, and γ is calculable from the conductance values for ammonium chromate.

With the help of the hydrolysis thus obtained the following considera-

tions will show that it is possible to determine the ionization-constant K_A for the hydrochromate ion. The equilibrium-constants involved in the hydrolysis of ammonium chromate, K_W the ionization-constant for water, K_B that for ammonium hydroxide, and K_A that for the hydrochromate ion may be combined into one constant, the so-called hydrolysis-constant, which equals

$$\frac{K_w}{K_A K_B} = \frac{NH_4OH \times \overline{HCrO_4}}{\overset{+}{NH_4} \times \overset{=}{CrO_4}}$$

In addition to this equation, which determines the equilibrium, may be formulated the following condition equations:

$$NH_4OH = \overline{HCrO_4} + NH_4HCrO_4$$

$$\overset{+}{NH_4} = 2\overset{=}{CrO_4} + \overline{HCrO_4}$$
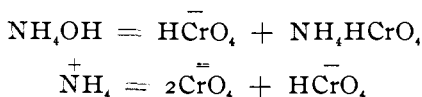
The concentration of ammonium hydroxide is given by the product of the hydrolysis h by the molal concentration C of the ammonium chromate solution; that of the $HCrO_4$ -ion is $\frac{1 + \gamma}{2}$ times as great[1], γ being the ionization of ammonium chromate at the concentration in question. The concentration of the ammonium-ion in equivalents per cubic centimeter is, as has already been stated, given by the ratio $\frac{\kappa_S}{A_{o(s)}}$ of the specific conductance of the salt to its equivalent conductance at zero concentration. Taking as values for K_W and K_B, 0.6×10^{-14} and 17.1×10^{-6} respectively[2], values for the ionization constant of the hydrochromate ion were calculated with the help of the above equations.

A summary of the results obtained from the measurements on the hydrolysis of ammonium chromate are given in Table 9.

TABLE 9.

Molal Conc. C	Ioniza- tion γ	Hydroly- sis h	NH_4OH	$\overline{HCrO_4}$	$\overset{+}{NH_4}$	$\overset{=}{CrO_4}$	$\frac{K_w}{K_A K_B}$	$K_A = \dfrac{\overset{+}{H} \times \overset{=}{CrO_4}}{\overline{HCrO_4}}$
0.02	0.75	0.029	0.00058	0.000508	0.0298	0.01464	5.75×10^{-4}	5.2×10^{-7}
0.01	0.80	0.029	0.00029	0.000261	0.01593	0.00783	6.05×10^{-4}	5.8×10^{-7}
0.005	0.84	0.030	0.00015	0.000138	0.00838	0.00412	6.00×10^{-4}	5.9×10^{-7}
0.0025	0.875	0.031	0.000078	0.000073	0.00436	0.00214	6.10×10^{-4}	5.8×10^{-7}
							(Mean)	5.7×10^{-7}

Though the values of K_A agree very well with one another, yet on account of the assumptions involved on the theoretical side, and of the sources of error on the experimental side no great accuracy can be claimed for the method.

[1] This follows from the assumption previously made that the unionized fraction of the hydrochromate is equal to one-half of that of the neutral ammonium chromate.

[2] Pub. of the Carnegie Inst., No. 63.

The Hydrolysis of Ammonium Chromate. Distribution Method.

Experiments by Donald E. Russ.

In this method, which was worked out by Abbott in an investigation soon to be published on the ionization of phosphoric acid, the hydrolysis is measured by determining the concentration of the ammonia produced in the neutral ammonium chromate solution. Briefly the method is this. First the distribution-ratio of ammonia between water and chloroform is found, and afterwards by distribution experiments the concentration of ammonia in chloroform which is in equilibrium with the free ammonia produced by hydrolysis in the aqueous ammonium chromate solution. The product of these quantities equals the desired concentration of ammonia in the ammonium chromate solution.

The procedure followed in determining the distribution ratio is here given. Into each of two bottles was poured about 300 cc. of chloroform and 100 cc. of 1.0-normal ammonia solution, and into each of two other bottles the same quantity of chloroform, but about 200 ccm. of 0.25 normal ammonia solution. The bottles were stoppered and rotated in a thermostat kept constant at 25°, and then left suspended in the thermostat until the layers became clear. From each water layer there was pipetted off 50 cc. portions for analysis. To avoid any loss of ammonia by volatilization each sample was run directly into a measured volume of normal hydrochloric acid known to be in excess, and the excess titrated for with standard ammonia solution, cochineal being used as indicator.

From the chloroform layers there was taken for analysis in the first two cases 100 cc., and in the latter cases 200 cc. of solution. As ammonia is much more soluble in water than in chloroform, any contamination of the chloroform layer with that of the aqueous layer would produce a large error in the distribution ratio. To prevent any such error the device suggested by Abbott was used for removing these portions for analysis. Into the neck of the bottle was inserted a stopper bearing tubes arranged exactly as in an ordinary wash bottle except that the longer tube was sealed at its lower end by a thin bulb. This tube was lowered through the solutions and the bulb broken by forcing it against the bottom of the bottle. The sample of the chloroform layer was then forced up through this tube by means of an air blast into a pipette connected with its upper end. The chloroform solutions thus removed were delivered beneath the surface of about 200 cc. of water contained in a bottle. To the water was added cochineal as indicator and the ammonia determined by titration with 0.1 normal hydrochloric acid and a standard ammonia solution.

The results are tabulated below. In the second column the slight correction for the ionization of the ammonium hydroxide is made.

TABLE 10.

Conc. NH$_3$ in H$_2$O-layer	Conc. Free NH$_3$ in H$_2$O-layer C$_1$	Conc. Free NH$_3$ in CHCl$_3$-layer C$_2$	Distribution Ratio K = C$_1$/C$_2$
0.9624	0.9596	0.03848	24.97
0.9616	0.9588	0.03876	24.84
0.2414	0.2400	0.00963	24.96
0.2404	0.2390	0.00962	24.90

24.92 (Mean)

In the experiments made to determine the concentration of free ammonia in the ammonium chromate solutions any displacement of the equilibrium due to removal of the ammonia by the chloroform, had to be avoided. Into a one-liter bottle was poured 500 cc. of chloroform and 250 cc. of the ammonium chromate solution under investigation. The bottle was shaken vigorously and then suspended in the thermostat until it had assumed the temperature of 25°. The aqueous layer was then poured off and discarded. A new portion of the ammonium chromate solution was added and the operation repeated. After four repetitions of this character a 400 cc. portion of the chloroform layer was withdrawn and analyzed according to the method already described. The standard hydrochloric acid used in this analysis was 0.01-normal.

The ammonium chromate solutions were prepared, as in the experiments of Merrill, by mixing exactly equivalent amounts of ammonium hydroxide and chromic acid and diluting to the desired volume. It is evident that to thus obtain exact neutrality, very careful analyses of the stock solutions are necessary.

The strength of the stock solution of ammonium hydroxide, free from carbonate, was determined by direct titration against standard hydrochloric solution. According to the experiments and theoretical considerations of Salm[1], the best available indicator to use in the titration of hydrochloric acid with ammonium hydroxide is cochineal, and the best condition is to have the solutions moderately strong. The titration was made accordingly, the stock solutions being about normal.

Since it was the strength of the stock solution of chromic acid as an acid which was desired, the following method for its analysis was employed. To a measured volume of the solution heated to boiling, was added an excess of pure barium acetate dissolved in hot water. The precipitated barium chromate formed was washed four times by decantation through a filter, finally thrown on the filter and washed again. The acetic acid in the filtrate, which never exceeded 200 cc., was determined by titration with a standard barium hydroxide solution, phenolphthalein being used as the indicator. Direct titration in the cold without intermediate filtration was also tried. The end point was sharp, and the results in good accord with the former method. The stock chromic acid solution was about normal in strength.

Z. physik. Chem., 57, 471 (1907).

The barium hydroxide solution used in the above analysis had been titrated against the hydrochloric acid used in the analysis of the stock ammonium hydroxide solution. By thus referring the analyses of the stock solutions to the same hydrochloric acid solution their relative strengths were accurately determined, and hence absolute neutrality on mixing the calculated volumes more certainly obtained.

Three independent series of experiments were carried out with two strengths of ammonium chromate. In the last case the following test was made as a further check on the absolute neutrality of the ammonium chromate solution.
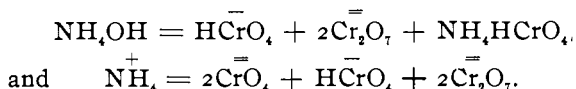
One hundred cubic centimeters of the solution were digested with solid pure neutral lead sulphate, and the solution decanted through a filter. To the filtrate, which should contain neutral ammonium sulphate formed by the metathesis, was added cochineal. The color indicated neutrality. One drop of a 0.05-normal ammonium hydroxide solution gave the pink color causd by an excess of ammonia, while one drop of a 0.05-normal hydrochloric acid solution gave the orange color characteristic of an excess of acid.

The results or the experiments are given in Table 11. The value of the distribution-ratio used in the calculations was taken equal to *25*.

TABLE 11.

Molal conc. $(NH_4)_2CrO_4$	Conc. ammonia in $CHCl_3 \times 10^5$	Conc. ammonia in H_2O-solution $\times 10^6$	Hydrolysis
I $\begin{cases} 0.050 \\ 0.050 \\ 0.025 \\ 0.025 \end{cases}$	5.51 5.33 2.67 2.70	137.8 133.3 66.65 67.39	0.0276 0.0267 0.0267 0.0270
II $\begin{cases} 0.050 \\ 0.050 \\ 0.025 \\ 0.025 \end{cases}$	5.33 5.24 2.60 2.70	133.3 131.1 65.15 67.39	0.0267 0.0262 0.0261 0.0270
III $\begin{cases} 0.050 \\ 0.025 \end{cases}$	5.33 2.67	133.3 66.65	0.0267 0.0267

In the formulation of the equilibrium conditions previously given for the calculation of the ionization-constant K_A for the hydrochromate ion from the hydrolysis of ammonium chromate the concentration of the dichromate ions in the solution was neglected. In these stronger solutions especially this concentration, though small, cannot be considered as negligible, and the more exact expressions for the condition equations used in the calculation become,

$$NH_4OH = \overline{HCrO_4} + 2\overline{\overline{Cr_2O_7}} + NH_4HCrO_4,$$

and $$\overset{+}{NH_4} = 2\overline{\overline{CrO_4}} + \overline{HCrO_4} + 2\overline{\overline{Cr_2O_7}}.$$

The concentration of ammonium hydroxide is known from the distribution experiments; that of the ammonium ions may be estimated by considering it to be equal to that present in the unhydrolyzed ammonium

chromate solution diminished by the concentration of ammonium hydrox--
ide formed by the hydrolysis. The ionization values used for the com-
putation of the ammonium ion concentration in the unhydrolyzed ammon-
ium chromate solution were calculated from conductivity data obtained
by extrapolation on a plot of measurements of Merrill for the conductance
of unhydrolyzed ammonium chromate. Though his measurements were
made at 18°, no serious error is here involved because of the fact that the
ionization of salts changes but little with the temperature. The ioniza-
tion values used in the calulation were for the chromate solutions, 0.05-
molal and 0.025-molal, respectively *0.66* and *0.72*.

The concentration of the dichromate ion in terms of the hydro-
chromate ion is given by the relation,

$$Cr_2O_7 = K_H \times (HCr_4O)^2.$$

Since the concentration of the dichromate ion occurs in the above equa--
tions only as a small correction term, an approximate value of K_H is suffic-
ient for its estimation. The value used was taken equal to *75*, that ob-
tained from the solubility experiments which follow. The concentration
of unionized ammonium hydrochromate may be estimated by assuming,
as was done before in the conductivity method, the unionized fraction
$(1-\gamma)$ of the ammonium hydrochromate in the mixture to be equal to one
half that of the neutral ammonium chromate; that is for the above concen-
trations of ammonium chromate *0.17* and *0.14* respectively. The total
concentration of ammonium hydrochromate in the mixture may be taken
equal to the concentration of ammonium hydroxide.

In Table 12 are presented the results of the calculations. The hydrol-
ysis values used were a mean of those given in the preceding table; the
values taken for K_W and K_B at this temperature were *0.8* × *10⁻¹⁴* and
18 × *10⁻⁶* respectively[1].

TABLE 12.

Molal conc.	NH₄OH 10⁷	NH₄	HCrO₄ × 10⁵	Cr₂O₇ × 10⁵	NH₄HCrO₄ × 10⁵	CrO₄	$\frac{K_W}{K_A K_B}$	K_A
0.05	134.0	0.0647	97.0	7.05	22.8	0.0318	6.3 × 10⁻¹	7.1 × 10⁻
0.025	66.7	0.0353	53.1	2.11	9.4	0.01736	5.8 × 10⁻¹	7.7 × 10⁻
							(Mean)	7.4 × 10⁻

The experiments were repeated at 18°. A summary of the results and
calculations is given in Table 13. The values for K_B, K_W, K_H, and the
distribution-ratio used in the calculations were *1.72* × *10⁻⁶*, *0.6* × *10⁻¹⁴*,
30 and *27*[2] respectively.

TABLE 13.

Molal conc. (NH₄)₂CrO₄	Hydrolysis	$K_W K_A K_B$	K_A
0.05	0.0252	5.7 × 10⁻¹	6.0 × 10⁻⁷
0.025	0.0253	5.4 × 10⁻¹	6.4 × 10⁻⁷

[1] Pub. of the Carnegie Inst. No. 63.

[2] This value for the distribution-ratio was taken from measurements of Abbott.

The values of K_A in the above table agree very well with those found by Merrill at the same temperature.

Solubility Experiments with Silver Chromate and Silver Dichromate.
Experiments by Donald E. Russ.

As is the case with all difficultly soluble salts of weak acids the solubility of silver chromate is increased by the presence of acids. This increase of solubility is caused by the decrease in the concentration of the chromate ion in the solution due to its conversion primarily into the hydrochromate ion, and secondarily into the dichromate ion. The increase of solubility is thus a measure of the extent to which these substances are formed. Accordingly the solubility of silver chromate in varying strengths of nitric acid was determined for the purpose of determining the equilibrium-constants for the reactions involved. An interpretation of the results, however, precludes a knowledge of the solubility-product for silver chromate. That this may be calculated from the solubility of silver chromate in an ammonia solution of known concentration the following considerations will show.

The solubility of silver chromate is increased by ammonia in virtue of the formation of the complex salt, $Ag(NH_3)_2CrO_4$. The product of the solubility-product, $K = \overset{+}{Ag}{}^2 \times \overset{=}{CrO_4}$ for silver chromate by the square of the complex-constant $K_C = Ag(\overset{+}{NH_3})_2/\overset{+}{Ag} \times (NH_3)^2$ for the complex ion $Ag(\overset{+}{NH_3})_2$ gives an equilibrium equation which must be satisfied in an ammonia solution saturated with silver chromate. This equation solved for the solubility-product for silver chromate gives the expression

$$K = \frac{\overset{=}{CrO_4} \times [Ag(\overset{+}{NH_3})_2]^2}{(\overset{-}{NH_3})^4 \times K^2_C}$$

In such a saturated solution the concentration of the silver ion is negligibly small due to the fact that the concentration of chromate ions is relatively large and the solubility-product for silver chromate very small. In other words the saturated solution may be considered as consisting entirely of $Ag(NH_3)_2CrO_4$ and free ammonia. The concentrations occurring in the above equation may be very simply calculated from the solubility, S, in mols per liter, the ionization values γ_1 and γ_2 for the complex-salt and the free ammonia in the solution respectively, and the total concentration of ammonia, C. Substituting these quantities in the equation it becomes,

$$K = \frac{4S^3\gamma_1^3}{(1-\gamma_2)^4(C-4S)^4 K^2_C}$$

The complex-constant K_C as determined by Bodländer and Fittig[1] is

[1] Z. physik. Chem., **39**, 610 (1902).

1.47×10^{7}.   The solubility of silver chromate in varying concentrations of ammonia solutions was accordingly determined in order to obtain a value for its solubility-product.

The silver chromate used in all of the solubility experiments was prepared by precipitating it from a silver nitrate solution by the addition of potassium chromate solution acidified with acetic acid.   The precipitate was washed thoroughly with water.

The procedure employed in the solubility experiments was invariably as follows: To an oil bottle of about 125 cc. capacity was added moist solid silver chromate to a depth of about one-half an inch, and then the desired ammonia solution until nearly filled.   The bottle was corked and rotated in the thermostat at 25° for a short while, then opened, and the solution poured off and replaced by a new portion of the same strength.   By this means the silver-chromate was freed of any possible impurity and a solution of ammonia of exactly the desired concentration introduced.   Equilibrium was approached from supersaturation as well as undersaturation. After rotating for from two to four hours to reach equilibrium the bottle was suspended in the thermostat to allow the precipitate to settle, and 50 or 100 cc. pipetted off through cotton filters for analysis.

The solution was acidified with nitric acid and the silver precipitated as the chloride by the addition of potassium chloride in slight excess. After heating to boiling, the silver chloride was filtered on a Gooch crucible, washed, thoroughly dried, and weighed. The chromate in the filtrate was determined volumetrically by adding an excess of potassium iodide, and, after standing five minutes to allow the reaction to complete itself, titrating for the iodine liberated with 0.05-normal sodium thiosulphate. Starch solution was added only after the brown color of the free iodine had almost disappeared, and the titration continued to a disappearance of the blue color.   The thiosulphate was standardized against potassium dichromate, the conditions followed being those used in the analysis.

In Table 14 are presented the results of the measurements and calculations.

TABLE 14.

Conc. NH$_4$OH (Volumetric) C	Solubility (Volumetric) S $\times$ 10^3	Solubility (Gravimetric) S $\times$ 10^3	Mean Solubility S $\times$ 10^3	γ_1	$1 - \gamma_2$	C—4S	$K = \dfrac{4S^3\gamma_1^3}{(1-\gamma_2)^4(C-4S)^4K^2_C}$
0.01	2.003	2.000					
0.01	2.010	2.005	2.004	0.91	0.91	0.001984	10.5×10^{-12}
0.02	4.165	4.170					
0.02	4.171	4.170	4.169	0.88	0.93	0.003324	10.0×10^{-12}
0.04	8.580	8.585					
0.04	8.587	8.625	8.595	0.84	0.95	0.005620	8.6×10^{-12}
0.08	17.57	17.58					
0.08	17.57	17.58	17.58	0.79	0.96	0.00968	6.6×10^{-12}
						(Mean)	8.9×10^{-12}

The values for the ionization γ_1 of the complex salt were obtained by assuming its ionization to be the same as that of potassium sulphate at the same concentration; those for the ionization γ_2 of the free ammonium hydroxide were calculated from the ionization-constant for ammonium hydroxide. The value of the solubility-product for silver chromate used for the subsequent calculation was taken equal to 9×10^{-12}. Except as otherwise indicated in the table the procedure followed in determining the solubility of silver chromate in nitric acid solutions was identical with that given above both as to the attainment of equilibrium and as to analysis of the saturated solutions. In the table giving the results of the measurements u signifies that equilibrium was approached from undersaturation, o from supersaturation. The concentrations of chromium and silver in the saturated solutions are expressed as milli-atomic in chromium and silver respectively.

TABLE 15.

	Conc. HNO₃		Conc. Total Chromium	Conc. Total Silver
	0.01	(u)	3.157	6.312
	0.01	(o)	3.158	6.318
	0.015	(u)	3.730	.....
	0.02	(u)	4.177	8.356
	0.02	(o)	4.177	8.356
	0.025	(u)	4.567	.....
I	0.03	(u)	5.200	.....
	0.04	(u)	5.800	11.62
	0.04	(o)	5.807	11.62
	0.05	(u)	6.380	.....
	0.06	(u)	6.833	.....
	0.07	(u)	7.333	.....
	0.075	(u)	7.477	.....
	0.075	(u)	.....	14.85
	0.08	(u)	7.260	15.46
	0.08	(o)	7.260	15.45
	0.10	(u)	5.647	19.00
II	0.10	(o)	5.647	19.02
	0.13	(u)	4.293	23.89
	0.13	(o)	4.296	23.90
	0.14	(u)	3.948	25.63
	0.14	(o)	3.948	25.63

[1] Shaken for three days.

An inspection of Table 15 shows that in the nitric acid solutions less than 0.08-normal the concentration of silver in the saturated solution is double that of the chromium, the proportions in which the two elements are present in silver chromate, while in the nitric acid solutions above 0.075-normal the concentration of dissolved chromium decreases, and that of silver increases with the increasing concentration of the acid. A consideration of the equilibrium equations will show that this phenomenon can be readily explained by the fact that the solubility-product for silver dichromate has been reached, and that this salt has begun to separate out as a second solid phase.

In order to be sure that this second solid phase really was silver dichro-

mate and not possibly the silver hydrochromate some of it was prepared and analyzed. It was made by adding chromic acid and silver nitrate in about equivalent amounts to form silver dichromate to a nitric acid solution about 0.1 normal. Under these conditions no silver chromate should precipitate. The precipitate was filtered and washed with nitric acid solution about 0.1 normal. One portion was dried at 110°, and a second portion was left for four days in a vacuum desiccator over sulphuric acid. Both samples were analyzed for their silver content. The first two results in the table refer to the sample dried at 110°, the other two to that dried in the desiccator. A comparison of the figures shows conclusively that the salt was silver dichromate.

TABLE 16.

Gms. Salt Analyzed.	Gms. AgCl Expm't Found	Gms. AgCl Calc. for $Ag_2Cr_2O_7$	Gms. AgCl Calc. for $AgHCrO_4$
1.0821	0.7188	0.7178	0.6893
1.1139	0.7385	0.7389	0.7098
1.523	1.0090	1.010	0.9703
1.8341	1.2171	1.216	1.169

A quantitative consideration of the foregoing results will be taken up in connection with the next series of solubility measurements. These experiments consisted in shaking pure silver dichromate, prepared as described above, with water, with nitric acid solutions of varying concentrations, and finally with a solution containing definite amounts of both nitric acid and silver nitrate till equilibrium was reached, and then analyzing the respective solutions for their content in silver and chromium. The method of establishing an equilibrium and of analysis was the same as that already described. The results of the measurements are given in Table 17. As before the concentrations of chromium and silver are expressed as milli-atomic.

TABLE 17

	Conc. HNO_3	Conc. $AgNO_3$	Total Conc. Chromium.	Total Conc. Silver.
I*	0.00	0.00	32.20	5.385
	0.00	0.00	32.19	5.395
	0.01	0.00	25.06	6.127
	0.01	0.00	25.06	6.135
	0.02	0.00	20.21	7.145
	0.02	0.00	20.21	7.152
	0.04	0.00	13.59	9.524
	0.04	0.00	13.59	9.524
II	0.06	0.00	11.10	11.10
	0.06	0.00	11.10	......
	0.08	0.00	11.11	11.10
	0.08	0.00	11.10	......
	0.08	0.01	6.625	......
	0.08	0.01	6.623	......

*Shaken for three days.

In the nitric acid solutions 0.06 normal and stronger the concentration of the chromium is seen to be equal to that of the silver, while in the less dilute solutions of nitric acid the concentration of the chromium ex-

ceeds that of the silver.   The explanation of this is that with water and
the more dilute nitric acid solutions, some of the solid silver dichromate
is converted to solid silver chromate with the formation of the excess of
chromium in the solution, while with the nitric acid solutions above
0.04 normal there is but one solid phase, silver dichromate, in equilib-
rium with the solution.

The discussion of the results of all of the solubility experiments with
the chromates of silver in nitric acid divides itself most naturally into
three parts.   First will be considered the case in which silver chromate
alone is in equilibrium with the solution, second that in which both silver
chromate and silver dichromate are present as solid phases, and third that
in which silver dichromate alone constitutes the solid phase.

In each case, before any final quantitative interpretation of results
could be made, it was necessary to estimate the concentration of all un-
ionized substances present in the respective solutions in appreciable
amount.   Here as in the freezing-point experiments of Eaton, the concen-
tration of any HCr_2O_7-ion or of unionized $AgHCr_2O_7$ was neglected.   It
is also to be noted that in every solution, due to the relatively large con-
centration of the hydrogen ion, that of the chromate ion, and hence also
that of unionized silver chromate can be considered as negligibly small in
comparison with those of the other substances. The unionized substances
in the solutions whose concentrations were considered were $AgNO_3$,
$AgHCrO_4$, $Ag_2Cr_2O_7$, HNO_3, H_2CrO_4, and $H_2Cr_2O_7$.   In computing these
concentrations the principle suggested by Noyes[1] that the ionization-
constant[2] for salts is a function of the total ion-concentration of the solu-
tion and that alone, and that salts of the same type have at equal ion-
concentrations the same value of the ionization-constant, was followed.
The ionization-constant for silver hydrochromate was considered to be
equal to that for silver nitrate at the same ion-concentration, that for
silver dichromate and dichromic acid as equal to that for potassium sul-
phate, and that for chromic acid as equal to that for nitric acid.

The method of making these computations was briefly this.   First with
the help of the experimental data and of the formulation given later, and
neglecting the concentration of all unionized substances, the concentra-
tion of the dichromate and the hydrochromate present was estimated.
Next a guess was made as to the concentration of each of the ions present,
and from these the total ion-concentration in the solution roughly deter-
mined.   Then the ionization-constants for silver nitrate, potassium sul-
phate, and nitric acid respectively in solutions with this ion-concentration
were calculated from the conductivity data of Kohlrausch for these sub-
stances alone.   Finally these approximate ion-concentrations in the solu-

[1] Science 20, 584 (1904); Z. physik. Chem., 52, 635 (1905).
[2] The term ionization-constant here signifies the ratio of the product of the
concentrations of the two ions of the salt to that of its unionized part.

tion were substituted in the expression for the ionization-constant, and using the corresponding value for the ionization-constant above obtained, the concentration of each of the unionized substances was calculated. From the experimental data, the concentration of the total silver, of the total chromium, and of the total nitrate in each solution were known By deducting the corresponding concentrations of the unionized substances from each of these values, were obtained for the concentration of the silver ion, that of chromium in the form of ions, and that of the nitrate ion. To gain separate values for the concentration of the hydrochromate ion and of the dichromate ion the formulation which follows was resorted to. The concentration of the hydrogen ion was calculated from the relation that the sum of the equivalent concentration of the cathions must equal that of the anions.

Having now obtained these more accurate values for the concentrations of each of the ions present, the whole process was repeated. An idea as to their nearness to the truth according to this principle may be obtained by observing how much the repetition changes the respective concentrations.

From the above estimation of the concentrations of the unionized substances present, there is known in each solution the concentration, $\overset{+}{Ag}$, of the silver ion, that, $\overset{+}{H}$, of the hydrogen ion, and the sum, $\overset{-}{HCrO_4} +$ $2\overset{=}{Cr_2O_7}$, of the hydrochromate ion concentration and twice that of the dichromate ion. In addition to these conditions of concentration there must be satisfied for the different cases certain equilibrium equations. For the first case, that in which silver chromate is the single solid phase, these equilibrium equations are:

$$K_1 = \overset{+}{Ag}{}^2 \times \overset{=}{CrO_4}$$

$$K_A = \frac{\overset{+}{H} \times \overset{=}{CrO_4}}{\overset{-}{HCrO_4}}$$

$$K_H = \frac{\overset{=}{Cr_2O_7}}{(\overset{-}{HCrO_4})^2}$$

For the case in which silver dichromate also saturates the solution the additional equation, the solubility-product K_2 for the silver dichromate is obtained:

$$K_2 = \overset{+}{Ag}{}^2 \times \overset{=}{Cr_2O_7}.$$

For the third case, that in which silver dichromate is the only solid phase, the solubility-product of the silver chromate is of course not involved, and since the ionization of the hydrochromate formed by the hy-

dration of the dichromate ion is prevented by the excess of acid present, its ionization-constant likewise need not be considered.

Since the value of the solubility-product K_1 for silver chromate has already been determined, it is evident that for the first case, if one of the constants, K_A or K_H, is given, the other may be calculated; or, if the known concentration conditions for any pair of these solutions are combined with the equilibrium equations it is possible to calculate values of both K_A and K_H.

Similarly for the second case, given one of the three constants K_A, K_H, or K_2, the others can be calculated, or from a consideration of any pair of solutions, values of all of these constants can be found.

Analogous considerations hold for the third case. It is to be noted here that the solubility, and hence the relative amounts of hydrochromate and dichromate in the solution are not much affected by increasing the concentration of the nitric acid. Addition of silver nitrate, a salt with a common ion, does, however, produce the desired effect. The values of the hydration-constant K_H, and the solubility-product K_2, for silver dichromate obtained from a consideration of pairs of solutions, would in this case be independent of any value for the ionization-constant K_A, for the hydrochromate ion.

A consideration of Table 18, which contains the final results of the calculations, shows that for the solutions obtained by shaking silver chromate with nitric acid, the concentration of the hydrochromate ion is large as compared with that of the dichromate ion. This signifies that the secondary reaction, the dehydration of the hydrochromate ion to form dichromate ion, plays but little part in producing the equilibrium conditions, and hence only an approximate value of the hydration-constant K_H is necessary to calculate a fairly reliable value for the ionization-constant K_A. The solutions which contain the dichromate ion in relatively the largest amount, and hence which provide the best data for calculating the most reliable value for the hydration-constant, are, as seen from the table, those obtained by shaking silver dichromate with water, and with nitric acid solutions so dilute as to cause separation of the second solid phase, silver chromate.

These considerations furnish the reasons for the method followed in calculating the results tabulated. For the first case by combining the conditions of concentration existing in solutions varying most widely in their chromium content, the first and fourth given in the table, with the equilibrium equations, were calculated values for both K_A and K_H. The values thus obtained were 5.5×10^{-7} and 21 respectively. Assuming this value for K_H, values of K_A were calculated from the concentration conditions prevailing in the second and third solutions. A mean of all values for the ionization-constant so obtained was then taken and used to

calculate values for the hydration constant from the ninth, tenth, eleventh and twelfth solutions.

A mean of these gave a more accurate value for the hydration-constant to use with the original first four solutions in order to obtain a new, more reliable value for the ionization-constant. By working back and forth according to this principle the values tabulated were obtained. In the table the constants enclosed in the parentheses were assumed in order to calculate the other constants given.

The constants agree well among themselves. Though perhaps the assumptions made in the various calculations do not warrant such a comparison, yet it is seen from the results that the value for the hydration-constant K_H obtained at this temperature is as might be expected somewhat greater than that found by Eaton at $0°$. The values for the ionization-constant K_A also agree well with those obtained from the experiments on the hydrolysis of ammonium chromate.

Discussion of the Results in Relation to Those of Other Investigators.

The measurements of Whetham[1] on the conductance at $0°$ of solutions of potassium dichromate are also in accordance with the results here presented. The following table derived from his measurements gives a comparison of the increase in the equivalent conductance observed for solutions of potassium dichromate between certain concentrations with the corresponding increase for solutions of potassium chloride and barium chloride.

Conc. Interval.	$\Delta\Lambda(K_2Cr_2O_7)$	$\Delta\Lambda(KCl)$	$\Delta\Lambda(BaCl_2)$
0.1 — 0.01	6.1	5.3	8.8
0.01 — 0.001	1.0	2.4	5.4
0.001 — 0.0001	10.9	0.7	2.3

In the first concentration-interval the change for the dichromate lies between that for the other two, in the second it is much smaller than either, and in the third it is very large compared with either of the other two. The abnormally small increase at first in the equivalent conductance is, as previously mentioned, probably due to the conversion of the dichromate ion into the slower moving hydrochromate ion, and the rapid increase in the very dilute solution to the ionization of the latter into hydrogen ion and the doubly charged chromate ion. This may be seen from a consideration of the freezing-point results of Eaton (See Table 5). These indicate that at $0°$ in a 0.1 normal solution of potassium dichromate the molal concentration of the dichromate ion is nearly equal to that of the hydrochromate ion, while in a 0.02 normal solution the ratio $Cr_2O_7/HCrO_4$ of their concentrations is only $1/2$. Approximate calculations neglecting the unionized parts of salts, and using 50 as an approximate

[1] Pr. Roy. Soc., 71, 332 (1903).

TABLE 18.

Solid phases	Conc. HNO₃	Ag × 10⁵	HCrO₄ × 10⁴	$\overset{=}{Cr_2O_7}$ × 10³	H × 10³	AgNO₃ × 10³	AgHCrO₄ × 10³	Ag₂Cr₂O₇ × 10⁵	HNO₃ × 10³	H₂CrO₄ × 10³	H₂Cr₂O₇ × 10³	K_A × 10⁵	K_z × 10⁷	K_II
Ag₂CrO₄	.01	5.808	2.245	0.3775	6.661	0.392	0.112	0.0012	0.1395	0.04	0.0014	7.9		(75)
	.02	7.488	2.775	0.577	15.15	0.730	0.134	0.0019	0.562	0.1034	0.0038	8.7		(75)
	.04	10.02	3.530	0.935	32.34	1.410	0.176	0.0032	1.63	0.2035	0.0103	8.2		(75)
	.075	12.41	4.220	1.333	62.94	2.345	0.193	0.0041	4.21	0.3465	0.0212	8.7		(75)
Ag₂CrO₄ and Ag₂Cr₂O₇	.08	12.64	4.120	1.273	66.73	2.62	0.195	0.004	4.68	0.349	0.021	9.1	2.0	(75)
	.10	15.29	3.410	0.8705	80.29	3.55	0.172	0.0027	6.02	0.292	0.0142	9.1	2.0	(75)
	.13	18.88	2.745	0.5640	101.2	4.88	0.141	0.0018	8.95	0.258	0.010	9.3	2.0	(75)
	.14	20.21	2.570	0.4965	107.7	5.29	0.131	0.0016	10.3	0.249	0.009	9.2	2.0	(75)
	.00	5.009	11.06	9.910	25.87	0.000	0.304	0.039	0.000	0.555	0.193	(8.4)	2.5	81
	.01	5.554	9.627	7.151	27.72	0.228	0.292	0.028	0.405	0.518	0.141	(8.4)	2.2	77
	.02	6.337	8.416	5.392	31.54	0.492	0.272	0.024	0.826	0.456	0.115	(8.4)	2.1	76
	.04	8.162	6.707	3.042	41.70	1.095	0.243	0.013	1.835	0.407	0.065	(8.4)	2.0	68
Ag₂Cr₂O₇	.06	9.26	5.610	2.365	56.18	1.61	0.209	0.0099	3.28	0.424	0.0594		2.0	(75)
	.08¹	13.47	3.855	1.117	74.36	2.98	0.172	0.0045	5.28	0.304	0.0256		2.0	(75)

¹ This last nitric acid solution was also 0.01 normal with respect to silver nitrate.

value for the hydration constant show that in a solution 0.001 normal this ratio is reduced to 1/20. These changes in the relative concentrations of the dichromate ion and hydrochromate ion, doubtless account for the small change in the equivalent conductance within the concentration interval of 0.1 — 0.001 normal. It is true that the ionization of the hydrochromate ion throughout this range of concentration is not entirely negligible; for example, in a 0.02 normal solution where the concentration of the hydrochromate ion is 0.009, its ionization calculated from $K_A = 7 \times 10^{-7}$ is almost one per cent.; but the much larger change in the proportion of hydrochromate ion and dichromate ion overbalances this. In the solutions more dilute than 0.001 normal the chromium is almost wholly present as hydrochromate ion, and the ionization of this rapidly becomes considerable, and, as above stated, accounts for the abnormally high conductance of the solutions. On account of these superimposed effects no quantitative interpretation of the results was attempted.

Sand and Kaestle[1] and Spitalsky[2] have investigated the constitution of chromates in solution by determining the concentration of the hydrogen ion in various chromate mixtures. The work of Spitalsky is of interest inasmuch as he takes into consideration the presence of the hydrochromate ion. The two reactions which he considers as determining the equilibria in chromate solutions are :

$$\overset{=}{Cr_2O_7} + H_2O = 2CrO_4 + 2\overset{+}{H}, \text{ and } \overset{+}{H} + CrO_4 = \overset{-}{HCrO_4}.$$
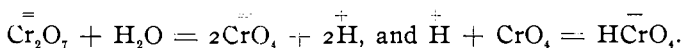
The method employed by him for measuring the concentration of the hydrogen ion was to determine the rate at which diazoacetic ester was catalytically decomposed by the different chromate solutions. Bredig and Fraenkel[3] have shown this to be a first order reaction, and that its rate is proportional to the concentration of the hydrogen ion.

From the concentration of the hydrogen ion thus found in two solutions of potassium dichromate, 0.0169 and 0.0302 molal respectively, Spitalsky calculates what he considers his best values for the equilibrium-constants of the above cited reactions. They are

$$K_1 \quad \frac{\overset{+}{H^2} \times (CrO_4)^2}{\overset{=}{Cr_2O_7}} = 5.1 \times 10^{-12} \text{ and } K_A \quad \frac{\overset{+}{H} \times CrO_4}{HCrO_4} \quad 2.7 \times 10^{-7}$$

The ionization-constant K_A is of the same order of magnitude as that found by us, 8×10^{-7}. The ratio (K_A^2/K_1) of the square of the latter constant to the former one, however, gives a value for the hydration-constant K_H equal to 0.014, which is not at all in accord with the value (75) given above. The discrepancy is due to the fact that serious error

[1] Z. anorg. Chem., **52**, 101 (1907).
[2] Ibid., **54**, 265 (1907).
[3] Z. physik. Chem.. **60**, 202 (1907); Z. Electrochem., **11**, 525.

was introduced into his calculation by the approximate assumptions that were made.

In order to determine how far our constants are in accord with Spitalsky's results, I have made certain calculations for four of the dichromate solutions investigated by him. The results are tabulated below.

By making the same assumptions as to the ionization relations in potassium dichromate solutions as were presented in detail under the freezing-point experiments of Eaton, and taking 75 as the value for the hydration constant K_h, the concentrations were calculated which are given in the fourth, fifth, sixth and seventh columns of the table. Since in a potassium dichromate solution the concentration of the chromate ion may be placed equal to that of the hydrogen ion[1], the relation holds that

$$\overset{+}{H}{}^2 = K_A \times \overline{HCrO_4}.$$

With the help of this equation taking K_A equal to 8×10^{-7}, the values of the hydrogen ion recorded in the next to the last column were calculated.

Conc. Total Cr.	Ionization $K_2Cr_2O_7$ (γ_1)	Ionization $KHCrO_4$ (γ_2)	Conc. $KHCrO_4$	Conc. $K_2Cr_2O_7$	Conc. $Cr_2O_7=$	Conc. $\overline{HCrO_4}$	Conc. $\overset{+}{H}$ (calc.)	Conc. $\overset{+}{H}$ (Obs.)
0.0338	0.795	0.905	0.00113	0.00225	0.00870	0.01077	0.000093	0.000095
0.0604	0.755	0.882	0.00198	0.00535	0.01647	0.01482	0.000109	0.000127
0.0964	0.722	0.861	0.00306	0.01035	0.02688	0.01893	0.000123	0.000170
0.1208	0.705	0.850	0.00374	0.01414	0.03377	0.02122	0.000130	0.000188

A comparison of the hydrogen ion concentrations thus calculated with those observed by Spitalsky (given in the last column) shows that there is nearly complete agreement in the most dilute solutions, and that even in the more concentrated solutions, where the quantities of the unionized substances are larger, the agreement is still a tolerable one[2], considering the estimates that were made in the computation of K_A.

Spitalsky in the interpretation of all of his results has underestimated the importance of the reaction, $\overset{+}{H} + \overset{=}{CrO_4} = \overline{HCrO_4}$, in determining the condition of chromates in solution. Thus his conclusion that in dilute solutions of potassium dichromate the concentration of the $HCrO_4$-ion is very small as compared with that of the Cr_2O_7-ion, is neither in accordance with the above calculations (see for example, the preceding table) nor consistent with the constants given by him. Thus, the concentra-

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[1] Assuming that any unionized K_2CrO_4 formed is compensated by the HCr_2O_7. H_2CrO_4, and H_2Cr_2O, formed, or that all of these quantities are negligible.

[2] Reference should, however, be made to the remarkable fact that the observed hydrogen-ion-concentration seems to be proportional to the concentration of the hydrochromate ion instead of to its square root. There seems to be no other explanation of this than that it arises from error in the assumption that $\overset{+}{H} = \overset{=}{CrO_4}$ especially in the more concentrated solutions where any estimate of the quantities of various unionized substances that may be produced, is very uncertain.

tion of the $HCrO_4$-ion in the potassium dichromate solution 0.0338-atomic in chromium calculated by substituting the hydrogen-ion concentration observed by him, and his value for the ionization-constant K_A in the ex-

pression $H^2 = K_A \times \overline{HCrO_4}$ is equal to 0.03342 ; that is, essentially all of the chromium is in the form of hydrochromate. Furthermore, if this did represent the constitution of the solution, the concentration of the Cr_2O_7-ion would be so small as to render its estimation by difference, and hence the evaluation of the hydrolysis-constant given by Spitalsky, very inaccurate.

Similarly Spitalsky concludes from the fact observed by him that in solutions of chromic acid the concentration of the hydrogen ion is essentially equal to that of the total chromium, that chromic acid exists as $H_2Cr_2O_7$ dissociating into only H-ion and Cr_2O_7-ion. This fact is equally well explained by assuming the existence of H_2CrO_4 dissociating into

H-ion and $HCrO_4$-ion. The ionization of the very weak acid ion, $\overline{HCrO_4}$, would be entirely prevented by the presence of the H-ion resulting from the primary ionization. As already pointed out, both hydrochromate and dichromate exist simultaneously in a proportion dependent on the concentration of the solution.

According to Spitalsky's results, the addition of potassium dichromate to chromic acid is analogous to the addition of potassium chloride to hydrochloric acid, and affects but little the concentration of the hydrogen ion. On the other hand, the addition of a small proportion of potassium chromate to chromic acid solutions removes quantitatively the hydrogen ion from the solution, primarily with formation of the weak acid anion,

$\overline{HCrO_4}$. Whether or not this hydrochromate ion remain as such, or be partly or wholly converted to dichromate ion through dehydration, would be without influence on the hydrogen ion concentration. Similarly the concentration of hydrogen ion in a potassium dichromate solution is largely decreased by the addition of a very small proportion of potassium chromate, owing to the formation of hydrochromate. These facts afford therefore, no confirmation of Spitalsky's interpretation since they are equally in accordance with the assumption of a large proportion of hydrochromate ion.

Summary.

In this article the view has been suggested and substantiated that in the equilibria prevailing in chromate solutions the intermediate hydrochromate ion plays an important part, the main equilibria involved being those of the reactions:

$$CrO_4 + \overset{+}{H} = \overline{HCrO_4} \text{ and } 2H\overline{CrO_4} = H_2O + Cr_2O_7.$$
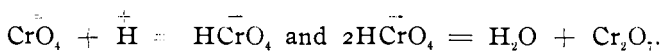
The relative amounts of chromate, hydrochromate, and dichromate

present are dependent upon the composition of the mixture and its concentration, and on the values of the equilibrium-constants for the two reactions.

Freezing-point determinations were made with solutions of chromic acid and of potassium dichromate varying in concentration from about 0.02 to 0.1 atomic in chromium. The observed lowering of the freezing-point in the most dilute solutions was actually greater than that which would correspond to complete ionization of these substances into dichromate ion and hydrogen ion or potassium ion, the van't Hoff factor i reaching 3.33 and 3.24 at the lowest concentrations, thus indicating the existence of hydrochromate ions in appreciable amount. From the results, approximate values of the equilibrium-constant for the second reaction,

i. e. of the hydration-constant $K_H = \overset{=}{Cr_2O_7}/(\overset{-}{HCrO_4})^2$ were calculated. The values of this constant obtained from the potassium dichromate and chromic acid experiments are 61 and 27, respectively.

The hydrolysis of ammonium chromate in dilute solutions was determined by two methods. The hydrolysis was assumed to be due mainly to the formation of ammonium-hydroxide and hydrochromate, the small amount of dichromate formed being subsequently taken into account as a correction term in the evaluation of the ionization-constant for the hydrochromate ion. In the first method the hydrolysis was derived from the increase in the conductance of a neutral ammonium chromate solution caused by the addition of enough ammonia to completely drive back the hydrolysis; and in the second method it was determined by distribution experiments from the concentration of ammonia in chloroform which was in equilibrium with the ammonium chromate solution in question. The distribution-ratio at 25° of ammonia between water and chloroform was incidentally determined, and found to be 25.

The values for the ionization-constant $K_A = \overset{+}{H} \times \overset{..}{CrO_4}/HCrO_4$ at 18° obtained by the two methods were 5.7×10^{-7} and 6.2×10^{-7} respectively, and that at 25° by the distribution method 7.4×10^{-7}. The constant is therefore only about 1/30 as great as that of acetic acid. Correspondingly, ammonium chromate in 0.05 molal solution was found to be 2.7 per cent. hydrolyzed.

The solubility at 25° of silver chromate in dilute ammonia solutions was determined, and from the results and the value of the complex-constant for the silver-ammonia-cation by application of the mass-action law, a value for the solubility-product, $(\overset{+}{Ag})^2 \times \overset{=}{CrO_4}$, for silver chromate was calculated. The value obtained was 9×10^{-12}, the corresponding silver-ion concentration in the saturated solution in water being 2.5×10^{-4} mols. per liter.

Solubility experiments at $25°$ were also made by shaking solid silver chromate with nitric acid solutions varying in concentration from 0.01 to 0.14 normal, and solid silver dichromate with water, with nitric acid solutions from 0.01 to 0.08 normal, and with an 0.08 normal nitric acid solution which was also 0.01 normal with respect to silver nitrate. In the experiments both the total silver and total chromium were analytically determined. The results showed that silver chromate in acid solutions stronger than 0.075 normal, is decomposed with separation of silver dichromate as a second solid phase. Correspondingly silver dichromate is decomposed by water and nitric acid solutions more dilute than 0.06 normal, with separation of solid silver chromate.

From these results and the solubility product for silver chromate above given values for the other equilibrium-constants involved, were calculated, namely the hydration-constant K_H, the ionization-constant K_A, and the solubility-product $K = (\overset{+}{Ag})^2 \times Cr_2O$, for silver dichromate. The final values obtained in this way for these three constants were $K_H = 75$, $K_A = 8.4 \times 10^{-7}$, and $K = 2 \times 10^{-7}$, respectively. This value of the solubility product corresponds to a silver concentration of 7.3×10^{-3} mols. per liter.

In the computation of these constants the concentrations of the unionized substances present in the solutions were estimated according to the following principle proposed by Noyes.[1] The ratio of the product of the concentration of the two ions of a salt to that of its unionized part is a function of the sum of the equivalent concentrations of all ions in the solution and of that alone ; and further, that this ratio is for any given ion-concentration approximately the same for salts of the same ionic type. Potassium sulphate was taken as a typical tri-ionic salt, and silver nitrate (or potassium chloride) as a typical di-ionic one. The ionization relations of dichromic acid H_2Cr_2O, were considered like those of potassium sulphate, while chromic acid H_2CrO_4 with respect to the dissociation of its first hydrogen was considered analogous to nitric acid. On account of these assumptions involved in their calculation, no great accuracy can be claimed for the values of the constants. The values obtained by the different methods do, however, agree well with one another, and verify the underlying conception that the hydrochromate ion is one of the important constituents of chromate solutions. With respect to the proportion of this ion present, it is of interest to note that the results lead to the conclusion that in a 0.1 molal solution of potassium dichromate, approximately 15 per cent. of the salt exists as hydrochromate and 85 per cent. as dichromate, while in a 0.01 molal solution approximately 45 per cent. exists in the former state.

[1] Science, **20**, 584 (1904) ; Z. physik. Chem., **52**, 635 (1905).

It has also been shown that the results of Whetham on the conductivity of potassium dichromate and those of Spitalsky on the catalysis of diazoacetic ester by chromate solutions are in substantial accord with the results from this investigation, and that the conclusion drawn by Spitalsky that his experiments indicated that the hydrochromate ion is not present in any considerable quantity in dilute solutions of chromic acid and potassium dichromate is an erroneous one.

In conclusion, I wish to thank Prof. A. A. Noyes for suggesting this investigation and for his ever-willing advice throughout its execution.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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THE PERMEABILITIES OF COLLODION, GOLD BEATER'S SKIN, PARCHMENT PAPER AND PORCELAIN MEMBRANES.

BY S. LAWRENCE BIGELOW.

Contents.

The object and scope of the investigation. Previous investigations. Apparatus. Method of measurement. The unit of permeability. The effect of changing the pressure upon the permeability of collodion, of gold beater's skin, of parchment paper, of porcelain. The results of the pressure experiment's and Poiseuille's formula. Permeability of collodion at different temperatures. Calculation to test the applicability of Poiseuille's formula. The effect of changing the temperature upon the permeability of parchment paper, of porcelain. Discussion of results and theory. Summary.

The Object and Scope of the Investigation.

Probably it will be conceded, without the presentation here of a summary, which, even if abbreviated until inadequate, would require too much space, that there are numerous theories, each accounting ingeniously for some of the facts included under the comprehensive title of osmotic phenomena and conflicting with others. One cause for the lack of unanimity of opinion on even the most fundamental propositions, such as the function of the membrane in an osmotic cell, is the number of unknown quantities in each single experiment. Unless we have a solvent, a solute, and a membrane, there is no osmosis in the ordinary sense of the term, but with all three present the number of possible interactions is large. It has seemed to the writer that results could be obtained, which might have an interesting bearing upon the problems of osmosis, by omitting the solute. The attention is thereby fixed on the function of the membrane.

My intention is to force a pure liquid (solvent) through several different membranes at different pressures and at different temperatures, and to force different pure liquids through one and the same membrane at different pressures and temperatures. After numerical values for these processes have been established, solutions may be put through the same treatment with some hope of elucidating valuable