This, however, would make a difference of 0.0026 cal./deg./mole at most in the thermodynamic quantities under consideration—in the specific heat of 0.0009 or less. The value of R given by the "International Critical Tables" is 1.9869 cal./deg./mole, which is 0.0005 in excess of the value used by us. This difference in the value of R produces considerable differences in the computed values of the entropy and $(-(F - E_0°)/T)$ less in the case of the specific heat. When the values of Johnston and Chapman are "corrected" for this difference in the value of R, it is found that the differences between our values and their values are just about what they should be according to Table II. This is a check on both calculations. Outside of the errors arising from their incorrect value of the doublet spacing, only one error has been found in their work. This is in the value of the specific heat at 4°K., where there should be almost complete agreement, since the $^2\Pi_{3/2}$ level is not yet excited at that temperature. Their value exceeds ours by 0.015 cal./deg./mole. Since we recomputed our value, this difference is apparently due to an error on their part.

It should be borne in mind, in considering the importance of the discrepancies arising from differences in the values of the physical constants, that the probable error due to uncertainty in the spectroscopic data of Jenkins, Barton and Mulliken is of the order of 0.005 cal./deg./mole, as estimated by Johnston and Chapman. The error introduced by the incorrect value of the doublet separation in the work of Johnston and Chapman is several times this probable error within a considerable range, and also exceeds, on the whole, the differences traceable to discrepancies in the values of the physical constants.

In conclusion, the writer wishes to thank Prof. E. C. Kemble, who suggested calculating the specific heat of nitric oxide, which was done at Harvard University in 1927; and the Faculty Research Committee of the University of Pennsylvania for providing funds for an assistant, Dr. A. V. Bushkovitch, who made the calculations of the entropy and the free energy.

Summary

The specific heat, entropy and free energy of nitric oxide in the ideal gaseous state have been computed for the temperature range from 1 to 500°K. from the spectroscopic data.

The values obtained do not agree entirely with those recently published by Johnston and Chapman. This is due principally to the fact that they used an incorrect value of the doublet separation in their computation; the effect of this error is distorted somewhat by differences in the respective values of the physical constants used by Johnston and Chapman and by us. The magnitude of the error affecting their values is several times larger than their estimated probable error throughout the greater part of the range from 1 to 500°K.

PHILADELPHIA, PA. RECEIVED JUNE 18, 1934

[CONTRIBUTION FROM THE LABORATORY OF CHEMICAL ENGINEERING, UNIVERSITY OF ILLINOIS]

The Solubility of Sulfur Dioxide at Low Partial Pressures. The Ionization Constant and Heat of Ionization of Sulfurous Acid[1]

BY H. F. JOHNSTONE AND P. W. LEPPLA

In some work on the rate of oxidation of sulfur dioxide by oxygen in stationary liquid films it has been necessary to know the solubility of the gas at partial pressures considerably lower than those previously reported. The opportunity has thus been given to make further application of the theory of interionic attraction to the field of intermediate electrolytes. Using the method of Sherrill and Noyes[2] the ionization constants of sulfurous acid have been calculated at 0, 10, 18, 25, 35 and 50° from the recent conductivity data of Maass and his co-workers.[3] By means of these constants the molalities of the un-ionized molecules, both in our dilute solutions and in the more concentrated solutions for which the vapor pressures were measured by Maass, have been

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[1] This paper contains a part of the results of a coöperative research, Project No. 34, with the Utilities Research Commission of Chicago, entitled "A Study of Stack Gases." Published by permission of the Director of the University of Illinois Engineering Experiment Station.

[2] Sherrill and Noyes, THIS JOURNAL, **48**, 1861 (1926); *cf.* also MacInnes, *ibid.*, **48**, 2068 (1926); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[3] Campbell and Maass, *Can. J. Research*, **2**, 42 (1930); Morgan and Maass, *ibid.*, **5**, 162 (1931).

calculated. The results show that an exact Henry's law relationship exists for this system over a range from 0.2 to 1000 mm. The variations of the ionization constant and of the Henry's law constant with temperature have been used to calculate, respectively, the heat of ionization and the heat of absorption.

Materials and Method

The water used was the usual grade of laboratory conductivity water distilled from alkaline permanganate through a block tin condenser. The hydrogen-ion concentration after the removal of the dissolved carbon dioxide was found to be $10^{-7.0}$ to $10^{-7.2}$. These measurements were easily made with the glass electrode.

The sulfur dioxide was from a tank of liquid sulfur dioxide of high purity that had been used until the more volatile gases were removed. No further purification was used other than distillation into a mercury-filled gas buret.

Ordinary cylinder nitrogen was used.

Procedure.—The low partial pressures were obtained by preparing mixtures of nitrogen and sulfur dioxide in a steel cylinder of 1700 cc. capacity at pressures up to 50 atmospheres. The cylinder was evacuated and flushed out several times to ensure complete removal of oxygen and carbon dioxide. The desired volume of sulfur dioxide was measured in a mercury-filled gas buret and passed into the cylinder under vacuum. The cylinder was then connected to a nitrogen tank with a high pressure adapter and nitrogen was introduced to the desired pressure. No stratification of the gases was experienced if the nitrogen was admitted rapidly so that a violent churning of the contents of the small cylinder occurred. Analyses showed that the mixture so prepared suffered no measurable deterioration over a period of a month.

The mixtures of sulfur dioxide and nitrogen were bubbled through the solvent in a Pyrex saturator of the type described by Bichowsky and Storch[4] until equilibrium had been reached, as indicated by successive analyses of the solution. Before each run the water was freed of dissolved gases by boiling and by passing nitrogen through the filled absorber for several hours. Somewhat less than the estimated amount of pure sulfur dioxide was passed into the absorber and the gas mixture turned on. The time required for equilibrium to be reached varied from twelve to twenty-four hours, depending upon the proximity to equilibrium reached by the first added sulfur dioxide, and also upon the concentration of the gas mixture. In several tests no differences were found regardless of from which side the equilibrium was approached.

Analyses.—After rejecting several other schemes, the following was adopted for the analysis of the very dilute solutions encountered. A sample of the solution was pipetted into excess standard potassium iodate solution, 1 to 3 normal with sulfuric acid, according to the procedure of Hendrixson.[5] The excess iodate was determined by adding excess potassium iodide solution and titrating the liberated iodine with standard thiosulfate solution using the starch indicator.

This procedure has the following advantages: (1) The standard potassium iodate solution may be made up directly by weight and is exceedingly stable even in dilute solutions. (2) The thiosulfate solution of the low concentration required (*i. e.*, down to 0.002 normal) is rather unstable and must be made up and standardized several times a day. This is conveniently done by the same procedure described for the solution analysis, using the same pipets and burets, thus eliminating any possible calibration errors. (3) The starch end-point in such dilute solutions is capable only of fair reproducibility, but the simultaneous standardization and analysis permit close comparison of the end-points in each case, practically eliminating any error due to inaccuracy in the recognition of the end-point.

The primary standard was potassium iodate prepared by twice recrystallizing the "C. P." product from conductivity water and drying at 130°.

The sulfur dioxide content was determined by drawing the gas through two absorbers in series containing acidified potassium iodate followed by the same procedure employed in the solution analysis. The volume of the sample was measured, after passing through the bubblers, in a mercury-filled gas buret containing a small quantity of water. The gas volume was corrected for the vapor pressure of water at the temperature of the water jacket of the buret, and also for the volume of sulfur dioxide removed in the absorber. The partial pressure of the gas in the absorber was calculated from the composition of the dry gas and the pressure over the solution corrected for the vapor pressure of the water, which in these dilute solutions is considered equal to that of pure water.

Results

The results of the solubility measurements at low partial pressures are shown in Table I. In the third column is given the molality of the hydrogen ion calculated from the equation

$$(m_+\gamma_\pm)^2 + Km_+ - Km = 0 \qquad (1)$$

by successive approximations as suggested by Randall and Failey.[6] In this equation, m_+ is the molality of the hydrogen ion, which is equal to the molality of the bisulfite ion; $\gamma_\pm$ is the mean activity coefficient of the ions which, for lack of further information, was taken equal to that of hydrochloric acid in solutions of the same ionic strength; m is the stoichiometric molality of the sulfur dioxide in the solution, and K is the ionization constant as determined from the conductivity data of Morgan and Maass, and of Campbell and Maass, which will be discussed below. In the fourth column of Table I the ratio of the molality of the un-ionized molecules to the pressure shows the agreement of the results with Henry's law. The small deviations are not considered to be of significance in view of the method of calculation of m_u, in which an

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[4] Bichowsky and Storch, THIS JOURNAL, **37**, 2696 (1915).

[5] Hendrixson, *ibid.*, **47**, 1319 (1925).

[6] Randall and Failey, *Chem. Reviews*, **4**, 293 (1927).

error of a fraction of a per cent. in the total molality is sufficient to account for a deviation of several per cent. in the ratio at these small concentrations.

TABLE I

SOLUBILITY OF SULFUR DIOXIDE IN WATER

p_{SO_2}, atm. × 10^3	Molality moles SO_2 per 1000 g. H_2O × 10^3	$m_+ \times 10^3$	$m_u/p = H$
25°			
0.27	2.484	2.156	1.21
1.20	6.203	4.718	1.24
2.29	9.546	6.663	1.26
2.67	10.84	7.35	1.31
6.71	20.59	11.87	1.30
9.11	25.61	13.86	1.29
13.50	33.28	16.65	1.23
			Av. 1.26
35°			
1.03	4.19	3.28	0.88
2.49	7.45	5.22	.90
4.12	9.99	6.54	.84
5.80	13.56	8.22	.92
9.55	19.87	10.83	.95
			Av. .90
50°			
2.30	4.67	3.42	0.54
3.83	6.37	4.28	.55
5.38	8.38	5.21	.57
8.79	10.57	6.20	.50
			Av. .54

The Ionization Constant of Sulfurous Acid

Sherrill and Noyes calculated the ionization constant of sulfurous acid from the conductivity data of Lindner[7] and of Kerp and Baur.[8] They corrected the limiting conductance for the change in ionic mobility with change in concentration in order to find the degree of ionization, and employed the Debye–Hückel limiting equation to find the activity coefficients of the ions. The best value obtained was 0.012. There was considerable variation, however, between the values for the different concentrations, which apparently was traceable to the conductance data.

Because of the importance of this constant from a theoretical viewpoint and the frequent need for more exact information on the equilibria in solutions of sulfurous acid in industry, Maass and his co-workers[3] were led to make an extensive study of this system, which included some very exact conductivity measurements. In the discussion of their data, however, Maass used concentrations rather than activities. The ionization constants so obtained varied considerably with concentration, as might be expected. At 25° the maximum increase was 24% of the value at the lowest concentration. Maass also attempted to calculate the equilibrium constant for the hydration of the dissolved sulfur dioxide molecules and from this a so-called "true ionization constant" in which the corrected concentration of the un-ionized sulfurous acid was used. Even these values at 25°, however, showed an increase of 21% as the stoichiometric concentration increased.

Evidence that unhydrated sulfur dioxide exists in solution has been found in the absorption spectra by Wright[9] and by Baly and Bailey,[10] and more recently in the Raman bands by Fadda.[11] Until an exact method is found for determining its concentration, however, it seems best to follow the custom proposed by Lewis and Randall[12] and assume standard states for the hydrated and unhydrated molecules such that at infinite dilution each activity is equal to the sum of the molalities of the separate molecular species. The equilibrium constant for the hydration is thus made equal to unity and the activities of the two substances remain equal as long as the activity of the water is unity, but in concentrated solutions their ratio is equal to the activity of water.

The thermodynamic ionization constant of sulfurous acid is given by the equation

$$K = \frac{a_{\mathrm{H}}\, a_{\mathrm{HSO_3}}}{a_{\mathrm{H_2SO_3}}} = \frac{\alpha^2 m}{1 - \alpha} \frac{\gamma^2_{\pm}}{\gamma_u} \qquad (2)$$

where a is the activity of the species indicated by the subscript, α is the degree of dissociation which may be obtained from conductance data by applying suitable corrections for the ionic strength, and γ_u is the activity coefficient of the un-ionized molecules. Since the salting-out effect of the ions of a weak acid on undissociated molecules is small,[6] γ_u may be considered approximately equal to unity for all concentrations of pure solutions of the acid. If this be true, then, in accordance with the convention of the preceding paragraph, the sum of the molalities of the hydrated and unhydrated molecules should be proportional to the partial pressure of the sulfur dioxide.

Following the principles of Sherrill and Noyes, we have recalculated the ionization constants

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[7] Lindner, *Monatsh.*, **33**, 613 (1912).

[8] Kerp and Baur, *Arb. kaiserl. Gesundheitsamt.*, **26**, 297 (1907).

[9] Wright, *J. Chem. Soc.*, **105**, 2097 (1914).

[10] Baly and Bailey, *ibid.*, **121**, 1813 (1922).

[11] Fadda, *Nuovo cimento*, [N. S.] **9**, 168 (1932).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 297.

from the conductivity data of Morgan and Maass at 0, 10, 18 and 25° and from those of Campbell and Maass at 35 and 50°, using interpolated values at 35°. Table II illustrates the method of calculation and shows the results obtained for 25°. The values for the individual measurements at the other five temperatures for the sake of brevity are not included.[13] The average values for the ionization constant and the Henry's law constant, however, are shown in Table III. The conductivity data for hydrochloric acid and sodium chloride solutions needed for the calculations were obtained from the "International Critical Tables"; those for sodium bisulfite solutions were interpolated for the correct temperatures from the measurements of Lindner. Fortunately errors in the latter values do not greatly affect the accuracy of the results. In column five of Table II is given the molality of the hydrogen ion found from the product of the total molality and the corrected conductance ratio; the molality of the un-ionized molecules in column six follows directly from columns one and five.

TABLE II

IONIZATION CONSTANT OF SULFUROUS ACID AT 25° FROM CONDUCTIVITY DATA

Molality, moles SO_2 per 1000 g. H_2O	p_{SO_2} atm. × 10^3	$\Lambda_{H_2SO_3}$	$\frac{\Lambda}{\Lambda_H + \Lambda_{HSO_3}} = \alpha$	m_+	m_u	$\gamma_\pm$	K	m_u/p
0.0271	10.40	201.9	0.524	0.0142	0.0129	0.891	0.0124	1.24
.0854	45.0	138.3	.363	.0310	.0544	.855	.0129	1.21
.1663	97.1	107.6	.285	.0474	.1189	.834	.0131	1.22
.2873	179.0	86.1	.230	.0661	.2212	.816	.0132	1.23
.5014	333.0	68.2	.184	.0922	.4092	.800	.0133	1.23
.7643	526.0	56.5	.1535	.1173	.6470	.789	.0132	1.23
1.0273	723.0	49.1	.1340	.1376	.8897	.783	.0130	1.23
1.290	919.0	43.9	.1204	.1553	1.1347	.778	.0129	1.23
1.496	1068.0	40.6	.1115	.1668	1.329	.776	.0126	1.24
						Av.	.0130	1.23

TABLE III

THE EFFECT OF TEMPERATURE ON THE IONIZATION CONSTANT AND HENRY'S LAW CONSTANT OF SULFUROUS ACID

t, °C.	K	m_u/p
0	0.0232	3.28
10	.0184	2.20
18	.0154	1.55
25	.0130	1.23
35	.0105	0.89
50	.0076	.56

The mean activity coefficient of the ionized portion of the sulfurous acid, shown in column seven, was calculated from the Hückel equation

$$\log \gamma_\pm = \frac{-1.2833 \times 10^6 \sqrt{\Gamma}}{(DT)^{3/2} + 3.557 \times 10^9\, aDT \sqrt{\Gamma}} + B\Gamma - \log(1 + 0.036\, m_+) \quad (3)$$

where D is the dielectric constant of water, T is the absolute temperature, and $\Gamma = \Sigma c_i z_i = 2\, \alpha c$, where c is the stoichiometric concentration expressed in moles per liter and z_i is the valence of the individual ions. The concentrations were taken directly as expressed by Maass. In all other places where molalities are used the conversion was made by means of the density data given also by Maass. The dielectric constants of water at temperatures other than 25° were taken from the equation of Drake, Pierce and Dow.[14] The value of the constant a was taken as 4.05×10^{-8} for all temperatures, and likewise the constant B was taken as 0.0713. These are the values given for hydrochloric acid.[15] In other words, we are making the reasonable assumptions that the activity coefficient of the ionized portion of this weak acid is the same as that for hydrochloric acid, and that the ionic diameter and the effect of the ions on the dielectric constant of water is approximately constant between 0 and 50°.

The values obtained for K justify this means of calculation. The deviations are small even at the lowest concentrations where the measurements on some of the series of data used might be considered doubtful. In some cases these have been omitted from the averages. There is a slight evidence of a maximum which is probably due to a decrease in the value of γ_u below unity. Deviations were somewhat greater at 35 and 50° where the less accurate data of Campbell and Maass were used.

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[13] The complete data may be obtained from the authors at the University of Illinois, Urbana, Illinois.

[14] Drake, Pierce and Dow, *Phys. Review*, **35**, 613 (1930).

[15] Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., 1931, Vol. I, p. 799.

Henry's Law Constant

The ratio of the molality of the un-ionized portion of the acid to the pressure is shown in column nine of Table II. At 25, 35 and 50° the values were in excellent agreement with each other and with those given in Table I for the lower concentrations. Since there is no variation in the ratio at these temperatures from $p = 0.00027$ atm. to $p = 1.068$ atm. we believe that the larger deviations at the low concentrations at 0, 10 and 18° were due to inaccuracies in some of the values used in the calculations. These were therefore omitted from the averages. At high concentrations the value of m_u/p should no longer be a constant because of the decrease in the activity of water. This activity was calculated from Raoult's law and the total molality of the solute particles, $(1 + \alpha)m$. The decrease, which amounts to 5.2% at the most, is sufficient to bring the values of the ratio to practical constancy at the low temperatures. We believe that it is better to omit this correction entirely, however, and state that the averages shown in Table III are probably correct to within 5%.

Heats of Ionization and of Solution

The logarithms of the constants obtained in the calculation are plotted against the reciprocal of the absolute temperature in Fig. 1. The individual points fall very near the straight lines. From the slopes we have calculated the heats of the two reactions

$$SO_2\,(\text{gas}) \rightleftarrows SO_2\,(\text{aq.})$$
$$\Delta H = -6260\ \text{cal.};\qquad \Delta F_{298} = -123\ \text{cal.}$$

and

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$
$$\Delta H = -3860\ \text{cal.};\qquad \Delta F_{298} = 2725\ \text{cal.}$$

The total heat of absorption of sulfur dioxide by water in infinite dilution is the sum of the heats of the two reactions, $\Delta H = -10{,}120$ cal. Stiles and Felsing[16] measured the total heat of absorption of sulfur dioxide for concentrations between $m = 0.0260$ and $m = 0.7356$. Their data may be extrapolated to infinite dilution by plotting ΔH against the corresponding values of the degree of dissociation, α, at 25° interpolated from Table II. Such a plot gives a straight line below $m = 0.127$. At $\alpha = 1$, ΔH becomes $-10{,}200$ cal. which is in excellent agreement with the value obtained by the indirect method.

The Solubility of Sulfur Dioxide in Aqueous Sulfuric Acid

As a part of the data needed, the solubility of sulfur dioxide at low partial pressures in several solutions of sulfuric acid was measured at 25°. The method and apparatus was the same as that used for the aqueous solutions. The results are shown in Table IV. If the degree of dissociation of the bisulfate ion were known for the concentrations used, or the activity coefficients of the individual ions were known, with the recently determined second ionization constant of sulfuric acid,[17] it should be possible to calculate the concentration of the ionized and un-ionized parts of the sulfurous acid in these solutions also. Since these quantities cannot be calculated with any degree of accuracy over such a long range of concentrations we are presenting here only the solubility data.

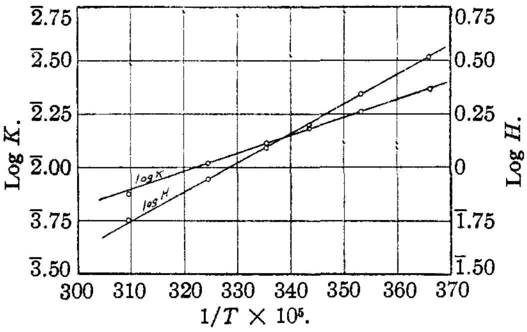

Fig. 1.—The effect of temperature on the ionization constant and Henry's law constant of sulfurous acid.

TABLE IV

SOLUBILITY OF SULFUR DIOXIDE IN SULFURIC ACID SOLUTIONS AT 25°

Molality of H_2SO_4, moles per 1000 g. H_2O	p_{SO_2}, atm. × 10^3	Molality of SO_2, moles per 1000 g. H_2O × 10^3
0.0879	1.30	1.93
.0879	5.71	11.29
.0879	10.22	18.78
.5174	1.30	1.61
.5174	5.71	7.96
.5174	10.22	13.45
1.103	1.31	1.34
1.103	5.73	7.19
1.103	10.22	12.53

Summary

The solubility of sulfur dioxide in water has been measured between 0.2 and 10.3 mm. at 25, 35 and 50°.

The ionization constants of sulfurous acid have been calculated from the conductance data

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(16) Stiles and Felsing, THIS JOURNAL, **48**, 1543 (1926).

(17) Hamer, *ibid.*, **56**, 860 (1934).

of Morgan and Maass and Campbell and Maass at 0, 10, 18, 25, 35 and 50°, using ion mobilities and activities corrected for the ionic strength of the solutions.

The ratio of the molality of the un-ionized molecules to the pressure is the same for the high concentrations measured by Maass and his co-workers as that found for the very dilute solutions by means of the equation, $(m_+ \gamma_\pm)^2 + Km_+ - Km = 0$.

The free energy and heats of ionization and of solution have been calculated from the equilibrium constants. The total heat of absorption of sulfur dioxide in infinite dilution is −10,120 cal. This value agrees with that obtained by extrapolating the data of Stiles and Felsing to infinite dilution.

URBANA, ILLINOIS RECEIVED JUNE 28, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

The Application of the Glass Electrode to a Study of Chromic Acid[1]

BY JACOB D. NEUSS AND WILLIAM RIEMAN III

Part I. The Second Dissociation Constant of Chromic Acid

The equilibria prevailing in aqueous solutions of chromates and dichromates have been the subject of numerous investigations. Up to the publication of Sherrill's important paper,[2] the constitution of such solutions was a matter of dispute. By means of freezing point, conductivity, distribution, and solubility experiments Sherrill demonstrated that the hydrochromate ion, $HCrO_4^-$, is an important constituent of dichromate solutions, and that the two important equilibria in such solutions may be represented by the equations

$$Cr_2O_7^{=} + H_2O \rightleftharpoons 2HCrO_4^- \qquad (1)$$

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^{=} \qquad (2)$$

He estimated from his results that at 25° the equilibrium constants of the two reactions are 0.013 and 8×10^{-7}, respectively. Other investigators[3] have failed to confirm these values, *e. g.*, the constant of reaction 2 has been reported as low[3b] as 0.88×10^{-7}, and that of reaction 1, as high[3a] as 70.

In the present paper is given a method for calculating more exact values of these constants from the activity of the hydrogen ion in solutions containing potassium chromate and dichromate in fixed proportions.

MacInnes and his co-workers[4,5] have perfected the technique of the glass electrode which is ideal for the measurement of *p*H in solutions containing oxidizing agents. Hence in this investigation the hydrogen ion activity in the chromate–dichromate solutions was computed from e. m. f. measurements using glass electrodes.

Britton[3e] and Hughes[3f] have also used the glass electrode, but in the interpretation of their results they assume complete conversion of the dichromate ion to hydrochromate ion.

Theoretical Considerations

Derivations of Equations.—The equilibrium constants of reactions 1 and 2 are, respectively

$$K = \frac{[HCrO_4^-]^2 \gamma^2_{HCrO_4^-}}{[Cr_2O_7^{=}] \gamma_{Cr_2O_7^{=}}} \qquad (3)$$

$$K_2 = \frac{(H^+) [CrO_4^{=}] \gamma_{CrO_4^{=}}}{[HCrO_4^-] \gamma_{HCrO_4^-}} \qquad (4)$$

where concentrations are expressed by brackets and activities by parentheses.

From equations 3 and 4 may be derived two new quantities, the apparent equilibrium constants, defined by the equations

$$K' = K \frac{\gamma_{Cr_2O_7^{=}}}{\gamma^2_{HCrO_4^-}} = \frac{[HCrO_4^-]^2}{[Cr_2O_7^{=}]} \qquad (5)$$

$$K' = K_2 \frac{\gamma_{HCrO_4^-}}{\gamma_{CrO_4^{=}}} = \frac{(H^+)[CrO_4^{=}]}{[HCrO_4^-]} \qquad (6)$$

Now consider a solution containing C moles of potassium chromate and C/n moles of potassium dichromate per liter. Neglecting the small amount of chromate produced by equation 2, it follows from stoichiometric considerations that

$$[CrO_4^{=}] = C \qquad (7)$$

$$[HCrO_4^-] = 2(C/n - [Cr_2O_7^{=}]) \qquad (8)$$

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[1] Further details concerning this work may be obtained from a thesis submitted in May, 1934, by Jacob D. Neuss to the Faculty of Rutgers University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Sherrill, THIS JOURNAL, **29**, 1641 (1907).

[3] (a) Spitalsky, *Z. anorg. Chem.*, **54**, 265 (1907); (b) Lundberg, *ibid.*, **55**, 426 (1907); (c) Beck and Stegmuller, *Arb. kais. Gesundh.*, **34**, 446 (1910); Beck, *Z. Elektrochem.*, **17**, 843 (1911); (d) Britton, *J. Chem. Soc.*, **125**, 1572 (1924); (e) Britton, *Trans. Faraday Soc.*, **28**, 531 (1932); (f) Hughes, *J. Chem. Soc.*, **491** (1928); (g) Saal, *Rec. trav. chim.*, **47**, 73, 264 (1928).

[4] (a) MacInnes and Dole, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 57 (1929); (b) MacInnes and Dole, THIS JOURNAL, **52**, 29 (1930).

[5] (a) MacInnes and Belcher, *ibid.*, **53**, 3315 (1931); (b) **55**, 2630 (1933).