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

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

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

---

[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).

By substituting these values in equations 5 and 6 and eliminating the quantity $[Cr_2O_7^{=}]$, one obtains the final equation

$$2(H^+)^2C = (2/n)(K_2)^2K' - K'K_2(H^+) \qquad (9)$$

If n is constant and (H^+) is determined in a series of solutions in which C is varied while the ionic strength is kept constant by the addition of a neutral salt, then the activity coefficients (equations 5 and 6) will remain constant. It follows that K' and K_2' will be constants whose values may be obtained from the linear plot of $2(H^+)^2C$ against (H^+). By repeating this procedure at other ionic strengths, a series of corresponding values for K' and K_2' is obtained.

Application of the Debye-Hückel equation[6] to equations 5 and 6 gives, respectively

$$pK' = pK + \frac{\sqrt{\mu}}{1 + 3.3\ a\ 10^7 \sqrt{\mu}} \qquad (10)$$

$$pK_2' = pK_2 - \frac{1.5\sqrt{\mu}}{1 + 3.3\ a\ 10^7 \sqrt{\mu}} \qquad (11)$$

where μ is the ionic strength of the solution, and a is related to the average effective diameter of all the ions. By adjusting the value of a, the experimental data can be made to fit the equations, and values of pK and pK_2 calculated.

Calculation of Ionic Strength.—The value of n chosen for actual experimental work was 2, since this produces a solution in the region of maximum buffer capacity.

By combining equations 5 and 8 one obtains

$$[HCrO_4^-] = (-K' + \sqrt{(K')^2 + 8K'C})/4 \qquad (12)$$

The ionic strength is then

$$\mu = m + (9C - [HCrO_4^-])/2 \qquad (13)$$

where the second term on the right is the contribution of the chromates to the ionic strength, and the first term the contribution of potassium chloride added in concentration m to maintain constant ionic strength as C is decreased.

It is clear from equations 12 and 13 that in order to calculate the ionic strength, K' must be known. However, it is not essential that this preliminary value of K' be accurate, since a large error in K' produces a relatively small error in μ. In the first series (series B, Table I) the value 0.014 was used. This choice proved fortunate since the value of K' calculated finally was 0.0135. In subsequent series equations 10, 12 and 13, in conjunction with the provisional value of pK obtained in series B, were used to calculate m. The approximations of the quantity, $(9C - [HCrO_4^-])/2$, were repeated until m was known within a few tenths of one per cent.

The Flowing Junction.—Scatchard has shown that the potential difference at a flowing junction between saturated potassium chloride and dilute hydrochloric acid is constant up to a concentration of 0.1 molal hydrochloric acid.[7] He also states that such constancy is to be expected if the hydrochloric acid were replaced by any other electrolyte. In addition Scatchard has calculated the value, 337.2 millivolts at 25°, for the potential of the 0.1 normal calomel electrode inclusive of the saturated potassium chloride bridge and the flowing junction. This value agrees with Clark's[8] value, 337.6, within the experimental error (0.5 millivolt) of the present work. By using the flowing junction and Clark's value for the calomel half-cell, the liquid junction correction is therefore automatically made.

Experimental Procedure

Salts.—Analyzed grades of potassium chromate and potassium dichromate were recrystallized once, and dried at 150°. Both salts gave negative tests for trivalent chromium. Direct iodimetric analysis of each showed a purity of 100% within 0.1%. An analyzed grade of potassium chloride was twice recrystallized and dried. A saturated solution showed no alkalinity toward phenolphthalein.

Solutions.—A stock solution was prepared by weighing the potassium chromate and potassium dichromate in the molar ratio 2:1. After suitable dilution, the solution was weighed and the concentrations calculated. Weighed portions of this stock solution were analyzed iodimetrically according to the directions of Popoff and Whitman,[9] using U. S. Bureau of Standards sodium oxalate (through 0.1 N potassium permanganate) as the ultimate standard. The total oxidizing normality agreed with the calculated within 0.1%.

The individual buffer solutions were prepared by delivering weighed quantities of the stock solution into calibrated volumetric flasks, adding the required weight of potassium chloride calculated by equation 13 as previously described, and diluting at 25° to the mark.

Calomel Electrodes.—Three 0.1 normal calomel electrodes were prepared and found to agree within 0.05 millivolt. The mercury was treated with purified air, dilute nitric acid, washed, dried, and twice distilled in a vacuum. The calomel was prepared electrolytically[10] from the pure mercury, and washed with exactly 0.1 normal potassium chloride before use.

Hydrogen Electrodes.—These were made according to the directions of Popoff, Kunz and Snow.[11] Tank hydrogen

---

[6] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[7] Scatchard, THIS JOURNAL, **47**, 696 (1925). On p. 703 Scatchard shows that this potential is constant up to 0.2 M hydrochloric acid within 0.1 millivolt.

[8] "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 3d ed., pp. 461–482, esp. p. 480.

[9] Popoff and Whitman, THIS JOURNAL, **47**, 2259 (1925).

[10] Ellis, *ibid.*, **38**, 740 (1916).

[11] Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

was purified by passing through a quartz tube filled with red-hot copper, and through sodium hydroxide solution.

Glass Electrodes.—The directions of MacInnes and Belcher[5a] were followed in preparing these electrodes. They were filled with dilute hydrochloric acid, and allowed to soak in distilled water. In this way the electrodes were simultaneously "aged" and tested for minute leaks by testing for chloride ion in the distilled water. The electrical resistance was then measured by the method of substitution.[4b] Electrodes with high or suspiciously low resistance were rejected. The internal filling of the glass electrode consisted of a quinhydrone electrode in 0.1 N hydrochloric acid. The upper opening of the glass electrode was sealed with paraffin.

Immediately before use in each run, the glass electrode was calibrated against a hydrogen electrode in a buffer of pH about 6. The exact composition of this solution is not of importance, since the difference in potential measured gives directly the required ϵ_G value in the equation

$$E_G = \epsilon_G + 59.15 \log (\mathrm{H}^+) \qquad (14)$$

where E_G is the potential of the glass electrode in millivolts, and ϵ_G is a constant which includes the asymmetry potential of the glass and the potential of the inner quinhydrone electrode. The potential of the hydrogen electrode was corrected to one atmosphere of hydrogen gas.

Cell Vessel.—The Pyrex flowing junction cell was a modification of that devised by Scatchard.[7] The modification consists in the introduction of two stopcocks. The first was inserted (at point H of his diagram) to replace his plunger; and the second, a three-way stopcock, was inserted (just below E of his diagram) to permit the formation of a junction between the saturated potassium chloride and the electrolyte of the 0.1 normal calomel electrode. The procedure was essentially the same as that used by Scatchard. Variations in the rate of flow from 3 to 12 drops per minute had no noticeable effect upon the e. m. f.

Temperature Control.—A 32-liter oil-bath was stirred efficiently by a mechanical stirrer. A Beckmann thermometer, the 25° point of which was determined by comparing with a certified thermometer, was used. The bath was kept within 0.02 of 25°.

Electrical Equipment.—The electrical apparatus consisted of a Leeds and Northrup type K potentiometer and type HS No. 2285-f galvanometer, and three mica condensers of one microfarad each. The ballistic method of Beans and Walden[12] for measuring the e. m. f. of cells of high resistance was slightly modified. With the potentiometer set a few millivolts above the estimated e. m. f., the condensers were charged for a given time and the galvanometer throw read. With the potentiometer set a few millivolts below the estimated e. m. f., the condensers were again charged for the same time and a second throw in the opposite direction was obtained. The true cell e. m. f. was then obtained by interpolation. The charging time was varied between sixty and ninety seconds, and was observed with a stop-watch. Five consecutive readings at ten-minute intervals usually agreed within 0.5 mv.

Results

The data of four series of measurements are shown in Table I. The pH was calculated by the equation

$$p\mathrm{H} = -\log (\mathrm{H}^+) = (E - 337.6 + \epsilon_G)/59.15 \qquad (15)$$

where E is the difference in potential in millivolts between the calomel electrode (positive) and the glass electrode (negative).

The equation of each series was obtained by the method of least squares.

TABLE I

No.	C	m	ϵ_G	E	pH	(H⁺) × 10⁷
Series A					$\mu = 0.1600$	
1	0.03684	0.0000	692.8	30.2	6.516	3.048
2	.01663	.08878	691.8	22.7	6.374	4.227
5	.008438	.1247	698.4	10.1	6.271	5.358
3	.004533	.1411	689.1	15.9	6.211	6.152
4	.002016	.1518	698.4	2.2	6.137	7.295
6	.0009992	.1560	697.3	−0.3	6.076	8.375
	$K_2' = 9.51 \times 10^{-7}$			$K' = 0.0114$		
Least squares	$2(\mathrm{H}^+)^2C = 1.033 \times 10^{-14} - 0.1086 \times 10^{-7}(\mathrm{H}^+)$					
Series B					$\mu = 0.0861$	
1	0.02011	0.0000	696.0	25.6	6.492	3.220
4	.01020	.04298	699.0	16.4	6.387	4.100
2	.005553	.06290	692.7	18.8	6.321	4.770
5	.001588	.07958[a]	696.0	8.6	6.205	6.230
3	.001223	.08109	699.5	4.5	6.195	6.380
	$K_2' = 7.41 \times 10^{-7}$			$K' = 0.0135$		
Least squares	$2(\mathrm{H}^+)^2C = 0.7432 \times 10^{-14} - 0.1003 \times 10^{-7}(\mathrm{H}^+)$					
Series C					$\mu = 0.04036$	
1	0.009587	0.0000	689.3	30.1	6.455	3.506
2	.005008	.01957	688.1	26.9	6.380	4.165
3	.002402	.03055	699.5	12.0	6.321	4.770
4	.000993	.03639	699.5	9.3	6.276	5.290
5	.000597	.03800	698.7	9.0	6.257	5.530
	$K_2' = 5.88 \times 10^{-7}$			$K' = 0.0170$		
Least squares	$2(\mathrm{H}^+)^2C = 0.5847 \times 10^{-14} - 0.0992 \times 10^{-7}(\mathrm{H}^+)$					
Series D					$\mu = 0.01040$	
1	0.002545	0.0000	699.5	20.4	6.463	3.445
5	.002478	.000274	694.1	24.9	6.448	3.562
4	.001740	.003329	697.3	20.2	6.423	3.776
2	.001068	.006092	697.7	18.8	6.406	3.926
3	.000567	.008130	699.7	16.1	6.394	4.036
	$K_2' = 4.37 \times 10^{-7}$			$K' = 0.0161$		
Least squares	$2(\mathrm{H}^+)^2C = 0.3125 \times 10^{-14} - 0.0715 \times 10^{-7}(\mathrm{H}^+)$					

[a] LiCl used instead of KCl.

The data are illustrated graphically in Fig. 1. Table II summarizes the results and gives the final values of the equilibrium constants.

Discussion

The experimental points of Fig. 1 lie on their respective lines within an error equivalent to 0.01

---

(12) Beans and Walden, THIS JOURNAL, **50**, 2673 (1928).

TABLE II

Line	$\sqrt{\mu}$	pK_2'	pK_2	pK'	pK
D	0.1020	6.359	6.500	1.79	1.70
C	.2014	6.230	6.494	1.77	1.59
B	.2934	6.130	6.496	1.87	1.63
A	.4000	6.023	6.492	1.94	1.63
		Mean	6.495		1.64
		K_2 =	3.20×10^{-7}	K =	0.023

$$pK_2 = pK + \frac{1.5\sqrt{\mu}}{1 + 0.7\sqrt{\mu}} \qquad pK = pK' - \frac{\sqrt{\mu}}{1 + 0.7\sqrt{\mu}}$$

pH unit. The estimated error in pK_2 is ±0.01 unit, and in pK ±0.04 unit.

Experiments at ionic strengths below 0.01 were not attempted due to the disturbing effect of carbon dioxide and the failure of the assumption underlying the derivation of equation 9.

The values for K and K_2 cannot be compared with previous results except as to order of magnitude. In the case of Saal's[3g] work on K, an interesting comparison can be made by a study of his original data given in Table III. For a discussion of the method, the reader is referred to the original paper.

TABLE III

Run	$[K_2Cr_2O_7]$	K'	K
A	0.125	0.015	0.019
B	.025	.018	.018
C	.0125	.021	.020
D	.0050	.022	.019
E	.00125	.024	.023
		Accepted value	0.019

Saal obtained, in his opinion, a true equilibrium constant (column 4) by applying the activity coefficient data of Brönsted[13] to the values of the apparent equilibrium constants (column 3). An inspection of the trend in column 3, however, shows that the true value of K is slightly greater than 0.024, since K' must approach K with increasing dilution as predicted by equation 10. A value in the vicinity of 0.024 would be in good agreement with our result, 0.023.

Part II. The First Ionization Constant

The second part of this study is concerned with the ionization of chromic acid according to the equation

$$H_2CrO_4 = H^+ + HCrO_4^- \qquad (16)$$

It was of interest to determine whether the ionization of chromic acid can be considered complete, or whether reaction 16 possesses a finite equilibrium constant. Early work had resulted in the conclusion that chromic acid is a strong acid.[14]

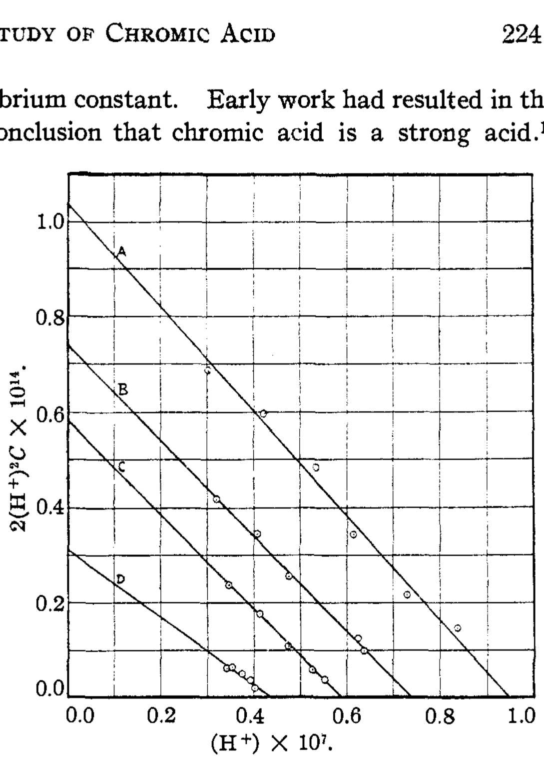

Fig. 1.—Plot of data according to Equation 9.

Experimental Method

The strength of chromic acid was compared with that of hydrochloric acid using the method of Lugg.[15] The cell measured was

$$\text{Pt, } H_2 \left| \begin{matrix} HCl(m_1) \\ KCl(m_3) \end{matrix} \right| \begin{matrix} H_2CrO_4(m_2) \\ KCl(m_4) \end{matrix} \left| \text{ Glass } \right| 0.1\ M\ HCl \left| AgCl \right| Ag$$

If m_3 is made much greater than m_1, and if m_1 and m_2 (also m_3 and m_4) are about equal, then the liquid junction potential should be negligibly small. The e. m. f., E, is then related to the hydrogen-ion concentration in each half-cell by the equation

$$\frac{E - \epsilon_G}{59.15} = \log \frac{[H^+]_{H_2CrO_4}}{[H^+]_{HCl}} + \log \frac{\gamma_{H^+(H_2CrO_4)}}{\gamma_{H^+(HCl)}} \qquad (17)$$

Since hydrochloric acid is completely dissociated,[15] $[H^+]_{HCl} = m_1$. Since the ionic strength is almost the same in both solutions, the activity coefficients of the hydrogen ion in both solutions should be identical, and the last term in equation 17 vanishes.[16]

Equation 17 may now be solved for $[H^+]_{H_2CrO_4}$, and a comparison of this value with m_2 gives a quantitative measure of the degree of ionization.

It was also desirable to study the effect of the

---

[13] Brönsted, *Z. physik. Chem.*, **102A**, 169 (1922).

[14] Ostwald, *Z. physik. Chem.*, **2**, 78 (1888); see also Refs. 3a and 3d.

[15] Lugg, THIS JOURNAL, **53**, 2554 (1931).

[16] According to the data of Scatchard (Ref. 7), the activity coefficient of the hydrogen ion changes but little in the vicinity of $\sqrt{\mu} = 0.4$; therefore small differences between the ionic strengths of both half-cells can be neglected.

addition of potassium dichromate to the chromic acid. If chromic acid is incompletely dissociated, the dichromate, when added in appreciable amounts, should decrease the hydrogen ion concentration.

Materials.—Doubly distilled constant boiling hydrochloric acid was used to prepare a stock solution. Weighed samples of the latter were titrated with standard sodium hydroxide solution. Kahlbaum chromium trioxide, free from trivalent chromium and sulfate, was used. Weighed samples of the stock solution were analyzed iodimetrically.[9] The solutions to be studied were prepared by diluting in calibrated volumetric flasks weighed amounts of the respective stock solutions. The concentrations of the two acids were made as nearly alike as practical. The required amounts of pure dry potassium chloride were weighed out and added to the flasks before dilution.

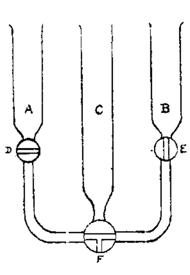

Fig. 2.—Cell vessel for stationary junction.

The electrical equipment and method were the same as in Part I. The glass electrodes were of lower resistance, and contained silver–silver chloride electrodes instead of quinhydrone electrodes. In this manner the experimental error was reduced to ±0.2 millivolt.

Since the liquid junction potentials are very small, a stationary junction was employed. The Pyrex cell vessel is shown in Fig. 2. Compartments A and B contained the hydrochloric acid and chromic acid, respectively. The liquid junction was made by stopcock F. Stopcock D was lubricated at the outer edges only. During the measurements the stopcocks were in the position shown in the diagram.

Before each measurement the glass electrode was calibrated against the hydrogen electrode in compartment A. Then, after washing, the glass electrode was transferred to B for the final measurement.

Calculations.—The ionic strength in the chromic acid solution to which no potassium dichromate was added was

$$\mu = (3m_2 - [\mathrm{HCrO_4^-}])/2 + m_4$$

where $[\mathrm{HCrO_4^-}] = (-K' + \sqrt{(K')^2 + 8K'm_2})/4$.

The values for $[\mathrm{HCrO_4^-}]$ were obtained by repeated approximation as described in Part I. The data are given in Table IV.

The results in column 12 would seem to indicate that a small but appreciable liquid junction potential, existent at the lower value of m_3/m_1, diminishes as the latter is increased. The conclusion that chromic acid is completely dissociated is therefore equivocal. The effect of the addition of potassium dichromate was next studied.

Calculations.—The ionic strength of chromic acid containing potassium dichromate in molar concentration, S, is

$$\mu = (3m_2 + [\mathrm{HCrO_4^-}] + 6S)/2 + m_4$$

TABLE IV

CELLS WITHOUT $K_2Cr_2O_7$

No.	m_3/m_1	m_1	m_3	$\sqrt{\bar{\mu}_{1,3}}$	m_2	m_4	$\sqrt{\bar{\mu}_{2,4}}$	ϵ_G	E	$[\mathrm{H^+}]_{\mathrm{H_2CrO_4}}$	$[\mathrm{H^+}]_{\mathrm{H_2CrO_4}}/m$
1	10	0.008333	0.08373	0.3034	0.008196	0.08377	0.3061	359.2	358.5	0.008109	0.989
2	10	.003724	.04024	.2097	.003978	.04024	.2116	360.1	361.0	.003857	.970
3	10	.01463	.1503	.4061	.01489	.1503	.4115	359.8	359.5	.01446	.971
4	10	.003740	.03972	.2085	.003905	.03972	.2087	358.6	359.2	.003828	.980
5	10	.01497	.1549	.4122	.01549	.1549	.4180	357.6	357.8	.01509	.974
6	20	.008204	.1640	.4150	.008213	.1640	.4173	359.0	358.7	.008109	.987
7	20	.004340	.08756	.3031	.004264	.08759	.3042	359.1	358.3	.004207	.987
8	50	.002601	.1305	.3648	.002610	.1305	.3652	354.6	354.6	.002601	.997
9	50	.003154	.1578	.4011	.003156	.1579	.4017	357.2	357.0	.003129	.992
10	50	.001503	.07547	.2774	.001508	.07550	.2777	357.3	357.4	.001509	1.001
11	50	.003850	.1927	.4433	.003855	.1928	.4442	357.7	357.6	.003835	0.995

TABLE V

CELLS WITH $K_2Cr_2O_7$

No.	m_1	m_3	$\sqrt{\bar{\mu}_{1,3}}$	m_2	m_4	S	$\sqrt{\bar{\mu}_{2,4}}$	ϵ_G	E	$[\mathrm{H^+}]$	$[\mathrm{HCrO_4^-}]$	K_1'
1	0.001972	0.1021	0.3226	0.002034	0.1021	0.004019	0.3388	357.9	357.8	0.001964	0.005344	0.15
2	.002059	.1580	.4000	.002063	.1581	.002015	.4067	358.1	357.7	.002027	.003665	.21
3	.001911	.1585	.4005	.001912	.1585	.004395	.4146	358.4	357.7	.001860	.005390	.19
4	.001996	.1557	.3971	.002001	.1558	.00206	.4038	358.9	358.3	.001950	.003684	.14
5	.001946	.1611	.4038	.001950	.1611	.006865	.4256	357.0	356.3	.001894	.006880	.23
6	.002423	.1610	.4042	.002423	.1611	.004846	.4197	357.6	357.1	.002376	.005840	.29
7	.002110	.1580	.4001	.002079	.1010	.01320	.3722	358.5	356.7	.001967	.01027	.18
8	.001974	.1580	.4000	.001974	.1000	.02100	.3992	357.6	355.4	.001812	.01312	.15
9	.002011	.1580	.4000	.002018	.0780	.03000	.4037	357.9	354.7	.001775	.01601	.12

Mean .18

Mean dev. ± .04

where $[HCrO_4^-] = (-K' + \sqrt{(K')^2 + 8K'(m_2 + 2S)})/4$

The results are given in Table V.

A comparison of the results of columns 11 and 5 indicates that chromic acid is incompletely dissociated. Column 13 gives the calculated values of the classical dissociation constant, $K_1' = [H^+][HCrO_4^-]/(m_2 - [H^+])$.

It is obvious that a small error in $[H^+]$ will cause a relatively large error in K_1'. However in all cases but one, the individual values of K_1' agree with the mean within a magnitude equivalent to the experimental error of 0.2 millivolt.

Calculations of the liquid junction potentials by the Henderson equation[17] gave values of about −0.2 millivolt for the first six cells of Table V. The maximum value, −1.0 millivolt, was calculated in the case of cell 9. It is realized that such calculations can give approximate values only. If a correction for the junction potential is applied, the mean value of K_1' becomes somewhat greater, but is still definitely finite, 0.29 ± 0.08.

Summary

The glass electrode has been applied to the measurement of hydrogen ion activity in solutions of chromic acid and its salts at 25°.

The second ionization constant of chromic acid is 3.20×10^{-7} with an estimated error of 3%.

The equilibrium constant of the reaction

$$Cr_2O_7^{=} + H_2O \rightleftarrows 2HCrO_4^-$$

is 0.023 with an estimated error of about 9%.

The ionization of the first hydrogen of chromic acid has been studied. The reaction is not quite complete. The classical ionization constant at an ionic strength of about 0.16 was found to be 0.18 ± 0.04.

NEW BRUNSWICK, N. J. RECEIVED JULY 2, 1934

[17] Henderson, *Z. physik. Chem.*, **63**, 325 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEBRASKA]

A Thermochemical Study of *d*-Gluconic Acid and its Modifications

BY ROYCE H. LEROY AND B. CLIFFORD HENDRICKS

Nef[1] showed that *d*-gluconic acid exists in two modifications other than the free acid form, *d*-gluconic-δ-lactone and *d*-gluconic-γ-lactone, and described methods of preparing them.

Hedenburg[2] used the polariscope to study the interconversion of each of these modifications into the equilibrium mixture in water solution. His data indicated that the free *d*-gluconic acid, when dissolved in water, is converted into *d*-gluconic-δ-lactone to the extent of about 20% at the end of twenty-four hours and that this quasi-equilibrium is maintained for three days. By that time the *d*-gluconic-γ-lactone is being formed at an appreciable rate. This change is shown by the specific rotation of the solution, which begins to increase slowly. At the end of eleven days the specific rotation reaches a constant value. This is interpreted as representing an equilibrium condition which exists between the three forms of the acid.

This same final equilibrium is reached at the end of fourteen days when *d*-gluconic-γ-lactone is dissolved in water. The specific rotation of the solution gradually and steadily decreases from the high initial value characteristic of the gamma form to that of the equilibrium mixture. When *d*-gluconic-δ-lactone is dissolved, two and one-half hours are required to attain an equilibrium point similar to that which is reached in twenty-four hours in the case of the free acid. This temporary equilibrium lasts for about twenty hours and then the specific rotation gradually increases and approaches the same final equilibrium point at the end of about eight days.

Hedenburg's findings were confirmed by Rehorst[3] and a third check was made of his results in the course of this investigation. Hedenburg's investigation also included *d*-mannonic acid and its lactones, and Upson, Sands and Whitnah[4] extended the study to *l*-mannonic and *l*-gluconic acid and their related lactones. In each case a relation similar to that encountered in the study of the *d*-gluconic acid was found to exist.

Levene and Simms[5] made a comprehensive examination of *d*-gluconic, *d*-glucoheptonic, *d*-

---

[1] Nef, *Ann.*, **403**, 273, 306 (1914).

[2] Hedenburg, THIS JOURNAL, **37**, 345 (1915).

[3] Rehorst, *Ber.*, **61**, 163 (1928).

[4] Upson, Sands and Whitnah, THIS JOURNAL, **50**, 519 (1928).

[5] Levene and Simms, *J. Biol. Chem.*, **65**, 31 (1925).