CONDUCTIVITY AND DENSITY OF CHROMIC ACID SOLUTIONS

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ABSTRACT

The conductivity and density of chromic acid solutions were determined for concentrations up to 10 molar (1,000 g/l of CrO_3). The density is practically a linear function of concentration. The conductivity increases to a maximum at about 5 molar and then decreases.

CONTENTS

I. INTRODUCTION

This study is a step in an investigation of the theory of chromium plating. The solutions used in this process have chromic acid as their principal constituent. In addition, they contain some other anion, such as the sulphate ion, which is introduced as sulphuric acid or as a sulphate. During operation there is always formed in the bath some trivalent chromium, commonly supposed to exist as "chromium chromates" of undefined composition. The ultimate purpose of this research is to determine the form and function of the sulphate and trivalent chromium in such solutions. The effects of these constituents upon the density and conductivity of chromic acid will be measured to see whether they throw light on this problem. First, however, it was necessary to determine the density and conductivity of pure chromic-acid solutions to serve as a basis of reference. This report is confined to the latter measurements.

The only values found in the literature for the conductivity of chromic acid are those of Walden [1] for dilute solutions, and of Jones [2]

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[1] Z. physik. Chem., **2**, p. 71; 1883.
[2] Am. Chem. J., **34**, p. 334; 1905.

for solutions from 0.8 to 7 M at 0° C. As no temperature coefficients were determined by Jones, the conductivities at higher temperatures could not be accurately computed. In this study the conductivities of chromic-acid solutions from 0.1 to 10 M were measured at 0°, 25°, and 45° C.

The densities of chromic-acid solutions, determined by several investigators, have been summarized by J. A. Beattie.[3] The data there given are for the densities at 15° C. of solutions containing from 1 to 60 per cent of CrO_3 (that is, from about 0.1 to 10 M). In this investigation the densities of solutions from 1 to 10 M in CrO_3 have been measured at 25° C., and a few values have been determined at other temperatures in order to estimate the temperature coefficients of density.

II. PREPARATION OF SOLUTIONS

1. PURIFICATION OF CHROMIC ACID

As a result of the demand in recent years for chromic acid for use in chromium plating, a product of relatively high purity is now available commercially. This material usually contains about 99.5 per cent of CrO_3 and small amounts of insoluble matter, sulphate, alkali salts, and trivalent chromium. The content of these impurities can be reduced by recrystallization, but it is difficult to remove them entirely. It was not found possible to completely eliminate trivalent chromium. In fact, unless precautions are used in the purification, there is a possibility of increasing the content of trivalent chromium, either through introduction of dust, or reducing gases from adjacent burners, or through local superheating of the solution or crystals. As will be shown, trivalent chromium is an especially objectionable impurity as it reduces the conductivity more than in proportion to its concentration. Efforts to reduce the content of trivalent chromium by evaporating in a stream of purified air or in a vacuum resulted in no marked improvement. By electrolysis with a platinum anode and a platinum cathode in a porous clay cup, the content of trivalent chromium could be reduced, as found by H. S. Lukens,[4] but not entirely eliminated.

After numerous trials it was found that the best product was obtained by dissolving the chromic acid in water, filtering through a porous porcelain filter, and evaporating on a steam bath until, on cooling, about half of the chromic acid crystallized out. The crystals were collected on a Büchner funnel. It was not necessary to thoroughly dry the product, which was used to prepare strong stock solutions from which the other solutions were then made. Two lots of chromic acid were thus purified. Analyses of the original and recrystallized acids (all dried at 110° C.) yielded the results shown in Table 1.

Inspection of these results shows that by one recrystallization the sulphate and insoluble matter were reduced to negligible concentrations. The content of "alkali salts" represents that of alkali ($Na_2O + K_2O$) combined as sulphate and chromate, chiefly the latter in the purified product. Sodium chromate contains only about 38 per cent of Na_2O, of which, therefore, the recrystallized acid contains

[3] International Critical Tables, **3**, p. 69.
[4] Trans. Am. Electrochem. Soc., **53**, p. 491; 1928.

not more than 0.04 per cent. The only significant impurity in the purified chromic acid is the trivalent chromium, of which lot B contains nearly three times as much as A. As it was not found practicable to prepare chromic acid with less Cr_2O_3 than in A, this lot was used in most of the measurements. Lot B was used in a few cases as a check upon the effect of trivalent chromium.

TABLE 1.—*Purification of chromic acid*

	Lot A		Lot B	
	Original	Recrystallization	Original	Recrystallization
CrO_3	99.49	99.75	99.37	99.74
Cr_2O_3	.22	.11	.40	.29
SO_4	.10	.01	.08	.01
Alkali salts	.18	.10	.15	.08
Insoluble	.21	.02	.17	.01
Total	100.20	99.99	100.17	100.13

2. METHODS OF ANALYSIS

In the analysis of the chromic acid before and after purification, and of the solutions used for making the density and conductivity determinations, the following methods were used.

(a) PREPARATION OF SAMPLES

The samples of solid CrO_3 were dried by heating to constant weight (usually for several hours) at 110° to 120° C. That this procedure removed practically all the water was shown by heating a sample of the same material to 120° C. in a current of dry air until constant weight was obtained and then heating it to a high temperature until the CrO_3 was entirely decomposed. The water evolved in the second heating and collected in a phosphorus pentoxide tube was equivalent to only 0.01 per cent of the weight of the sample.

The solutions for the measurements of conductivity and density were prepared and standardized on a volumetric basis with a precision of at least 1 part in 500. This procedure was used because of the greater convenience, and the fact that subsequent determinations of the effects of other constituents may be more readily interpreted on a volume concentration than a weight concentration basis.

(b) INSOLUBLE

The sample (5 to 25 g) was dissolved in water and the solution was filtered through asbestos on a Gooch crucible, previously dried at 130° C. The residue was washed with dilute hydrochloric acid (1:5) and then with water, dried at 130° C. and weighed. No attempt was made to determine the composition of the residue, part of which was a black powder, insoluble in concentrated nitric or hydrochloric acid. The treatment with dilute hydrochloric acid was used to remove any Cr_2O_3 (or chromium chromate) which might dissolve in preparing the more concentrated solutions of chromic acid. To some extent, therefore, this definition and method of determining "insoluble matter" is arbitrary.

(c) SULPHATE

The sulphate was determined in 5 to 10 g samples of CrO_3 by the method described in B. S. Tech Paper No. 346 (1927), which involves reduction of the chromic acid with alcohol in the presence of a regulated excess of hydrochloric acid, and precipitation of barium sulphate. After these analyses were completed, Willard and Schneidewind [5] showed that in this method the precipitation of barium sulphate is not complete unless the solution is allowed to stand for about 18 hours or more before filtration. They found that in the presence of acetic acid complete precipitation is much more rapidly obtained. In all of the analyses reported in this paper the solutions were allowed to stand overnight.

(d) ALKALI SALTS

The chromic acid was strongly ignited, leaving a residue consisting of Cr_2O_3 plus any alkalis ($Na_2O + K_2O$) that were present. In the residue, the latter were combined with SO_3 so far as this sufficed, and then with CrO_3 to form Na_2CrO_4 or K_2CrO_4. The green residue of Cr_2O_3 was extracted with hot water, and the filtrate evaporated to dryness. The salts thus obtained were usually contaminated with undecomposed CrO_3 and finely divided Cr_2O_3 that passed through the filter in colloidal form. The first residue was therefore ignited strongly and again extracted. The final residue, which was white or yellow, was weighed and reported as "alkali salts." No attempt was made to determine its content of Na_2O and K_2O.

(e) CHROMIC ACID

The content of Cr^{VI} was determined electrometrically by titration with ferrous sulphate. A 3,000-ohm rheostat and portable galvanometer were used. The platinum wire electrode and the tip of a calomel electrode were introduced into the beaker containing the chromic acid. A permanent deflection of 1 mm was produced at the end point by an addition of 0.02 ml of 0.1 N ferrous ammonium sulphate. As about 40 ml of the latter solution was used in each titration, a precision of 1 part in 2,000 was attainable. In order to attain this precision in the analysis of the solid chromic acid, the titrations were made with weight burettes. As indicated above, the concentrations of the chromic-acid solutions were determined with volume burettes.

The ferrous ammonium sulphate solution was standardized daily against a 0.1 $K_2Cr_2O_7$ N solution. The latter was prepared from potassium dichromate that was recrystallized from water and dried.

(f) TRIVALENT CHROMIUM

(1) *Differential titration.*—This method, described in B. S. Tech. Paper No. 346, depends upon (*a*) titration of the Cr^{VI} originally present and (*b*) titration of the total Cr^{VI} after any Cr^{III} has been oxidized. This oxidation was conducted with ammonium persulphate in the presence of silver nitrate. The Cr^{III} originally present was computed from the difference between these two titrations. It was found that the method is reliable and convenient for relatively large concentrations of Cr^{III}, but like all such differential titrations, it is not suitable for determining small amounts of Cr^{III}, especially if these are of the same order as the reproducibility of each titration.

[5] Trans. Am. Electrochem. Soc., **56**, p. 333; 1929,

(2) *Direct precipitation.*—A slight excess of ammonium hydroxide was added to the diluted solution of chromic acid, which was boiled for some time and kept slightly alkaline by small additions of ammonia. The precipitate of chromic hydroxide was filtered and washed, dissolved in dilute nitric acid, and reprecipitated with ammonia. This treatment was repeated until no tests for chromate (with lead acetate) could be obtained in the filtrate. The precipitate was ignited and weighed as Cr_2O_3.

No attempt was made to define exactly the optimum conditions for this precipitation and ignition. Tests made by this method and by differential titration upon chromic acid containing 0.5 to 5 per cent of Cr_2O_3 showed good agreement. Direct precipitation was used for concentrations of Cr_2O_3 below 0.5 per cent for the above-mentioned reasons.

III. CONDUCTIVITY MEASUREMENTS

1. APPARATUS AND METHOD

A Kohlrausch slide-wire (Leeds & Northrup) with extension coils and a 3-dial resistance box were used. An alternating current with a frequency of 1,000 cycles was supplied by a microphone hummer (General Radio Corporation) with an output of 0.06 watt when set for high intensity. This power was too low to secure a sharp minimum on the bridge, consequently the telephone current was increased fiftyfold by means of a 2-stage vacuum tube amplifier.[6] The interval of silence on the slide-wire was thereby decreased from 3 divisions to 0.1 division, thus yielding a precision of about 1 part in 3,000.

The conductivity bridge was made symmetrical by having the lead wires of equal length to the resistance box and conductivity cell. These conductors consisted of double-stranded No. 12 copper wire, inclosed in a grounded metal-sheathed cable. In other respects, the recommendations of E. W. Washburn[7] were followed. In order to eliminate the effects of any asymmetry in the arrangement or in the sine wave, a reversing switch was included in the circuit. Readings taken with the two positions of the switch did not usually differ by more than 1 part in 2,500. The mean of the two readings was used.

The integrity of the bridge assembly was confirmed by substituting a calibrated a. c. resistance box for the electrolytic cell. Values of the resistance computed from the bridge settings agreed within 1 part in 2,000 with the standard values over the range from 75 to 900 ohms.

Baths containing an oil of low viscosity and motor-driven stirrers were kept at 25° and 45° C., respectively, by means of "metastatic" mercury regulators. During the summer a cooling coil was used in the 25° bath. The heating elements were operated by relays actuated by a 3-electrode tube.[8] The Beckmann thermometers used for setting the regulators were calibrated for total immersion. The application of emergent stem corrections showed that the true bath temperatures were 24.98° C. ±0.02°, and 44.96° C. ±0.02°. As the divergences of the true temperatures from 25° and 45° C., respectively,

[6] Similar to that used by Hall and Adams, J. Am. Chem. Soc., **41**, p. 1515; 1919.
[7] J. Am. Chem. Soc., **38**, p. 2452; 1916; Leeds & Northrup Catalogue, No. 48, p. 24; 1919.
[8] Beaver and Beaver, Ind. Eng. Chem., **15**, p. 359; 1923.

produced effects smaller than the reproducibility of the conductivity measurements, the results have been reported as for 25° and 45° C. Finely shaved ice was used to secure the temperature of 0° C. used in some of the measurements.

Washburn type C cells with platinized electrodes were used. The heat transfer from these cells is very efficient, and their change in temperature during passage of the bridge current for a few minutes was less than the fluctuations in bath temperature. Hence, it was unnecessary to wait any appreciable time before making the final readings.

2. DETERMINATION OF CELL CONSTANTS

As most of the solutions of chromic acid to be used were relatively concentrated and had high conductivities, it was necessary to determine the cell constant with a solution of comparably high conductivity. For this purpose sulphuric acid of maximum conductivity was selected. The density and concentration of such acid have not been very precisely defined. Klohrausch and Holborn [9] specify 30 per cent sulphuric acid, with a density of 1.223 at 18° C. In International Critical Tables the density of 30 per cent sulphuric acid is given as 1.2150 at 25° C. The value of 0.8242 reciprocal ohm-cm is given by Eastman [10] as the specific conductivity at 25° C. of sulphuric acid with maximum conductivity. Using this value, a cell constant of 86.98 was obtained for cell A, as the average of closely concordant determinations with solutions of sulphuric acid ranging in density at 25° C. from 1.2180 to 1.2243. In like manner for cell B a constant of 63.15 was obtained.

The above values were checked approximately by means of "demal" potassium chloride solution, prepared according to Parker and Parker,[11] and with 1 *N* potassium chloride solution prepared according to Kohlrausch, Holborn, and Diesselhorst.[12] The potassium chloride was twice recrystallized, sintered, powdered, and heated for three hours at 150° C. Kohlrausch's solution and data yielded a cell constant for A of 87.03, and Parker's a constant of 87.10. Both of these are in fair agreement with the value of 86.98 obtained with sulphuric acid. Since the resistivities of sulphuric and chromic acid are comparable, the latter value was used. Similarly for cell B, the constant 63.15 was chosen as the correct value. The values 63.17 and 63.13, secured with the Parker and Kohlrausch solutions, respectively, were considered as checks on this result. When the conductivity of a given chromic-acid solution was measured in cells A and B, the values computed from the selected constants agreed to within about 1 part in 1,000.

IV. DENSITY MEASUREMENTS

The density determinations were made by E. L. Peffer, of this bureau. Glass sinkers, partially filled with mercury, were immersed in tall cylinders containing the chromic-acid solutions. The cylinders were kept in a bath maintained at 25 ±0.02° C. For the stronger, more viscous solutions pycnometers were used. Appropriate correc-

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[9] Leitvermögen der Elektrolyte, p. 75; 1916.
[10] J. Am. Chem. Soc., 42, p. 1651; 1920.
[11] J. Am. Chem. Soc., 46, p. 332; 1924. A "demal" solution contains 1 equivalent in 1 cubic decimeter, not in 1 liter.
[12] Ann. Physik., 64, p. 440; 1898. The corrected Kohlrausch conductances which were used are given in I. C. T., 4, p. 230.

tions for the air buoyancy of the pycnometer and weights were applied. The values submitted were adjudged to be accurate to within 1 part in 2,000.

V. RESULTS OBTAINED

The data for concentration, density, and conductivity are assembled in Table 2. The concentrations in the first column are those obtained by actual analysis. A preliminary plot of these concentrations against the measured densities indicated that the relation is practically linear. The "revised concentrations" in the second column were obtained from a straight line drawn through the points in such a way as to make the average percentage deviations from the experimental concentrations as small as possible. This condition was satisfied by the equation $D = 1.00644 + 0.06606\ C$, the constants of which were evaluated by plotting the function

$$F = \frac{D-1}{C} \text{ against } \frac{1}{C}$$

where D = density and C = concentration.[13]

This equation was found to represent the experimental data closely for the range 2 to 10 M. These "revised concentrations" have been used in the other tables and plots. (Densities obtained with 2 and 5 M cromic acid solutions prepared from lot B fell on this line, indicating that small concentrations of trivalent chromium exert no perceptible effect on the density.) Table 3 gives the densities and conductivities for integral volume concentrations.

TABLE 2.—*Experimental data on density and conductivity of chromic-acid solutions*

Experimental concentration mols/L at 25° C.	Revised concentration	Density, 25° C.	Conductivity (reciprocal ohm-cm)		
			0° C.	25° C.	45° C.
0.0994	---------	---------	---------	0.0372	0.0467
.199	---------	---------	---------	.0726	.0913
.497				.1723	.2162
.995	[1](0.995)	1.0731	0.2187	.3152	.3911
[a].501	---------		.2846	.4287	.5285
1.972 B	1.969	1.1365	---------	.5044	.6204
2.146	2.134	1.1474	.3581	.5345	.6561
2.504	---------		.3905	.5752	.7078
2.995	2.998	1.2045	.4183	.6164	.7631
3.982	3.991	1.2701	.4398	.6573	.8184
4.640	---------		.4381	---------	---------
4.963	4.964	1.3344	---------	.6621	.8341
5.055 B	5.075	1.3417	.4283	.6582	.8325
6.001	6.018	1.4040	.4195	.6397	.8152
7.028	7.011	1.4696	.3866	.5999	.7685
7.972	7.956	1.5320	.3468	.5477	.7112
8.939	8.937	1.5968	.2928	.4796	.6306
9.791	9.759	1.6511	---------	.4215	.5522

[a] As the linear relation between concentration and density does not hold below about 2 M, the equation given in the text does not apply to this concentration or to others below 2 M.

[13] International Critical Tables, **3**, p. 52.

TABLE 3.—*Interpolated data on density and conductivity of chromic-acid solutions*

Concentration mols/L at 25° C.	Density, 25° C.	Conductivity (reciprocal ohm–cm)		
		0° C.	25° C.	45° C.
1.00	1.0725	0.219	0.315	0.389
2.00	1.1383	.342	.513	.632
3.00	1.2041	.418	.616	.763
3.20	----------	.425	.628	.778
3.40	----------	.430	.639	.790
3.60	----------	.434	.647	.801
3.80	----------	.438	.653	.810
4.00	1.2699	.440	.657	.818
4.10	----------	[1].440	----------	----------
4.20	----------	.440	.659	.824
4.40	----------	.439	.661	.828
4.60	----------	.439	.662	.831
4.80	----------	.437	[1].662	.833
5.00	1.3358	.435	.662	[1].834
5.20	----------	.433	.661	.833
5.40	----------	.431	.659	.831
5.60	----------	.428	.653	.828
5.80	----------	.424	.648	.823
6.00	1.4016	.420	.641	.817
6.20	----------	.414	.633	.808
6.40	----------	.408	.626	.799
6.60	----------	.401	.618	.789
6.80	----------	.394	.609	.780
7.00	1.4674	.387	.600	.769
8.00	1.5332	.345	.545	.708
9.00	1.5990	.289	.477	.625
10.00	1.6648	.225	.402	.528

[1] Maximum.

A comparison of the density data for 25° C. with those compiled by Beattie for 15° C. shows substantial agreement. When Beattie's values for weight-concentration [14] are converted to volume concentrations, his data also fall upon a straight line, with slightly higher densities at 15° C. (as would be expected) than those here reported for 25° C. A few measurements of density at 15°, 25°, and 35° C. yielded, for M CrO$_3$, temperature coefficients of density of 0.00023 (15° to 25°) and 0.00032 (25° to 35°) which are very close to those of pure water (0.000205 and 0.000302, respectively). For 5 M CrO$_3$ the corresponding coefficients are 0.00075 and 0.00078. The differences between the density values for 15° and 25° correspond approximately to these coefficients. These differences are too small to affect the practical control of chromium-plating solutions.

In Figure 1 the conductivities have been plotted against the revised concentrations. These curves show that there is a maximum in the conductivity of chromic acid, the position of which varies with the temperature; that is, from about 4.1 M at 0° C. to 4.8 M at 25° C. and to 5.0 M at 45° C. This shift, especially from 0° to 25° C. is greater than can be accounted for on the basis of the change in density and hence in volume concentration, that is caused by the difference in temperature. It must, therefore, involve a difference in the degree or type of the dissociation of the chromic acid.

The temperature coefficients of conductivity computed from the data in Table 3 show that in the range from 25° to 45° C., such as is used in chromium plating, the average coefficient is from 1 to 1.5 per

[14] International Critical tables, 3, p. 69.

cent per °C. The temperature intervals were too great to permit
accurate computation of the coefficients for small intervals.

The data in the tables and curves were all obtained with lot A of
chromic acid except the few points marked *B*, which were obtained
with lot B which has a trivalent chromium content nearly three
times as great as A. It is not possible from these few observations
to estimate closely the effects of trivalent chromium upon the density
or conductivity. This will be the subject of a future investigation.
A few preliminary experiments were made with solutions containing
known larger concentrations of trivalent chromium, introduced as
chromium hydroxide. These indicated that the decrease in con-
ductivity produced by trivalent chromium, calculated as Cr_2O_3, is
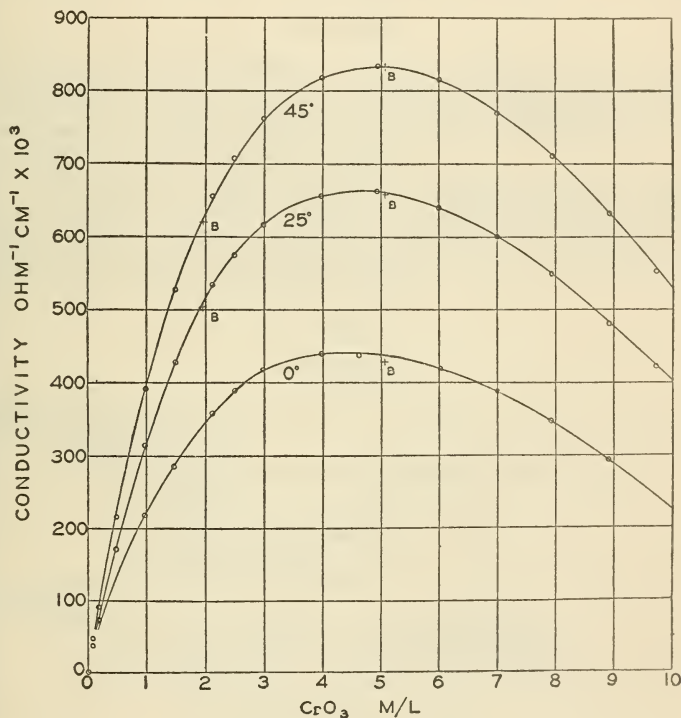roughly three times as great as its proportional content. It is at least

FIGURE 1.—*Conductivity of chromic acid*

possible, therefore, that the conductivities here recorded for lot A
(which contained 0.11 per cent Cr_2O_3) may be too low by 0.3 per cent.
Pending more exact measurements, no such correction has been
applied to the data.

VI. CONCLUSIONS

The only general conclusions that can be drawn from these measure-
ments are that (1) the density of chromic-acid solutions is practically
a linear function of the volume concentration, and (2) the conduc-
tivity of chromic-acid solutions reaches a maximum at from 4 to 5 *M*,
depending upon the temperature. Further experiments will be made

to determine more exactly the effect of trivalent chromium upon the conductivity.   At least it is evident that the presence of a maximum in the conductivity of practically pure chromic acid shows that the curve of similar shape reported by E. A. Ollard[15] for a solution of chromic acid with a high content of trivalent chromium has no necessary bearing upon the form or function of the latter constituent in such solutions.

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[15] Electroplaters' and Depositors' Tech. Soc., 3, p. 5; 1929.