ELECTROMETRIC TITRATION
OF CHROMIUM
WITH
POTASSIUM PERMANGANATE

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By

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ELECTROMETRIC TITRATION OF CHROMIUM WITH POTASSIUM PERMANGANATE

Introduction

While working on the electrodeposition of metallic chromium, Ewing and Malloy[1] found no method available in the literature for readily determining the chromium content and state of oxidation of the constituents of the solutions which were used in the investigation. The present work is an attempt to surmount this difficulty, presenting a short, rapid method, capable of a high degree of accuracy in the hands of a trained experimenter.

The solution containing chromium is poured through a modified Jones reductor, the reduced solution caught in an air-free container and titrated with standard potassium permanganate solution, the end point being determined by means of a potentiometer.

The technique of the potentiometric titration of oxidizing and reducing substances has been modified and improved and the chemistry of divalent chromium has been investigated, leading to an appreciation of the possibilities of reduced chromium as one of the most intense reducing agents known.

H. D. Newton[2] reduced titanium by means of metallic zinc and titrated the resulting solution with potassium permanganate. The method required elaborate precautions to insure complete solution of the zinc and an atmosphere of hydrogen was constantly kept above the liquid during the determination.

Shimer and Shimer[3] modified the method of Newton by replacing the reduction in a flask with the use of a Jones reductor. However, the slow passage of the liquid through the long, thin tube presented little advantage over the tedious method proposed by Newton. Here also, there still remained the difficulty of preventing reoxidation of the reduced titanium by the air.

C. Van Brunt[4] has described a method for the reduction of potassium dichromate by means of an electrically heated Jones reductor, the reduced solution being caught in a beaker containing excess of ferric ammonium sulphate and the resulting ferrous salt oxidized with standard potassium permangenate solution, using the color of excess permanganate to determine the end point. He indicates an accuracy of three parts per thousand. This method obviates the difficulty of keeping the reduced solution from being oxidized by the air and presents an avenue of escape from the slowness and inconvenience of the long column used by Shimer and Shimer.

On the other hand, it has the disadvantage of being indirect, ferrous iron being the intermediate compound formed in the reaction, A direct method would have inherent advantages which are obvious.

The method proposed by the writer combines the advantages of the Newton and the Shimer and Shimer methods by reduction of the chromium in a beaker with zinc-mercury amalgam and pouring the mixture through a long, thin Jones reductor, the column retaining particles of amalgam unconsumed in the preliminary reduction. Electrical heating is supplanted by steam heating, a process more adaptable to ordinary laboratory practice, The ferric sulphate of Van Brunt gives way to potassium permanganate for anticipating the action of the air on the reduced chromium and an atmosphere of carbon dioxide replaces the lighter hydrogen used by Newton.

The electrometric method used by the writer for determining the end point of the reaction: $Cr^{++} \rightarrow Cr^{+++}$ is very accurate, one drop of reagent permanganate in excess of the required quantity changing the potential reading of the cell by as much as six-tenths of a volt. Since the resulting chromic sulphate solution isgreen, the end point could not have been detected by color change, even on the addition of a large excess of permanganate.

- GENERAL THEORY -

Jean Piccard[5] studied the autooxidation of chromous salts and concluded that in neutral or acid solution atmospheric oxygen in excess forms not only chromic salts but chromic acid and compounds of an intermediate degree which are stable for a measurable time.

Traube and Passarge[6] found that salts of divelent chromium reduce water directly when the latter is warmed or acidified. The divalent salts also reduce the carbon compounds having double or triple bonds, in acid solution.

These investigations show the instability of chromous chromium and explain the precautions necessary in the work of Newton, Shimer and Shimer, and VanBrunt.

When a platinum wire is immersed in a solution containing chromous and chromic ions and connected by means of an external circuit with a mercurous sulphate cell, which in turn makes contact with the chromous-chromic solution by means of a salt bridge, a potential difference is established between the platinum wire and the metallic electrode of the mercurous sulphate cell. This potential difference may be measured by means of a potentiometer.

The equation -

$$E = E_0 - \frac{RT}{NF} \log_e \frac{\text{activity of product of oxidation}}{\text{activity of product of reduction}}$$

expresses the electromotive force of this cell, where -

$E =$ the observed potential difference

$E_0 =$ the potential difference of a like cell when the ratio $\frac{\text{activity of product of oxidation}}{\text{activity of product of reduction}}$ is exactly 1.

$R =$ the gas constant in the van't Hoff equation. Measured in volts X coulombs.

$T =$ the absolute temperature

$N =$ the difference in valence of the metal in final and initial states.

$F =$ the value of the Faraday, or 96,500 coulombs.

In the case of chromium, the equation takes the form

$$E = E_0 + .059 \log_{10} \frac{Cr^{++}}{Cr^{+++}}$$

Forbes and Richter[7] have determined the value of E_0 and found a deviation from the theoretical value of the coefficient of the logarithm. They give the value, referred to the normal hydrogen electrode as zero, of

$$\pi = 0.400 + 0.065 \log \frac{Cr^{++}}{Cr^{+++}}$$

This determination was made at mercury electrodes, the potentials on platinum reaching a maximum about 0.16 volts lower, with evolution of hydrogen.

The value of E is a measure of the ratio of the concentrations of Cr^{++} and Cr^{+++} ions. On adding the oxidizing agent the value of this ratio changes until the concentration of the Cr^{++} ion becomes vanishingly small, when there is a corresponding sudden rise in potential. This point represents the end point of the reaction.

If the measured electromotive force isplotted as ordinate against quantity of oxidizing agent added, as abscissa, a curve, which expresses the given function, results. The point where the second derivative equals zero is taken as the end point of the reaction.

The absolute value of the potential reading will vary from the value obtained against the hydrogen electrode by the value of this half-cell:-

$Pt/Hg/Hg_2SO_4$ (s), H_2SO_4 (.5), Na_2SO_4 (.3), $H^+(1)/H_2(g)/Pt$

The initial readings actually recorded in this work were around -0.8 volt and the end point around -0.3 volt, the final readings around +0.15 volt.

- MATERIALS AND APPARATUS -

The apparatus used **is** illustrated in the accompanying diagram,(Fig.1). It was especially designed for this work and will be found to be very easy to duplicate. It consists essentially of a beaker(A) of 500 cc. capacity, fitted with a rubber stopper. An inlet tube for carbon dioxide gas; an outlet tube for the gas; a thermometer (T); a platinum wire (pt), six inches in length; a stirrer (S), run by a small 1/50th horse power motor; the end of the delivery tube of the reductor and the longer arm of the salt bridge extend through the rubber stopper into the beaker(A). The delivery tube reaches three-fourths of the way to the bottom of the beaker.

The half-cell consists of a hard glass test tube (C), into the bottom of which a small platinum wire has been fused, the tube containing sufficient mercury to cover the protruding end of the platinium, then a paste of mercurous sulphate and mercury, on top of which is a paste of mercurous sulphate and normal sulphuric acid. The rest of the space in the tube is filled with normal sulphuric acid which had been saturated with mercurous sulphate.

A glass arm filled with the cell acid, sulphuric acid saturated with mercurous sulphate, makes contact with an intermediate vessel (I), containing a solution of sodium sulphate, 49 grams per liter. An ⊓ shaped bridge (B) filled with the solium sulphate solution makes contact with the vessel (A) by means of an arm curved upward at the extremity. This curve prevents the admittance of air bubbles when the vessel (A) is removed.

The function of the intermediate vessel (I) is to allow for any desired change in the acidity of the solution in the reaction vessel (A). In fact, a basic solution in (A) would not invalidate the applicability of the cell(C) as the half-cell. Thus the set-up is very elastic in its application.

The vessel (D) consists of a 5-liter bottle containing the sodium sulphate solution used in the salt arm (B). On opening the pinch clamp, the arm (B) may be flushed into the reaction vessel, insuring no loss of its contents, due to diffusion. The density of the sodium sulphate was so chosen as to cut down the possible diffusion to a minimum.

The reductor column (E) consists of a Pyrex tube, to one end of which a stop-cock length is fused. The other end carries a Pyrex test tube fused to a piece of glass of the same bore as the reductor tube. The upper end of the column is fitted with a stopper with an inlet tube for carbon dioxide, for forcing the charge down through the reductor column. The column contains a large plug of glass wool (F) just above the stop cock and is filled to a height of 50cm. with Zn-Hg amalgam. The tube is encased with a rubber sack into which steam is admitted. The steam and water of condensation leave through the opening in the bottom of the sack.

The platinum electrode from the reaction vessel (A) and the platinum electrode from the mercurous sulphate half-cell are connected to two of the terminals of a Leeds and Northrup Student Type Potentiometer. Being standard equipment, no attempt will be made here to explain the potentiometer set-up.

- PREPARATION AND ANALYSIS OF MATERIALS -

The burettes used were calibrated at the Bureau of Standards, Washington D.C., and checked. The pipettes were calibrated at the Bureau of Standards and also checked. The weights were calibrated in strict accordance with the method of T.W. Richards[8] on a very good Voland and Sons Analytical Balance, using the method of weighing by vibrations.

The water used was laboratory re-distilled water and Baker's best chemicals were used.

The permanganate used was made up a month in advance and allowed to "age". Tt was then kept in a black bottle to prevent change in strength. The normality of the solution was determined against sodium oxalate, certified by the Bureau of Standards and containing 99.9% sodium oxalate.

The potassium dichromate was standardized against Mohr's salt, the Mohr's salt being previously checked by analysis with the standard permanganate and found to be 99.6% pure.

The chromic acid solution was standardized against the same Mohr's salt.

In order to standardize the solution of chromic sulphate it was found necessary to use iodimetric methods.

A standard sodium thiosulphate solution was made up and checked against the potassium dichromate, which had been previously standarized in terms of the primary standard used in this work, the sodium oxalate.

The chromic sulphate was then oxidized with sodium peroxide and the chromium estimated by means of the thiosulphate solution.

As a final check, the thiosulphate was standardized against the standard permanganate.

- STANDARDIZATION DATA -

Standardizing $KMnO_4$ against Sodium Oxalate

Sample No.	#1	#2	#3	#4	#5
Weight of sample gms.	.25415	.25635	.25574	.25480	.25484
Corr. weight sample	.25390	.25609	.25548	.25455	.25459
cc $KMnO_4$	43.50	43.87	43.77	43.60	43.61
Normality	.087120	.087130	.087121	.087143	.087136

Sample calculation of normality -

$$\frac{Na_2C_2O_4}{2} = 66.997 = \text{equivalent weight}$$

$$N = \frac{.25390 \times 1000}{66.997 \times 43.50} = .087120$$

Average of 5 determinations of normality = .08713 ± .00009

Standardizing $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ against the standard permanganate.

Sample No.	#6	#7	#8	#9
Weight of sample gms.	1.53661	1.53634	1.53638	1.53744
cc $KMnO_4$	44.79	44.78	44.77	44.79
Percent Fe	14.182	14.181	14.178	14.174

Sample calculation of percent iron:

$$\text{Percentage} = \frac{55.84 \times 44.79 \times .08713 \times 100}{1.53661 \times 1000} = 14.182$$

Average of 4 determinations of percent iron = 14.179 ± .005

Standardizing $K_2Cr_2O_7$ against Mohr's salt.

Sample No.	#10	#11	#12	#13
Weight of sample gms.	11.38567	11.38526	11.38459	11.38572
cc$K_2Cr_2O_7$	44.81	44.80	44.79	44.81
Normality	.64519	.64531	.64541	.64519

Sample calculation of normality -

$$N = \frac{11.38567 \times .14179 \times 1000}{55.84 \times 44.81} = .64519$$

Average of 4 determinations of normality = .6453 ± .0001

Standardizing H_2CrO_4 against Mohr's salt.

Sample no.	#14	#15	#16
Weight of sample gms.	5.1021	5.1019	5.1017
cc H_2CrO_4	40.60	40.57	40.54
Normality	.3191	.3193	.3195

Sample calculation of normality -

$$N = \frac{5.1021 \times .14179 \times 1000}{55.84 \times 40.69} = .3191$$

Average of 3 determinations of normality = .3193 ± .0002

Standardizing Sodium Thiosulphate Solution Against Standard Potassium Dichromate Solution.

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Sample No.	#17	#18	#19	#20	#21
cc$K_2Cr_2O_7$	10.00	10.00	10.00	10.00	10.00
cc Thiosulphate	33.81	33.82	33.80	33.82	33.80
Normality	.19086	.19081	.19092	.19081	.19092

Sample calculation of normality -

$$N = \frac{10.00 \times .6453}{33.81} \pm .19086$$

Average of 5 determinations of normality = .19086 ± .00006

Standarizing $Cr_2(SO_4)_3$ against Thiosulphate

Sample No.	#22	#23	#24
cc $Cr_2(SO_4)_3$	10.00	10.00	10.00
cc Thiosulphate	30.49	30.50	30.50
Normality	.29097	.29106	.29106

Sample calculation of normality -

$$N = \frac{.19086 \times 30.49}{2 \times 10.00} = .29097$$

Average of 3 determinations of normality = .29103 ± .00006

Standardizing Thiosulphate against standard $KMnO_4$

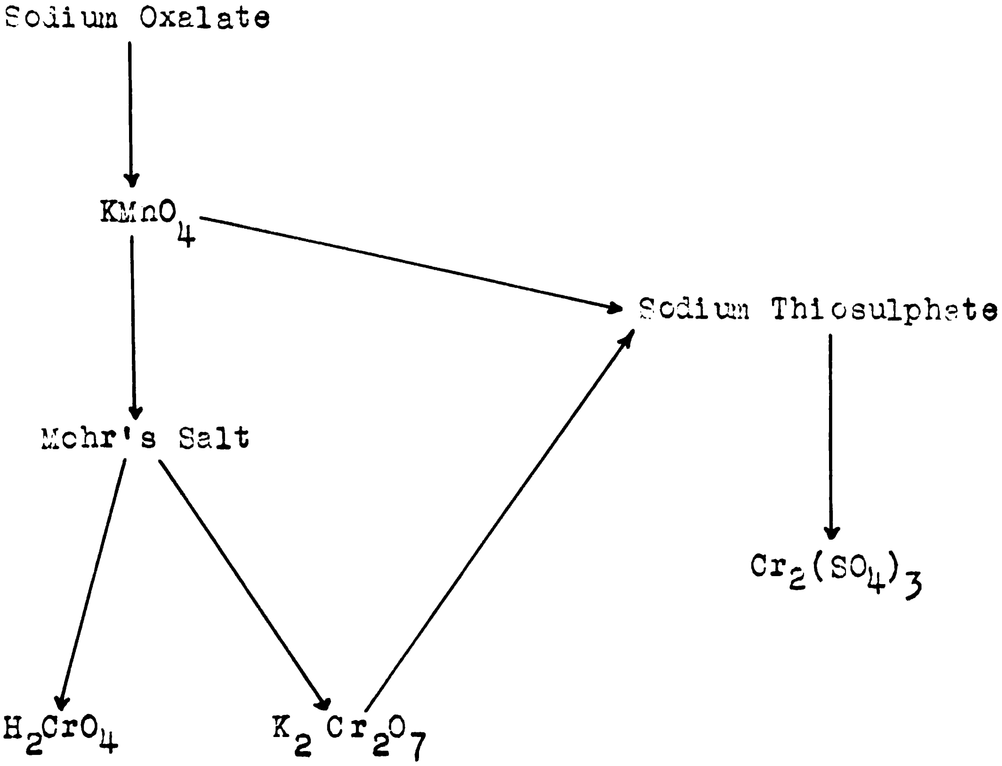
Sample No.	#25	#26	#27	#28
cc $KMnO_4$	100.00	100.00	100.00	100.00
cc Thiosulphate	45.80	45.82	45.82	45.79
Normality	.19024	.19016	.19024	.19028

Sample calculation of normality -

$$N = \frac{100.00 \times .08713}{45.80} = .19024$$

Average of 4 determinations of normality = .19023 ± .00007

SCHEME OF STANDARDIZATION



- Figure 2 -

The above scheme shows quite clearly the method of standardization employed. Since in the actual data taking during the body of this thesis the potassium permanganate is taken as the standard, there can be very little chance for error in this entire work.

It will be noted that whereas the normality of the thiosulphate by the $K_2Cr_2O_7$ oxidation is .19086, it is found to be .19023 by the $KMnO_4$ oxidation, a discrepancy of .33%. However, this need occasion no alarm, for the dichromate oxidation of KI to iodine differs from the permanganate oxidation of KI to iodine in the rate of reaction and degree of efficiency. Since the thiosulphate was standardized against dichromate and the chromic sulphate was first oxidized to dichromate and then caused to react with the thiosulphate, thus behaving the same as dichromate, the value to be accepted for the thiosulphate is that obtained on standardization against dichromate, rather than that obtained with potassium permanganate.

The Zn used in the reductor column consists of particles which pass a 10-mesh sieve but are retained by a 20-mesh sieve. It was amalgamated by stirring in a mixture of 25 cc of normal mercuric chloride solution, 25 cc of hydrochloric acid (specific gravity 1.12) and 250 cc of water for three minutes. The solution was then poured off and the zinc washed repeatedly with water. The Zn-Hg amalgam was kept under water when not in use.

The carbon dioxide gas was purified by passing through a U-tube filled with calcium chloride and then through a column filled with glass wool, the latter removing solid particles.

The sodium sulphate solution in the storage bottle (D) used for flushing out salt bridge (B) was treated with just sufficient permanganate to oxidize the slight amount of reducing substances present, in order to prevent the subsequent reaction of these with the contents of the reaction vessel (A).

- PROCEDURE -

The reductor column was first washed with 400 cc. of 5% sulphuric acid (5 cc. concentrated acid in 100 cc. of solution), thus removing all traces of foreign material and remains of previous runs. Then 25 cc. of 16% sulphuric acid was run through the column. The side arm of the salt bridge (B) was then flushed thoroughly, after which the platinum electrode in beaker (A) was washed with acid and flamed to remove adherent impurities.

Meanwhile, the steam was started through the rubber sack enclosing the column and allowed to issue freely from the lower opening. The beaker (A) was rinsed and in it was placed 20 grams of C.P. anhydrous, fused sodium acetate and 20 cc. of water. The carbon dioxide gas was then allowed to sweep through the vessel for five minutes, displacing the air.

When the vessel was free from air, the mixture to be analyzed was diluted to 50 cc., 4 cc. of concentrated sulphuric acid and about 5 grams of Zn-Hg amalgam added and the whole boiled for five minutes, the solution assuming first a green color (formation of chromic sulphate), and then a light blue color (formation of chromous sulphate). The solution was then poured into the hot reductor column and allowed to enter the reaction vessel at a slow rate, in no case faster than rapid dripping.

The beaker in which the preliminary reduction took place was rinsed with a 5% sulphuric acid solution, the washings being added to the contents of the column.

The column was washed with 100 cc. of 5% sulphuric acid, the air at no time having access to the top of the Zn-Hg column, although now this precaution is believed to be unnecessary. A final rinsing was accomplished with distilled water. The passage of the wash acid through the column was often hurried by applying pressure to the top by means of a cylinder of compressed carbon dioxide.

The reaction vessel was kept air-free by continually blowing carbon dioxide through it during a run. The reduced chromium solution was then titrated with the permanganate from burette (G), the reading of the potentiometer being recorded at each addition.

When near the end point of the titration, the salt bridge (B) was flushed into the vessel (A) to include any solution which may have diffused into the side-arm of (B).

The vessel was kept at 70° C. during the entire run by means of a small micro-burner.

The voltage readings were then plotted on coördinate paper against cc $KMnO_4$ added, the end point being taken as the abscissa corresponding to the point one-half of the way up the rise in the titration curve. From the normality of the permanganate used, the number of grams of chromium per cc of the solution analysed is readily obtained.

If the oxidizing power of the solution were previously determined against any standard reducing agent, a simple calculation would give the proportion of hexavalent chromium to trivalent chromium in the original solution, providing it were free from divalent chromium. This can be assured by aerating the sample for a few minutes, when the divalent chromium is immediately oxidized completely to trivalent chromium. However, in the opinion of the writer, divalent chromium cannot exist in the presence of the strongly oxidizing hexavalent chromium, so the precaution noted is not at all necessary.

In the later work it was found advantageous to introduce 1 cc less than the required amount of $KMnO_4$ in the beaker (A) and to allow the reduced chromium solution to enter, thus anticipating any oxidizing action of residual air. The end point was then determined by adding the rest of the $KMnO_4$ and taking potential readings, as before.

To prevent the slight diffusion of the contents of beaker (A) into the salt bridge, the side-arm of bridge (B) was lowered into the beaker only when potential readings were to be taken. This procedure was used in connection with the method in the above paragraph. In the earlier work, where the $KMnO_4$ was added drop by drop to the contents of the beaker, the side-arm remained in position throughout the entire experiment.

It was found necessary to wait for the potential readings near the end point to remain constant, requiring in some cases as long as twenty minutes. It is not permissible to add more $KMnO_4$ until equilibrium is established, when the potential reading remains fairly constant.

In a portion of the work it was found of decided advantage to add the $KMnO_4$ continuously, keeping a little excess in the beaker up until the last stages of the reduction.

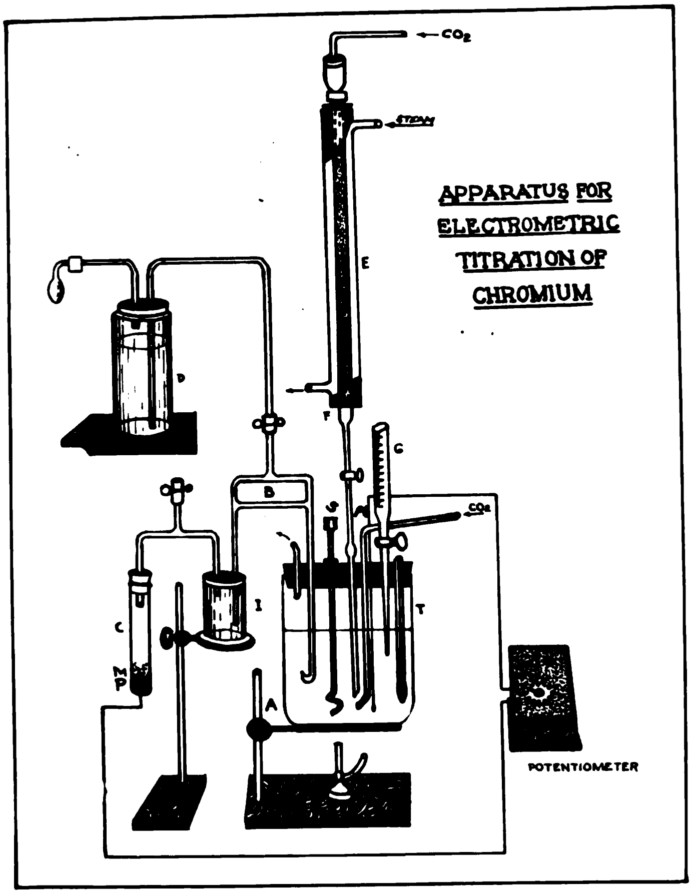

CO$_2$
STEAM
APPARATUS FOR ELECTROMETRIC TITRATION OF CHROMIUM
E
D
F
G
B
CO$_2$
I
C
T
M
P
A
POTENTIOMETER

Fig. 1

- DATA -

Table I

Using 20.00 cc. $Cr_2(SO_4)_3$; Normality = .29103

Sample No.	Theoretical cc $KMnO_4$	Actual cc Required	Grams Cr Added	Grams Cr found	Percent error
1.	44.54	44.60	0.2018	0.2021	+.15
2.	44.54	44.39	0.2018	0.2011	-.35
3.	44.54	44.55	0.2018	0.2018	±.00
4.	44.54	44.52	0.2018	0.2017	-.05
5.	44.54	44.52	0.2018	0.2017	-.05
6.	44.54	44.52	0.2018	0.2017	-.05
7.	44.54	44.52	0.2018	0.2017	-.05
8.	44.54	44.50	0.2018	0.2016	-.10
*9.	22.27	22.26	0.1009	0.1009	±.00

* Using 10.00 cc. $Cr_2(SO_4)_3$

Normality in divalent chromium = 2/3 of .29103 = .19402

Equivalent weight of Cr = 52.0

Weight of Cr in one liter of solution = 10.08904

Weight of Cr in 20.00 cc of solution = 0.20178

Mean (omitting sample #2 as in error) of eight determinations -

Reduction = 99.98%

Table II

Using 20.00 cc. $K_2Cr_2O_7$; Normality = .6453

Sample No.	Theoretical cc $KMnO_4$	Actual cc Required	Grams Cr Added	Grams Cr found	Perc. Error
10.	49.37	49.30	0.2237	0.2234	-.13
11.	49.37	49.37	0.2237	0.2237	±.00
12.	49.37	49.35	0.2237	0.2236	-.04
13.	49.37	49.33	0.2237	0.2235	-.09
14.*	24.69	24.67	0.1119	0.1118	-.09

* Using 10.00 cc. $K_2Cr_2O_7$

Normality in divalent chromium - 1/3 of .6453 = .2151

EQuivalent weight of Cr = 52.0

Weight of Cr in one liter of solution = 11.1852

Weight of Cr in 20.00 cc. of solution = 0.2237

Mean of five determinations ; Reduction = 99.93%

Table III

Using 40.00 cc. H_2CrO_4 - Normality = .3193

Sample No.	Theoretical cc $KMnO_4$	Actual cc Required	Grams Cr Added	Grams Cr found	Percent error
15.	48.86	48.78	0.2213	0.2209	-.18
16.	48.86	48.84	0.2213	0.2212	-.05
17.	48.86	48.84	0.2213	0.2212	-.05
18.*	24.43	24.41	0.1106	0.1105	-.09

* Using 20.00 cc. H_2CrO_4

Normality in divalent chromium - 1/3 of .3193 = .1064

Equivalent weight of Cr = 52.0

Weight of Cr in one liter of solution = 5.5328

Weight of Cr in 40.00 cc. of solution = 0.2213

Mean of four determinations - Reduction = 99.91%

- DISCUSSION OF DATA -

Samples of the standard $Cr_2(SO_4)_3$, $K_2Cr_2O_7$ and H_2CrO_4 solutions were analyzed in accordance with the procedure outlined. The method of anticipation by means of $KMnO_4$ was used and the results were excellent.

It is seen from Table I that the mean of eight consecutive determinations of chromium in chromic sulphate yielded 99.98% of the quantity actually taken for analysis.

Table II shows the results in the case of potassium dichromate, the quantity of chromium found being 99.93% of that added.

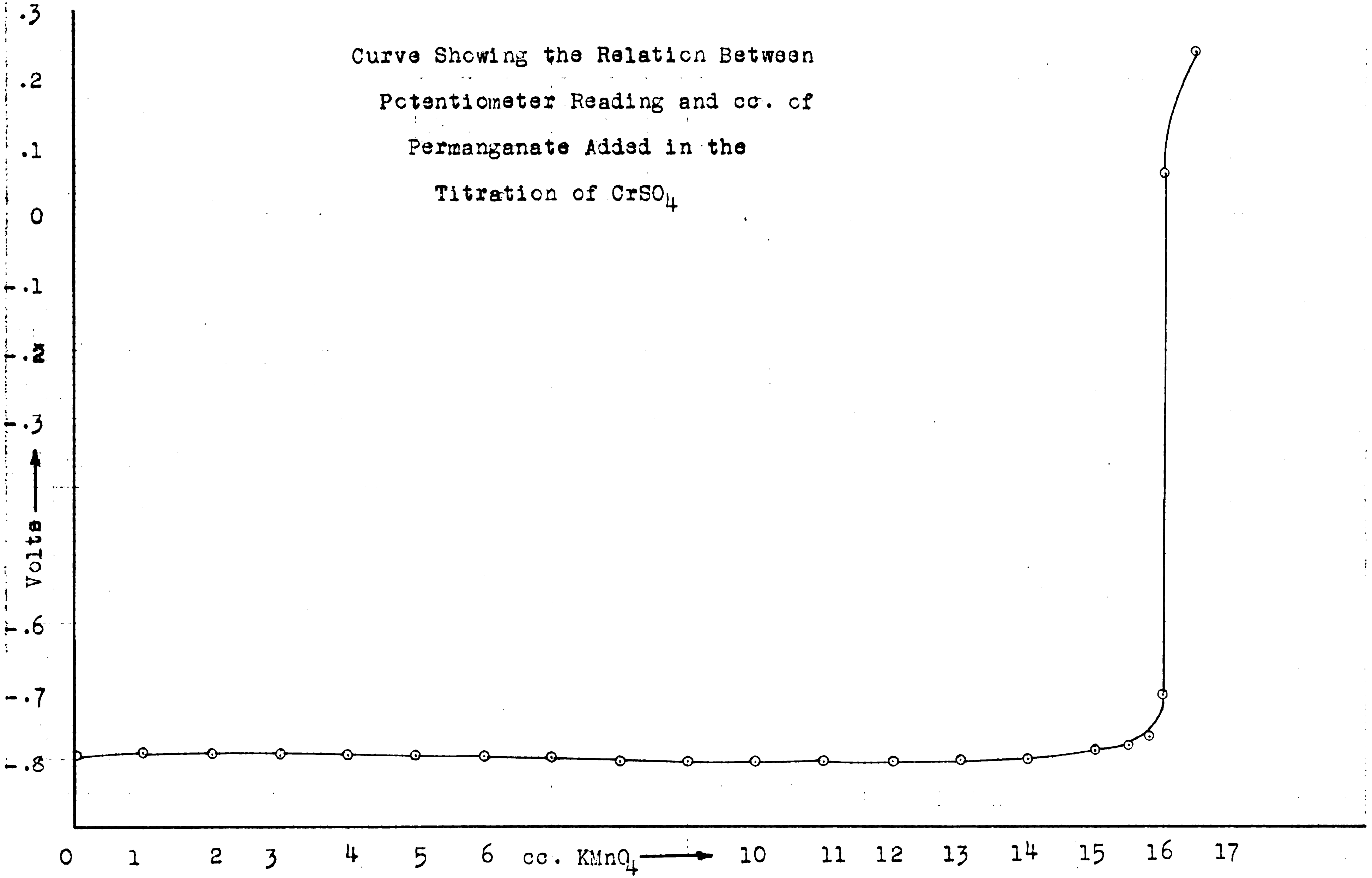
Table III shows like figures for chromic acid, the quantity of chromium found being 99.91% of that added. On decreasing the quantity of chromium taken for analysis as in samples #9,#14 and #18 equally excellent results are obtained.

A blank of .01 cc. $KMnO_4$ has been subtracted from all the tabulated figures. This represents the quantity of $KMnO_4$ consumed by the reagents.

It was found that the quantity of sulphuric acid used during the reduction is of little importance, provided enough is present to effect the reduction. Of course, too much acid tends to sulphate the column and consequently is deleterious to the reductor.

During the titration with $KMnO_4$ it was found that a solution only slightly acid prevented to a large degree the oxidation of chromous chromium, which was often found to occur even in the presence of the inert carbon dioxide. This oxidation is explained by supposing the presence of oxygen in the partially purified gas and the small oxidizing effect of the sulphuric acid in more concentrated solutions. The acidity was decreased by using sodium acetate, which yields NaOH on hydrolysis. The difficultly soluble and slightly ionized chromous acetate formed is less affected by atmospheric oxygen than the sulphate. Thus the sodium acetate accomplishes a twofold purpose.

In the course of this work,chromous acetate was isolated and found to be red in color. Chromous sulphate is light blue in color. The change from acetate to sulphate could be readily followed by means of this color change.



Curve Showing the Relation Between Potentiometer Reading and cc. of Permanganate Added in the Titration of $CrSO_4$

Figure 3.

The curve in Fig. 3 represents the analysis of a sample of $K_2Cr_2O_7$ and is typical of all the titration curves obtained with all the compounds of chromium investigated.

On stopping the carbon dioxide stream during a titration the potential was found to rise as much as 0.2 volt, showing the necessity for excluding even traces of atmospheric oxygen from the reaction vessel.

- CONCLUSIONS -

It was found that chromium compounds were quantitatively reduced to chromous chromium in a modified Jones reductor and were determined volumetrically with standard potassium permanganate. The course of the titration was followed by means of potentiometer readings and the end point accurately determined from the rise in the titration curve at this point.

The method of anticipation of atmospheric oxidation, by means of permanganate was found preferable to that of keeping a little excess of permanganate in the titration vessel up until the later stages of the reduction.

The activity of chromous sulphate was found to be so great that the method of total titration after complete

reduction was discarded in favor of the method of anticipation by means of permanganate.

The titration curves for chromous sulphate were found to be ideal, one drop of permanganate causing a sudden rise in potential of 0.5-0.8 volt.

In a given sample of hexavalent and trivalent chromium, the former may be determined by means of ordinary laboratory methods and the total chromium content by means of the method proposed by the writer. A simple calculation will then yield the quantity in each of the two states of oxidation.

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