

## CONSTITUTION OF CHROMIC ACID.

[PART I.]

BY ASWINI KUMAR DATTA AND NILRATAN DHAR.

Received March 21, 1916.

From observations on the depression of the freezing point of aqueous solutions of chromium trioxide and the colorimetric study of the watery solutions of chromic acid, chromates and dichromates, and from the results of electrical conductivity measurements, Ostwald concludes that chromic acid solutions contain the strong acid  $\text{H}_2\text{Cr}_2\text{O}_7$  which forms neutral salts not appreciably hydrolyzed in aqueous solution. Costa,<sup>1</sup> from ebullioscopic measurements of chromic acid in aqueous solutions, shows that solutions not too concentrated contain the acid  $\text{H}_2\text{Cr}_2\text{O}_7$ . Spitalsky<sup>2</sup> arrived at similar conclusions from a study of the concentration of  $\text{H}^\circ$  in solutions of free chromic acid. Sabatier<sup>3</sup> tried to establish the identity of the spectra of chromic acid and dichromates, but no definite conclusion can be drawn from this work.

Sherril,<sup>4</sup> from an elaborate and careful study, considers that dilute solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  contain almost exclusively the ions  $2\text{K}^+$  and  $\text{Cr}_2\text{O}_7^{--}$  but that strong solutions of  $\text{K}_2\text{Cr}_2\text{O}_7$  are slightly acid owing to slight hydrolysis. Evidently Sherril has tried to amalgamate the two opposing views.<sup>5</sup>

Dubrisay<sup>6</sup> has shown that chromic acid differs from a strong dibasic acid, such as sulfuric acid, in exhibiting a constant surface tension only until the first acid function is neutralized, after which the surface tension decreases gradually but slightly until the second is neutralized.

Walden,<sup>7</sup> from conductivity measurements, adduces strong reasons in favor of the formula  $\text{H}_2\text{CrO}_4$ . Abegg and Cox<sup>8</sup> took the same view as that taken by Walden and they also add further reasons in support of this formula.

The present investigation is an attempt to assist in the solution of the problem by a study of further physical properties of chromium trioxide ( $\text{CrO}_3$ ) and  $\text{R}_2\text{Cr}_2\text{O}_7$  in solution.

## Molecular Volume in Solution.

If  $m$  is the molecular weight of a dissolved substance in grams,  $l$  the quantity of solvent which is present for every mol of solute,  $d$  the density

<sup>1</sup> *Gaz.* 36 (1906).

<sup>2</sup> *Z. anorg. Chem.*, 54, 265 (1907).

<sup>3</sup> *Compt. rend.*, 103, 49.

<sup>4</sup> *THIS JOURNAL*, 29, 1614 (1907).

<sup>5</sup> See also Dehn, *THIS JOURNAL*, 36, 829 (1914) for a colorimetric investigation of the chromates.

<sup>6</sup> *Compt. rend.*, 156, 1902 (1913).

<sup>7</sup> *Z. physik. Chem.*, 2, 70 (1888).

<sup>8</sup> *Ibid.*, 48, 725 (1904).

of the solvent and  $d_s$  the density of the solution, the "Molecular solution volume"  ${}_sV_m$  is related to these as follows:

$${}_sV_m = \frac{m + l}{d_s} - \frac{l}{d}$$

From the molecular solution volume of a large number of substances, Traube calculated the atomic volume of the elements and the volume effects of a few of the chief modifications of structure and he also deduced from his extensive work a process for ascertaining the molecular weight of a substance in dilute aqueous solution. For dissolved substances we have the relation

$${}_sV_m = \Sigma nC + \phi_s,$$

where  ${}_sV_m$  is the molecular solution volume of the substance and  $\phi_s$  the molecular solution co-volume, which is approximately constant. In calculating  $\Sigma nC$  the atomic and structural constants for the substance in solution are used and, further, if the substance is an electrolyte, allowance is made for dissociation. This method has been successfully used in ascertaining the association factor of many substances.

The two possible formulas for chromic acid are  $H_2CrO_4$  and  $H_2Cr_2O_7$ . Now, all the above substances are strong electrolytes, chromic acid being a strong acid as has been determined from conductivity measurements and its chemical behavior.  $H_2CrO_4$  and  $K_2CrO_4$  are evidently of similar structure and so are  $K_2Cr_2O_7$  and  $H_2Cr_2O_7$ , and the difference between the molecular solution volume of  $K_2CrO_4$  and chromic acid, on the supposition that its formula is  $H_2CrO_4$ , should be equal to the difference between the solution volume of 2 atoms of potassium and 2 atoms of hydrogen. This also would be the difference between the molecular solution volume of  $K_2Cr_2O_7$  and chromic acid if its formula be  $H_2Cr_2O_7$ . It was found that the relation stated above holds good only when we take the formula for chromic acid as  $H_2Cr_2O_7$ .

TABLE I.  
Chromic Acid.

Density.	Acid per cc. as $H_2CrO_4$ (g.).	${}_sV_m$ .	Acid as $H_2Cr_2O_7$ (g.).	${}_sV_m$ .
1.01480	0.02420	45.1	0.02250	73.6
1.00749	0.01210	44.6	0.01135	72.4
1.00503	0.00806	44.1	0.00750	72.0
1.00385	0.00605	43.0	0.00562	69.5
1.00256	0.00403	42.8	0.00375	69.0
		Mean, 44.0		70.9

The materials used were prepared in several ways and carefully purified by repeated crystallization and were dissolved in "Conductivity water" and kept in "Resistance glass" bottles. The strength of chromic acid was ascertained by adding excess of pure KI and titrating the iodine by

standard sodium thiosulfate. The density was determined by means of a Sprengel pycnometer as modified by Ostwald, following the details as given by him. The densities recorded above are the means of three determinations, agreeing to the fifth decimal place.

TABLE II.

Potassium dichromate.			Potassium chromate.		
Density.	Salt per cc. (g.).	$sV_m$ .	Density.	Salt per cc. (g.).	$sV_m$ .
1.01859	0.027144	90.9	1.01184	0.01488	39.5
1.00932	0.013572	91.4	1.02340	0.02976	40.5
1.00465	0.006786	92.2	1.01449	0.01863	42.0
1.00990	0.028240	87.0	1.00728	0.00931	41.9
1.00497	0.14120	87.0			
Mean, 89.7			Mean, 41.0		

Traube found the atomic volume, in solution, of hydrogen = 3.1 and of sodium = 1.8. He does not seem to have calculated that for potassium. We calculated the atomic volume in solution of potassium from the following data taken from "Physikalisch-chemische Tabellen":<sup>1</sup>

TABLE III.

Sodium Chloride.			Potassium Chloride.		
Density.	Salt per cc. (g.).	$sV_m$ .	Density.	Salt per cc. (g.).	$sV_m$ .
1.0401	0.0585	17.5	1.0444	0.0746	28.9
1.0788	0.01170	17.8	1.0887	0.1492	27.8
1.1164	0.01755	17.7	1.1317	0.2238	27.4
Av., 17.6			Av., 28.0		

Now sodium chloride and potassium chloride are both salts of similar nature. Their "structural constants" and "allowance for ionization" may be taken to be equal. The difference between their molecular volumes in solution is evidently that between the atomic volume in solution (A) of one atom of potassium and one atom of sodium. The atomic volume in solution of potassium is therefore 28 ( $sV_m$  for KCl) — 17.6 ( $sV_m$  for NaCl) + 1.8 (A for Na) = 12.2. This atomic constant of potassium may also be deduced as follows:

Traube<sup>2</sup> found the atomic volume (A) in solution of chlorine to be 13.2. Therefore

$$28.0 = 13.2 + A \text{ (for K)} + x \quad (1)$$

$$17.6 = 13.2 + 1.8 \quad + x \quad (2)$$

$x$  is a constant dependent on the nature of the salt and is the same for both KCl and NaCl, they being salts of the same nature.

From (1) and (2) we get A (for K) = 12.2. The two results are identical, showing the validity of our assumptions. The atomic volume

<sup>1</sup> Landolt and Bornstein, p. 177.

<sup>2</sup> *Loc. cit.*

in solution of potassium can therefore be taken to be 12.2. The difference between the solution volume of 2 atoms of potassium and 2 atoms of hydrogen is therefore  $12.2 \times 2 - 3.1 \times 2 = 18.2$ . The molecular volume in solution of potassium dichromate as has been found is 89.7 and that of chromic acid on the supposition that its formula is  $H_2Cr_2O_7$  is 70.9. The difference is 18.8 in good agreement with the calculated number 18.2. The molecular volume in solution of potassium chromate is 41.0 and that of chromic acid on the supposition that its formula is  $H_2CrO_4$  is 44. The difference is  $-3$  instead of  $+18.2$ . We are thus led to conclude that formula for chromic acid is  $H_2Cr_2O_7$  and not  $H_2CrO_4$ . The above line of reasoning seems to be clear and satisfactorily confirmed by experimental evidence. But we should mention here that it has been found that this method does not always yield the right result. Gioletti<sup>1</sup> has applied the method to some tautomeric compounds, and on the whole the results are not very encouraging. Acetoacetic ester has the molecular volume 126.9, while the calculated<sup>2</sup> volume for the enolic form is 127.9 and that for the ketonic structure is 132.8. Accordingly it might be supposed that the sample consisted entirely of the enolic tautomeride; but this is contrary to chemical experience and to the evidence from other physical sources.

### Refractivity.

Refractivity is both additive and constitutive.<sup>3</sup> The molecular refraction of a compound is the sum of the refraction equivalents of the elements which enter into the compounds, modified by the manner of combination. So by an examination of their refractive equivalent of a substance we may gain a knowledge about the molecular condition of the substance.

Molecular refractivity of a solid electrolyte is slightly altered by solution in water. The behavior of different salts is not uniform, some increase and others decrease in refractivity on passing into solution. The effect of dilution is pronounced with concentrated solution. It tends to be constant with dilution and in a moderately dilute solution it becomes fairly constant.

We determined the molecular refractivity of various solutions of chromates, dichromates and chromic acid by Pulfrich's refractometer, using a sodium flame as the source of light. A certain amount of the substance was dissolved in water and the refractive index and density of the solution were taken. From this the refractive equivalent,  $n - 1/d = m$  was calculated, where  $n$  is the refractive coefficient,  $d$  the density and  $m$

<sup>1</sup> *Gazz. chim. ital.*, 34, 208 (1904).

<sup>2</sup> Traube, *Ber.*, 29, 1715 (1896).

<sup>3</sup> Gladstone, *Proc. Roy. Soc.*, 439 (1868); 60, 140 (1896); Gladstone and Hibbert, *Trans. Chem. Soc.*, 67, 831 (1895).

the molecular weight of the compound. The refractive equivalent of the dissolved salt is obtained by deducting from the refractive equivalent of a solution of the form  $s + p\text{H}_2\text{O}$ , where  $s$  signifies one molecule of the salt—the value which corresponds with  $p \times \text{H}_2\text{O}$ . That is the refractive equivalent of the salt =  $\frac{u - I}{d} (m + x) - \frac{u' - I}{d'} x$ , where  $u$  is the refractive coefficient of the salt solution,  $d$  its density,  $m$  the molecular weight of the salt,  $x$  the weight of the solvent containing the gram molecular weight of the salt,  $u'$  the refractive coefficient of the solvent and  $d'$  its density.

TABLE IV.  
Chromic Acid.

Density.	$\mu$ of solution.	$\mu'$ of water.	Acid per cc. calculated as $\text{H}_2\text{CrO}_4$ .	Refractive equiv.	Acid per cc. cal. as $\text{H}_2\text{Cr}_2\text{O}_7$ .	Refractive equiv.
1.01480	1.336765	1.33174	0.02420	39.7	0.0225	73.4
1.00749	1.33431	1.33182	0.01210	39.1	0.01125	72.5
1.00507	1.33347	1.33174	0.00806	39.7	0.0075	73.4
1.00382	1.33313	1.33182	0.00605	39.9	0.00562	73.8
1.00256	1.33259	1.33182	0.00403	39.4	0.00375	72.8
Av., 39.5						73.2

TABLE V.  
Potassium Chromate.

Density.	$\mu$ for solution.	$\mu'$ for water.	Salt per cc.	Refractive equivalent.
1.02340	1.33782	1.33182	0.02976	53.0
1.01184	1.33475	1.33182	0.01488	51.2
1.01449	1.33539	1.33182	0.018627	51.4
1.00728	1.33379	1.33182	0.009314	52.7
1.00361	1.33275	1.33182	0.0046567	52.9
Av.,				52.2

Potassium Dichromate.

Density.	$\mu$ of solution.	$\mu'$ of water.	Salt per cc. calculated as $\text{K}_2\text{Cr}_2\text{O}_7$ .	Refractive equivalent.
1.01859	1.336745	1.33197	0.027144	82.5
1.00932	1.33431	1.33193	0.013572	82.2
1.00465	1.33315	1.33195	0.006786	82.8
1.00303	1.33267	1.33193	0.004524	82.6
1.01909	1.33685	1.33197	0.028239	82.5
1.00990	1.33455	1.33197	0.014119	82.8
1.00497	1.33326	1.33197	0.00706	82.7
Av.,				82.6

In the present case the solvent is water, its density is taken to be unity at the temperature of the experiments, which was about 26°. The density of the solutions is of course determined at the same temperature. The refractivity of water used in the solution was observed separately each time

the refractivity of the solution was observed. It was found that the refractivity of the water varied from day to day very slightly, the maximum deviation being 1' (one minute) in the reading of the scale of the instrument which affected the refractive coefficient only in the fifth decimal place. This slight variation was evidently due to slight change of temperature and partly to errors of experiments.

Gladstone and others have found the refractive equivalent of potassium atom = 8.1 and of hydrogen in acids = 3.5. The refractive equivalent of hydrogen in water and other nonionizable substances is 1.5, but the value for hydrogen in strong acids is 3.5.<sup>1</sup> The difference between the refractive equivalents of 2 atoms of potassium and two atoms of hydrogen is therefore  $16.2 - 7 = 9.2$ . By similar lines of reasoning as indicated in the case of molecular solution volume we can expect the difference between the refractive equivalents of potassium dichromate and chromic acid, on the supposition that its formula is  $H_2Cr_2O_7$ , to be 9.2. By actual experiments we find the difference to be  $82.6 - 73.2 = 9.4$ . If the formula of chromic acid be  $H_2CrO_4$  we should get the same difference between the refractive equivalents of potassium chromate and chromic acid ( $H_2CrO_4$ ). By experiment we find it  $52.2 - 39.5 = 12.7$  in place of 9.2. The formula of chromic acid is therefore  $H_2Cr_2O_7$  and not  $H_2CrO_4$ . This is also the conclusion arrived at from the study of volume relations.

Thus we see that two most important physical properties of chromic acid in solution are in support of the formula  $H_2Cr_2O_7$ , which also seems to be the more probable one from various other investigations.

In a subsequent paper, some other physical properties will be discussed.

PHYSICOCHEMICAL LABORATORY,  
PRESIDENCY COLLEGE, CALCUTTA.  
IMPERIAL COLLEGE OF SCIENCE,  
LONDON.

---

#### NOTE.

**A Bottle for the Iodimetric Titration of Copper.**—Since L. W. Andrews<sup>2</sup> first described the use of iodate as a substitute for many iodimetric determinations, the method has been extended and is finding additional uses constantly. In technical practice particularly, the application to copper ores as described by Jamieson, Levy and Wells,<sup>3</sup> and by Brostrom<sup>4</sup> is finding much favor; in this method, there is formed hydrocyanic acid—a feature that militates against the use of the original shaking bottle as described by Andrews because of the pressure developed in shaking and the consequent forcible ejection of particles of liquid on removing the

<sup>1</sup> LeBlanc, *Z. physik. Chem.*, 4 (1889); Gladstone, *Phil. Mag.*, 15 (1870).

<sup>2</sup> *This Journal*, 25, 756 (1903).

<sup>3</sup> *Ibid.*, 30, 760 (1908).

<sup>4</sup> *Eng. Mining J.*, 98, 215 (1914).