deep, closed at top and bottom with Teflon-gasketed Kel-F plates for visibility. The top window was removable. Connections to a reflux condenser of coiled polyethylene tubing, to drainage and to an inlet for liquid HF were provided through magnesium fittings in the walls. These were protected from atmospheric moisture with anhydrous $CaSO_4$ and could be closed by means of magnesium bodied stopcocks with Teflon plugs held in place by spring tension. The drainage outlet was used for obtaining samples of supernate. The HF (General Chemical Company, sulfur-free) was led through a copper coil condenser to a cooled calibrated magnesium reservoir with a Kel-F window from which measured quantities of HF could be delivered to the cell. The cell itself was provided with a cooling coil which maintained the temperature close to −10°.

Thorough mixing of the solutions was ensured by use of a magnetic stirrer. The internal magnet was sealed in a polyethylene capsule for protection.

The Nickel–Acetonitrile Complex.—A portion of pure nickel powder weighed with the magnet, and known volume of acetonitrile, measured by pipet, were placed in the dry cell through the top window, which was then closed tightly. One hundred ml. of HF was now delivered to the cell and stirring begun. In most cases the evolution of hydrogen, brisk at first, was no longer observable after 30 minutes. Stirring was maintained for a longer period (Table III) to ensure attainment of equilibrium. When equilibrium was deemed to have been reached, the cell was drained and washed out with HF until the washes were colorless. The magnet with the unreacted nickel clinging to it was then removed quickly to an anhydrous potassium fluoride desiccator and subsequently weighed. From the loss in weight of the nickel the concentration of nickel in solution was calculated. In two blank runs in the absence of acetonitrile and with different weights of nickel, it was found that complete transfer of the nickel could be accomplished by this method. Because of the formation of a fluoride coating on the metal, the weight increased each time exactly 3.62%, agreeing within the accuracy of the analytical balance. All weights of nickel found during the course of the investigation were corrected by this amount before calculation of the concentration of nickel in solution. The data so obtained are those appearing in Fig. 1 and Table III.

Reagents.—The complexing agents used were of reagent grade in all cases except that of the diglycolic acid, which was of technical grade.

The metal powders were of reagent grade. The metal fluorides were commercial materials obtained from Penn Salt. The $Ni(CO)_4$ was obtained from the International Nickel Company, and the $Fe(CO)_5$ from Chemical Commerce.

Analytical.—All analyses were done by the analytical laboratories of the Central Research Department of Minnesota Mining and Manufacturing Company.

In all cases where analyses were carried out on solutions, the solution of complexing agent was treated with an excess of the solid metallic fluoride.

St. Paul, Minn.

[Contribution from Cobb Chemical Laboratory, University of Virginia]

Heats of Formation of Potassium Chromate, Potassium Dichromate, Chromate and Dichromate Aqueous Ions. Entropy of Dichromate Ion

By C. N. Muldrow, Jr., and L. G. Hepler

Received February 28, 1957

We have determined the heats of solution of $K_2CrO_4(c)$, $K_2Cr_2O_7(c)$ and $(NH_4)_2Cr_2O_7(c)$ and the heats of reaction of $K_2Cr_2O_7(c)$ and $CrO_3(c)$ with aqueous alkali and of $K_2CrO_4(c)$ with aqueous acid. From the results of these determinations we have calculated the heats of formation of $K_2CrO_4(c)$, $K_2Cr_2O_7(c)$, $(NH_4)_2Cr_2O_7(c)$, $CrO_4^=(aq)$ and $Cr_2O_7^=(aq)$ to be, respectively, −331.9, −486.4, −425.0, −207.6 and −345.2 kcal./mole. From our heats of formation and reaction, equilibrium constants and entropy data from the literature, we have calculated the entropies of $Cr_2O_7^=(aq)$ and $HCrO_4^-(aq)$ to be 70.5 and 47.8 cal./deg. mole, respectively. The standard free energies of $CrO_4^=(aq)$, $Cr_2O_7^=(aq)$ and $HCrO_4^-(aq)$ have also been calculated to be −170.1, −303.4 and −179.0 kcal./mole, respectively.

Investigation of the experimental data on which the thermodynamic properties of $CrO_4^=(aq)$ and $Cr_2O_7^=(aq)$ as given by the Bureau of Standards,[1] Bichowsky and Rossini[2] and Latimer[3] are based showed that these values were not reliably known. Especially, it became apparent that the heats of formation of these ions and of various chromates and dichromates (*e.g.*, K_2CrO_4, $K_2Cr_2O_7$, etc.) were based on questionable heats of reaction of CrO_3 and heats of solution of chromates and dichromates. Calculation of standard heats of formation at 298°K. from the results of many of the pertinent earlier investigations is difficult because most of that work was carried out under such conditions that heats of dilution and heat changes in correcting observed heats of reaction to 298°K. are both large and uncertain. Therefore we have undertaken an investigation of the thermochemistry of $K_2Cr_2O_7(c)$, $Cr_2O_7^=(aq)$, $K_2CrO_4(c)$ and $CrO_4^=(aq)$ by means of solution calorimetry. This work also has involved the study of $CrO_3(c)$ and $(NH_4)_2Cr_2O_7(c)$.

Experimental

Our high-precision solution calorimeter used in previous investigations[4,5] has been improved by several changes. The rate of stirring has been increased and more efficient stirrers have been used. This improved stirring has markedly lessened the time required to attain thermal and reaction equilibrium in the calorimeter, without significantly changing the calorimetric drifts, and has therefore reduced extrapolation uncertainties. A second improvement has been more accurate timing of the heating periods. The calibrated stopwatch has been replaced by a Standard electrical timer read to 0.01 second. The timer is wired through a triple pole-double throw switch that is used to switch the electrical power from the dummy heater to the calorimeter heater. We estimate that the total uncertainty in elapsed time for the heating periods due to variation in the frequency of the local 60 cycle a.c. current, etc., is no more than 0.05 second.

All of the reactions investigated have been rapid. In every experiment the reaction was completed and steady after-period drifts were obtained less than five minutes after breaking the sample bulbs. The heating periods varied from 55–200 seconds.

All of the heats have been determined at 25.0 ± 0.3°.

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(1) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards, 1952.

(2) F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1936.

(3) W. M. Latimer, "Oxidation Potentials," Second Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

(4) R. L. Graham and L. G. Hepler, This Journal, **78**, 4846 (1956).

(5) C. N. Muldrow, Jr., and L. G. Hepler, *ibid.*, **78**, 5989 (1956).

Materials.—The potassium dichromate ($K_2Cr_2O_7$) used was Mallinckrodt primary standard analytical reagent and the potassium chromate (K_2CrO_4) was Mallinckrodt A.C.S. Reagent. The ammonium dichromate [$(NH_4)_2Cr_2O_7$] was Mallinckrodt analytical reagent. All of these reagents were thoroughly dried before use.

Two brands of CrO_3 were used: Coleman and Bell C.P. and Baker and Adamson Reagent. Samples of both were analyzed by reaction of CrO_3 with standardized ferrous ammonium sulfate solution and titration of the excess ferrous ions with standardized potassium dichromate solution. The titrations were carried out in sulfuric acid–phosphoric acid solution with sodium diphenylaminesulfonate indicator. The two samples of CrO_3 were found to be 99.7 and 99.6% pure, respectively. By making use of a dry box, we were able to load CrO_3 into a weighed calorimeter bulb, weigh the bulb plus CrO_3 and fasten the bulb to the calorimeter stirrer without exposing the CrO_3 to the atmosphere.

The perchloric acid and potassium hydroxide solutions used in the calorimetric runs were prepared by dilution of previously standardized stock acid and alkali solutions.

Results

The difference in the heats of formation of $Cr_2O_7^=(aq)$ and $CrO_4^=(aq)$ was determined in two different ways, each of which involved the calorimetric determination of two different heats of reaction. We have expressed the difference in these heats of formation in terms of the standard heat of reaction 1 at infinite dilution. This has been done for two

$$2CrO_4^=(aq) + 2H^+(aq) = Cr_2O_7^=(aq) + H_2O \quad \Delta H_1^\circ \qquad (1)$$

purposes: (a) for the calculation of several heats of formation, (b) for the calculation of ΔS_1° from ΔH_1° and ΔF_1°. Because the entropy of every species in (1) except $Cr_2O_7^=(aq)$ is known, a value for ΔS_1° makes possible the calculation of the partial molal entropy of $Cr_2O_7^=(aq)$.

The first method for the experimental investigation of the heat of reaction 1 involved determination of the heat of solution of potassium chromate to give potassium and chromate ions and determination of the heat of reaction of potassium chromate with aqueous perchloric acid to give potassium and dichromate ions. The calorimetric reactions are given by eq. 2 and 3, respectively. In the case of reaction 3, the solutions were in every experiment

$$K_2CrO_4(c) = 2K^+(aq) + CrO_4^=(aq) \quad \Delta H_2 \qquad (2)$$

$$K_2CrO_4(c) + H^+(aq) = 2K^+(aq) + {}^1/_2Cr_2O_7^=(aq) + {}^1/_2H_2O \quad \Delta H_3 \qquad (3)$$

so dilute that no potassium perchlorate was precipitated.

The results of these experiments are given in Table I. The starred heats for reaction 2 indicate solution in 7.5×10^{-4} *M* potassium hydroxide and the others refer to solution in pure water.

TABLE I

HEAT OF SOLUTION (2)				HEAT OF REACTION (3)		
Moles K_2CrO_4/950 ml. soln.	ΔH_2 (kcal./mole)	Moles K_2CrO_4/950 ml. soln.	ΔH_2 (kcal./mole)	Moles K_2CrO_4 $\times 10^3$/950 ml. soln.	Moles $HClO_4$ $\times 10^3$/950 ml. soln.	ΔH_3 (kcal./mole K_2CrO_4)
0.01084	4.32	0.02571	4.32	4.724	5.256	4.37
.01506	4.30	.02714	4.35*	8.432	9.557	4.03
02064	4.33*			10.427	14.34	3.97
				11.463	14.34	3.89
				14.481	19.11	3.76
				15.604	19.11	3.77

We have extrapolated the heats of (2) and (3) to infinite dilution in order to obtain ΔH_2° and ΔH_3°, which are, respectively, 4.2 and 4.6 kcal./mole K_2CrO_4. We have also calculated $\Delta H_1^\circ = 2\ \Delta H_3^\circ - 2\ \Delta H_2^\circ = +0.8$ kcal. The estimated uncertainty in the measured heats ΔH_2 and ΔH_3 is 0.05 kcal./mole and the uncertainties in the extrapolated values for ΔH_2° and ΔH_3° are 0.1 and 0.2 kcal., respectively.

The second method for the experimental investigation of the heat of reaction 1 involved the heat of solution of potassium dichromate to give potassium and dichromate ions and determination of the heat of reaction of potassium dichromate with aqueous potassium hydroxide to give potassium and chromate ions. The calorimetric reactions are given by eq. 4 and 5, respectively.

$$K_2Cr_2O_7(c) = 2K^+(aq) + Cr_2O_7^=(aq) \qquad \Delta H_4 \quad (4)$$

$$K_2Cr_2O_7(c) + 2OH^-(aq) = 2K^+(aq) + 2CrO_4^=(aq) + H_2O \quad \Delta H_5 \quad (5)$$

The results of these experiments are given in Table II. All of the heats of solution of potassium dichromate to give $Cr_2O_7^=(aq)$, except one, were carried out in very dilute perchloric acid (10^{-3} to 10^{-4} *M*). The starred run indicates solution in pure water. No potassium perchlorate was precipitated in any of these runs.

TABLE II

HEAT OF SOLUTION (4)				HEAT OF REACTION (5)		
Moles $K_2Cr_2O_7$/ $\times 10^3$/950 ml. soln.	ΔH_4 (kcal./mole)	Moles K_2CrO_7 $\times 10^3$/950 ml. soln.	ΔH_4 (kcal./mole)	Moles $K_2Cr_2O_7$ $\times 10^3$/950 ml. soln.	Moles KOH $\times 10^3$/950 ml. soln.	ΔH_5 (kcal./mole $K_2Cr_2O_7$)
1.139	19.87	5.330	18.72	7.221	17.04	−7.29
2.005	19.77	5.342	18.80	7.234	17.04	−7.29
2.610	19.86	5.806	18.60*	8.747	24.34	−7.39
3.445	19.18	5.829	18.76	10.100	48.72	−7.36
5.199	18.80	6.870	18.59	15.320	48.72	−7.45
				19.999	48.72	−7.40

We have extrapolated the heats of reactions 4 and 5 to infinite dilution in order to obtain ΔH_4° and ΔH_5°, which are, respectively, 20.0 and −7.3 kcal./mole $K_2Cr_2O_7$. We estimate the uncertainties in the measured heats ΔH_4 and ΔH_5 to be 0.1 and 0.05 kcal./mole. The estimated uncertainties in the extrapolated values for ΔH_4° and ΔH_5° are 0.2 and 0.1 kcal. In order to calculate ΔH_1° from our values for ΔH_4° and ΔH_5° we need to know the standard heat of reaction 6 and have therefore

$$H^+(aq) + OH^-(aq) = H_2O(l) \quad \Delta H_6^\circ \qquad (6)$$

calculated $\Delta H_6^\circ = -13.36$ kcal. from Bureau of Standards[1] heats of formation. From the relation $\Delta H_1^\circ = \Delta H_4^\circ + 2\ \Delta H_6^\circ - \Delta H_5^\circ$ we have calculated $\Delta H_1^\circ = 0.6$ kcal. This heat is in satisfactory accord with the value obtained by our first method and we take as a best value $\Delta H_1^\circ = +0.7$ kcal. It is difficult to estimate the uncertainty in this heat because so much of the uncertainty arises from the various extrapolations to infinite dilution rather than from calorimetric or reaction difficulties. However, we believe that the uncertainty in the average ΔH_1° given above is less than 0.3 kcal.

A large number of workers have investigated the various equilibria between $CrO_4^=(aq)$, $Cr_2O_7^=(aq)$ and intermediate species. In particular, Neuss and Rieman,[6] Tong and King,[7] and Davies and Prue[8] have investigated the equilibrium constant for reaction 7 and have obtained values in

$$Cr_2O_7^{=}(aq) + H_2O = 2HCrO_4^-(aq) \quad K_7 \qquad (7)$$

satisfactory agreement. On the basis of these investigations we take $K_7 = 0.029$ and $\Delta F_8^\circ = +2.10$ kcal. Neuss and Rieman[6] also have investigated the acid dissociation of hydrogen chromate ion ($HCrO_4^-$) as in eq. 8. They report K_8

$$HCrO_4^-(aq) = CrO_4^{=}(aq) + H^+(aq) \quad K_8 \qquad (8)$$

$= 3.2 \times 10^{-7}$ and we calculate $\Delta F_8{}^\circ = +8.86$ kcal.

We have used these equilibrium constants and free energies to calculate $K_1 = 3.37 \times 10^{14}$ and $\Delta F_1^\circ = -19.82$ kcal. We further calculate $\Delta S_1^\circ = (\Delta H_1^\circ - \Delta F_1^\circ)/T = 68.8$ cal./deg.mole. We take entropies of H_2O, H^+ and $CrO_4^{=}$ from the Bureau of Standards and calculate from ΔS_1° that the partial molal entropy of $Cr_2O_7^{=}(aq)$ is 70.5 cal./deg. mole.

The heats of solution and reaction reported above are sufficient to determine the heat of hydrolysis of $Cr_2O_7^{=}(aq)$ to $CrO_4^{=}(aq)$ and thence the entropy of $Cr_2O_7^{=}(aq)$. However, in order to obtain heats of formation of $CrO_4^{=}(aq)$, $Cr_2O_7^{=}(aq)$ and the potassium salts, it is necessary to carry out at least one additional calorimetric investigation. Accordingly, we have measured the heat of reaction of CrO_3 with aqueous potassium hydroxide to give chromate ions. This heat of reaction, with the heat of formation of CrO_3 and the Bureau of Standards heats of formation of the other substances involved, suffices to give us the heat of formation of $CrO_4^{=}(aq)$. The calorimetric reaction is given by eq. 9 and the results are given in Table

$$CrO_3(c) + 2OH^-(aq) = CrO_4^{=}(aq) + H_2O \quad \Delta H_9 \qquad (9)$$

III. We have extrapolated these heats to infinite dilution and take $\Delta H_9^\circ = -28.0$ kcal./mole CrO_3. The estimated uncertainty in ΔH due to extrapolation to infinite dilution and the small amount of impurity in the CrO_3 is 0.2 kcal.

TABLE III

REACTION OF $CrO_3(c)$ WITH $OH^-(aq)$

Moles $CrO_3(c) \times 10^3$/ 950 ml. soln.	Moles $OH^- \times 10^3$/ 950 ml. soln.	ΔH_9 kcal./ mole CrO_3
4.881	12.11	−28.01
5.692	14.60	−28.09
7.447	17.04	−28.10

The largest error involved in this procedure comes from the uncertainty in the heat of formation of CrO_3. This heat of formation depends upon the heat of oxidation of Cr_2O_3 to CrO_3 as determined by Roth and Becker[9] and on the heat of formation of Cr_2O_3. The heat of formation of Cr_2O_3 has been investigated recently by Mah[10] (combustion calorimetry) and by Ramsey and co-workers[11] (temperature coefficient of dissociation pressure), who have discussed the earlier work on Cr_2O_3. On the basis of the results of these investigations we have chosen −270.0 kcal./mole as the standard heat of formation of $Cr_2O_3(c)$.

This is identical with the heat of formation chosen earlier by Brewer[12] and close to that adopted by the Bureau of Standards[1] (−269.7). We calculate from this heat of formation and Roth and Becker's heat of oxidation that the heat of formation of $CrO_3(c)$ is −138.0 kcal./mole.

We have used the above values of ΔH_9° and the heat of formation of CrO_3 with the Bureau of Standards[1] heats of formation of H_2O and $OH^-(aq)$ to calculate the standard heat of formation of $CrO_4^{=}(aq)$ to be −207.6 kcal./mole. By combining this heat of formation with heats of formation of $K^+(aq)$, H_2O and $OH^-(aq)$ as given by the Bureau of Standards[1] and our ΔH_1°, ΔH_2°, ΔH_3°, ΔH_4° and ΔH_5° we have calculated the heats of formation of $Cr_2O_7^{=}(aq)$, $K_2CrO_4(c)$ and $K_2Cr_2O_7(c)$ to be, respectively, −346.2, −331.9 and −486.4 kcal./mole.

We have also determined the heat of solution of $(NH_4)_2Cr_2O_7$ in very dilute perchloric acid (10^{-3} to 10^{-4} *M*). The calorimetric reaction is given by eq. 10 and the results are given in Table IV.

$$(NH_4)_2Cr_2O_7(c) = 2NH_4^+(aq) + Cr_2O_7^{=}(aq) \quad \Delta H_{10} \qquad (10)$$

We have extrapolated the observed heats to infinite dilution to obtain $\Delta H_{10}^\circ = 15.3 \pm 0.2$ kcal./mole. This heat was used with our heat of formation of $Cr_2O_7^{=}(aq)$ and the Bureau of Standards[1] value for $NH_4^+(aq)$ to calculate the heat of formation of $(NH_4)_2Cr_2O_7(c)$ to be −425.0 kcal./mole. Kapustinskii and Shidlovskii[13] investigated the heat of combustion of $(NH_4)_2Cr_2O_7$ to give N_2, H_2O and Cr_2O_3 and reported the heat of formation of $(NH_4)_2Cr_2O_7$ to be −430 ± 6 kcal./mole. This is seen to be in satisfactory agreement with our heat of formation. In so far as our work is concerned, the only likely large source of error is the appreciable uncertainty in the heat of formation of CrO_3. The combustion work avoids this difficulty and therefore it would be desirable to have a better heat of combustion of $(NH_4)_2Cr_2O_7$.

TABLE IV

HEAT OF SOLUTION OF $(NH_4)_2Cr_2O_7(c)$

Moles $(NH_4)_2Cr_2O_7(c) \times 10^3$/ 950 ml. soln.	ΔH_{10} (kcal./mole $(NH_4)_2Cr_2O_7$)
4.256	15.21
4.976	15.02
8.426	14.59
9.610	14.55

We have calculated the standard free energies of formation of $CrO_4^{=}(aq)$ and $Cr_2O_7^{=}(aq)$ from our heats of formation and entropies to be, respectively, −170.1 and −303.4 kcal./mole. It would also be desirable to calculate the standard oxidation potential of the $Cr^{+++}/Cr_2O_7^{=}$ couple. There are several possible ways to carry out this calculation. The heat of formation of $Cr^{+++}(aq)$ can be used with an estimated entropy to calculate the

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(6) J. D. Neuss and W. Rieman, THIS JOURNAL, **56**, 2238 (1934).

(7) J. Y. Tong and E. L. King, *ibid.*, **75**, 6180 (1953).

(8) W. G. Davies and J. E. Prue, *Trans. Faraday Soc.*, **51**, 1045 (1955).

(9) W. A. Roth and G. Becker. *Z. physik. Chem.*, **A145**, 464 (1929).

(10) A. D. Mah, THIS JOURNAL, **76**, 3363 (1954).

(11) J. N. Ramsey, D. Caplan and A. A. Burr, *J. Electrochem. Soc.*, **103**, 135 (1956).

(12) L. Brewer, *Chem. Revs.*, **52**, 27 (1953).

(13) A. F. Kapustinskii and A. A. Shidlovskii, *C. A.*, **50**, 9849*c* (1956).

free energy of formation of Cr^{+++}(aq) which can then be combined with our free energy of formation of $Cr_2O_7^{=}$(aq) to give $\Delta F°$ and $E°$ for the $Cr^{+++}/Cr_2O_7^{=}$ couple. Or the heat of reduction of $Cr_2O_7^{=}$(aq) to Cr^{+++}(aq) can be combined with an estimated entropy of Cr^{+++}(aq), and our entropy of $Cr_2O_7^{=}$(aq) to give $\Delta F°$ and $E°$ for the $Cr^{+++}/Cr_2O_7^{=}$ couple. Data from the literature for the pertinent heats[3,14] are so unreliable as to make these calculations virtually meaningless.

From the results of the investigation by Davies and Prue[8] of the temperature dependence of the equilibrium constant for reaction 7 we calculate ΔS_7° = 8.5 cal./deg. mole $Cr_2O_7^{=}$ and ΔH_7° = 4.64 kcal./mole $Cr_2O_7^{=}$. These data have been combined with our heat of formation and entropy of $Cr_2O_7^{=}$(aq) and the National Bureau of Standards values for water to give the heat of formation of $HCrO_4^-$(aq) as −205.0 kcal./mole and the entropy as 47.8 cal. deg./mole. We also have calculated the standard free energy of formation of $HCrO_4^-$ to be −179.0 kcal./mole.

Discussion

Latimer[3] and the National Bureau of Standards[1] have taken the entropy of $HCrO_4^-$(aq) to be 16.5 cal./deg.mole. Our value (47.8) is much more nearly in accord with what one should expect from comparison with MnO_4^- (45.4),[3] ReO_4^- (48.3),[15] and ClO_4^- (43.2).[3] We also see that the entropy of ionization of $HCrO_4^-$ (−38.6) as calculated from our entropy is in accord with the entropies of ionization of HSO_4^- (−26.2), HSO_3^- (−33), $H_2PO_4^-$ (−29.9), HCO_3^- (−35.4) as taken from Latimer.[3]

Our heat of solution of K_2CrO_4(c) (ΔH_2°) is in good agreement with the results obtained by earlier workers.[1] Our heat of solution of $K_2Cr_2O_7$(c) (ΔH_4°) is about 3 kcal./mole more positive than heats reported by earlier investigators.[1] It is impossible to compare our heats of reaction of K_2CrO_4(c) with H^+(aq) (ΔH_3°) and of $K_2Cr_2O_7$(c) with OH^-(aq) (ΔH_5^0) with the older heats[1,2] because the older work was carried out in relatively concentrated solutions and at temperatures lower than 25°. Our heat of reaction of CrO_3(c) with OH^-(aq) (ΔH_9°) is several kcal./mole more exothermic than earlier heats. We attribute this to the fact that the older work was carried out in more concentrated solutions at temperatures lower than 25° and possibly with less pure CrO_3.

Acknowledgments.—We are pleased to express our gratitude to Mr. Robert L. Graham for help with some of the calorimetric work and to the Research Corporation for financial assistance.

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[14] M. W. Evans, Paper 3.30 "Nat. Nuclear Energy Series," Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 282.

[15] J. W. Cobble, G. D. Oliver and W. T. Smith, Jr., THIS JOURNAL, **75**, 5786 (1953).

CHARLOTTESVILLE, VA.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

A Copper Analog of the Alkali Tungsten Bronzes

BY LAWRENCE E. CONROY AND M. J. SIENKO[1]

RECEIVED FEBRUARY 5, 1957

Non-stoichiometric solids of the form Cu_xWO_3 have been prepared by electrolytic reduction at 800° of molten mixtures of $CuWO_4$ and WO_3. Copper content has been varied from $x = 0.26$ to $x = 0.77$. Two kinds of crystals have been found—orthorhombic with a = 3.88 Å., b = 3.73 Å., and c = 7.74 Å., taken from the preparation for which $x = 0.26$, and triclinic with a = 5.85 Å., b = 6.65 Å., c = 4.88 Å., α = 134°45′, β = 91°40′, and γ = 93°37′, taken from the preparation for which $x = 0.77$. The molar magnetic susceptibility at 26° of the powder for which $x = 0.26$ was observed to be $+34 \pm 1 \times 10^{-6}$. Conductivity measurements from −160° to +80° made on single triclinic crystals taken from the preparation for which $x = 0.77$ showed typical semi-conductor behavior. At 26° the specific resistance was 12.6 ohm-cm. perpendicular to the c-axis and 17.2 ohm-cm. parallel to the c-axis. Energies of activation for the conduction process were found to be 0.147 and 0.149 electron volt, respectively. Attempts to measure the Hall voltage of a single crystal indicated 13 cc. per coulomb as an upper limit for the Hall constant, from which it is deduced that the minimum concentration of current carriers is 5×10^{17} particles per cc. It is proposed that these materials are analogous to the tungsten bronzes.

The alkali tungsten bronzes are non-stoichiometric solids of composition M_xWO_3, where M is an alkali metal and x can vary from 0 to 1. Although known since their discovery by Wöhler[2] in 1824, it is only recently that these bronzes have been well characterized.[3] The sodium tungsten bronzes, for which the data are most extensive, have been shown to have a cubic perovskite structure[4] if x is greater than about 0.35, a high electronic[5] conductivity which passes through a maximum[6] at x = 0.75, and a feeble paramagnetism[7,8] which is independent of temperature.[8] The Hall coefficient is negative, and its magnitude indicates that there is approximately one free electron per sodium atom.[5] Chemically, all the alkali tungsten bronzes are quite inert, being attacked only by strong alkalies.

As discussed in a previous paper,[9] the tungsten

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[1] On leave of absence at the Laboratorie de Chimie Minérale, University of Toulouse, Toulouse, France.

[2] F. Wöhler, *Pogg. Ann.*, **2**, 350 (1824).

[3] G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); G. Hägg, *Nature*, **135**, 874 (1935); M. F. Straumanis and S. S. Hsu, THIS JOURNAL, **72**, 4027 (1950); A. Magneli, *Arkiv. Kemi*, **1**, 213 (1949); A. Magneli and B. Blomberg, *Acta Chem. Scand.*, **5**, 377 (1951).

[4] W. F. de Jong, *Z. Krist.*, **81**, 314 (1932).

[5] E. J. Huibregtse, D. B. Barker and G. C. Danielson, *Phys. Rev.*, **84**, 142 (1951).

[6] B. W. Brown and E. Banks, *ibid.*, **84**, 609 (1951).

[7] F. Kupka and M. J. Sienko, *J. Chem. Phys.*, **18**, 1296 (1950).

[8] P. M. Stubbin and D. P. Mellor, *Proc. Roy. Soc. N. S. Wales*, **82**, 225 (1948).

[9] L. E. Conroy and M. J. Sienko, THIS JOURNAL, **74**, 3520 (1952).