The results of Noyes and Garner are also compatible with our interpretation. If the dimers involve oxide or hydroxide bridges, increasing the nitric acid concentration will tend to decrease the free cerium(IV) concentration by forming nitrate complexes but at the same time will tend to increase free cerium(IV) by decreasing the extent of dimerization and apparently the two effects are comparable. This of course is similar to the suggestion of Yost, Russell and Garner[2] involving hydroxide complexes. The very small change in the standard formal potential when the ratio of Ce^{IV} to Ce^{III} is varied keeping total cerium constant can be accounted for on the basis of the fact that as the ratio is changed, the expected change in free cerium(IV) which would result from a change in the per cent. of dimerization of cerium(IV) is approximately balanced by a change in the amount of cerium(IV)–cerium(III) dimerization. The small residual change is in the direction which would be expected if the cerium(IV)–cerium(IV) association constant were larger than the cerium(IV)–cerium(III) association constant.

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BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

The Thermal Decomposition of Aqueous Chromic Acid and Some Properties of the Resulting Solid Phases[1]

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Aqueous chromic acid solutions in closed containers evolve oxygen at an appreciable rate at 300 to 325°. The equilibrium has been investigated at oxygen pressures between 50 and 200 atmospheres. The decomposition is first order at 300° but it is approximately of order $1^1/_2$ at 325°. The solid decomposition products are chromium dioxide (cassiterite structure, $a_0 = 4.421 \pm 0.002$ Å., $c_0 = 2.916 \pm 0.001$ Å.) and $HCrO_2$ (diffraction symbol $\bar{3}mR$---, $a_0 = 4.787 \pm 0.005$ Å., $\alpha = 36.3 \pm 0.1°$, $Z = 1$).

Introduction

The kinetics of the decomposition of chromic acid in sulfuric acid solutions and the effect of the resulting chromic sulfate have been studied by Snethlage[2] and Aynsley[3] in the range 14 to 100% oleum. Birjukov[4] observed that boiling aqueous chromic acid evolved oxygen, but no measurements appear to have been made of the decomposition equilibrium or kinetics in this system, nor have the decomposition products been identified. Such data are reported herein as the result of experiments conducted on aqueous chromic acid solutions in a closed system at 300 and 325°. The solid decomposition products, chromium dioxide and $HCrO_2$, were studied by chemical, X-ray, optical and morphological methods.

Thermal Decomposition of Aqueous Chromic Acid

Experimental.—The solutions used in the experiments were prepared from Mallinckrodt Analytical Reagent CrO_3 and distilled water, and the chromate content of all solutions used in the experiments or obtained therefrom was determined volumetrically. The experiments were performed with the solutions contained in bombs made of Type 347 Stainless Steel. The inside of the bomb had a protective platinum cladding in only one experiment but in all experiments corrosive attack on the wall was slight. Temperatures were measured with a calibrated chromel–alumel thermocouple inserted in a well in the bomb wall and connected to a Brown recorder. The recorder controlled the voltage to the electric furnace containing the bomb, thus controlling the bomb temperature to within $^1/_2$° of the desired temperature. The upper end of the bomb was connected to a water-filled Heise pressure gage by capillary tubing of negligible volume.

For each equilibration the bomb was filled exactly half full with the chromic acid solution to be equilibrated at the elevated temperature. On reaching the temperature at which equilibration was to be made the bomb was rocked continuously. It is estimated that in each equilibration less than 1% of the hexavalent chromium had decomposed by the time the equilibration temperature had been reached. No samples were taken during the equilibration period. Hence the reaction proceeded in a closed system. Pressure readings indicated the degree of completion of the reaction and provided information on reaction kinetics. After constant pressure readings over several days indicated that equilibrium had been attained, the bomb was allowed to cool to room temperature, the liquid phase was filtered and analyzed for its hexavalent chromium content, and the solid phases were identified.

Results and Conclusions.—Data pertinent to the equilibrium state are presented in Table I. In each equilibration all or part of the oxygen present at equilibrium had been produced by the decomposing chromic acid. Column E of Table I was

TABLE I

THERMAL DECOMPOSITION OF AQUEOUS CHROMIC ACID

	A	B	C	D	E	F
Run	CrO_3 molality[a] of the aqueous charge	Gaseous charge (room temp.)	Temp. (°C.) at equilibration	CrO_3 molality[a] as removed from bomb	Equil. CrO_3 molality[a], equilibration temp.	Equil. O_2 pressure (atm.), equilibration temp.
1	1.590	Helium, 1 atm.	300	0.116	0.120	50.5
2	3.348	Helium, 1 atm.	300	.473	.489	84.8
3	3.348	Oxygen, 68.4 atm.	300	.784	.810	209.2
4	3.348	Helium, 1 atm.	325	.384	.400	91.5

[a] The molality is the number of gram formula weights of CrO_3 per 1000 grams of water.

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] H. C. S. Snethlage, *Rec. trav. chim.*, **57**, 1341 (1938); **57**, 459 (1938); **55**, 874 (1936).

[3] E. E. Aynsley, *J. Chem. Soc.*, 368 (1950).

[4] N. D. Birjukov, *J. Gen. Chem. U. S. S. R.*, **10**, 942 (1940).

calculated from column D by correcting for water lost to the vapor phase at the equilibration temperature.[5] For this purpose the steam pressure was estimated from the initial pressure of the solution before appreciable decomposition had taken place, and the expansion of the liquid was taken to be 1.30 at 300° and 1.40 at 325° from observations on such solutions in sealed silica glass tubes. Column F of Table I is the difference between gage pressure at equilibrium and gage pressure before decomposition. Pressure data are presented in Fig. 1.

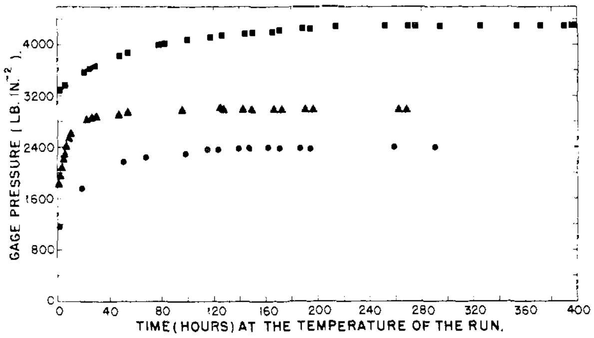

Fig. 1.—Representative pressure data: ●, run 2 at 300°; ■, run 3 at 300°; ▲, run 4 at 325°.

The solutions obtained from the equilibrations possessed after filtering the orange color characteristic of aqueous chromic acid solutions but there sometimes was a brown tinge possibly due to a small amount of dissolved chromium having an oxidation state of less than six. The bulk of the decomposition product was solid $HCrO_2$, occurring as a layer of dark material on the bomb wall. This is the phase described by Shafer and Roy[6] as stable under these conditions in the system Cr_2O_3–H_2O. The material adjacent to the wall was earlier-formed chromium dioxide, covered with a larger amount of $HCrO_2$. It is thought the aqueous phase came to equilibrium with the latter solid to yield the data of Table I.

It seems reasonable to represent the decomposition products by solid $HCrO_2$, oxygen and water, but it is doubtful if Table I contains enough data to determine uniquely the ionic form of the chromic acid at 300°. It is certain that the effects of polymerization, acid ionization and varying ionic strength are among the important factors in explaining the equilibrium data. Studies at 25° by Tong and King[7] indicate that a dominant species is the dimer in the form of the dichromate ion $Cr_2O_7^{-2}$ even in chromic acid solutions more dilute than the equilibrated solutions of the present study. More highly condensed acids might also be present at room temperature in the latter solutions.[8,9] A three molal chromic acid solution sealed in a silica glass capillary tube and heated underwent a change in color from orange to deep scarlet as it was heated to 200° and above, although no perceptible decomposition had taken place. The color intensification probably is associated with increased polymerization because the red color of solid chromium trioxide and solid tetrachromates is more pronounced than that of solid dichromates.[8] Hence it seems likely that the average polymerization of the chromic acid in the solutions of Table I at 300 and 325° is well beyond the dimeric stage. In the acids H_2CrO_4 and $H_2Cr_2O_7$ as well as H_3PO_4 and $H_4P_2O_7$ there is one strongly ionizing proton per chromium or phosphorus atom.[7] If this trend were extended to the present solutions at 300° the average Cr(VI) species might be represented by the polymer $(HCrO_4)_n^{-n}$ of acid chromate ion, although the hydration of the polymeric anion would be unknown. Thus the decomposition reaction would be represented by

$$nH^+ + (HCrO_4)_n^{-n} = nHCrO_2(s) + 3n/4O_2(g) + n/2H_2O(l) \quad (1)$$

In order to correlate any such postulated equilibrium as that of equation 1 with the data at 300° in Table I, activity coefficients would have to be estimated for the ionized species. Such estimates could be attempted by using the Debye–Hückel equation[10] in the form

$$\log \gamma_{\pm} = \frac{-1.283 \times 10^6 z_+ z_- (DT)^{-3/2} \sqrt{\Gamma}}{1 + 35.57\mathring{a} (DT)^{-1/2} \sqrt{\Gamma}} \quad (2)$$

where $\mathring{a}$ is the mean distance of closest ionic approach in Å., z_+ and z_- are ionic charges, and Γ is the ional concentration.

Values for the dielectric constant D could be taken from the values for pure water as calculated from the equation of Akerlof and Oshry[11] giving $D = 19.56$ at 300° and 16.09 at 325°. These low values of D give rise to low values of DT in equation 2, resulting in calculated activity coefficients far less than unity. If $\mathring{a}$ in equation 2 is assumed to be 5 Å. a value of 4 for n in equation 1 would allow calculation of an equilibrium constant from which the three equilibrium molalities at 300° in Table I could be calculated within 25%. (The value chosen for n would not be changed significantly if the equilibrium solid phase were assumed to be CrO_2.) However, determination of the best value for n depends on the value used for $\mathring{a}$. It is questionable if equation 2 is suitable for a highly charged ion like $(HCrO_4)_4^{-4}$. An extended form[10] of the Debye–Hückel equation might be preferable to equation 2, but it would be subject to some of the same uncertainties, such as distribution of charge in the polymeric anion. The equilibration concentrations of runs 2 and 4 of Table I indicate that the change of heat content or enthalpy, ΔH, for the decomposition reaction is slightly positive, *i.e.*, the reaction is slightly endothermic.

An attempt was made to reproduce one of the equilibrium conditions of Table I starting with solid $HCrO_2$ and chromium dioxide, water and

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(5) J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1951.

(6) M. W. Shafer and R. Roy, *Z. anorg. u. allgem. Chem.*, **276**, 275 (1954).

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(9) M. C. Sneed and J. L. Maynard, "General Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1942, p. 1008.

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd edition, Reinhold Publ. Corp., New York, N. Y., 1950, pp. 36–41.

(11) G. C. Akerlof and H. I. Oshry, THIS JOURNAL, **72**, 2844 (1950).

oxygen. A platinum-clad bomb was used and the mode of equilibration was similar to that of the runs in Table I. After 312 hours at 300° under an oxygen pressure of 100 ± 4 atmospheres the concentration of chromate reached only 0.030 molal. This low concentration is believed to be due to a slow recombination rate. At the end of the experiment an appreciable amount of both $HCrO_2$ and chromium dioxide remained.

The data of Fig. 1 yield information on the kinetics of the decomposition because, to a close approximation, the molality of the chromic acid that has decomposed is linearly related to the pressure of oxygen that has been produced; *i.e.*

$$[Cr(VI)]_0 - [Cr(VI)]_t = \text{(constant) (no. of atm. pressure of oxygen produced)} \quad (3)$$

The hexavalent chromium molality at the beginning of decomposition, $[Cr(VI)]_0$, and its value after equilibration, $[Cr(VI)]_{eq}$, can be used with the difference between the final and initial pressure readings to allow evaluation of the constant in equation 3. The hexavalent chromium molality at any time t after the equilibration is begun, $[Cr(VI)]_t$, can then be calculated from equation 3 knowing the pressure at time t. The validity of equation 3 rests in part upon the assumption that Henry's law is obeyed for oxygen in these solutions. Pray, Schweickert and Minnich[12] have shown that this is the case for oxygen in contact with pure water at these temperatures. It is also assumed that the total volume of the condensed phases does not change during the decomposition. The slight diluting effect on the liquid phase of water liberated by the decomposition (equation 1) is ignored.

For each equilibration run the decomposition rate over most of the experimental range can be represented as

$$\frac{d[Cr(VI)]_t}{dt} = -k([Cr(VI)]_t - [Cr(VI)]_{eq})^r \quad (4)$$

The data of Fig. 2 all were obtained with the same unclad stainless-steel bomb. The data of runs 2 and 3 at 300° indicate that, in the first stages at least, the decomposition reaction was of the first order, *i.e.*, $r = 1$ in equation 4. The reason for the difference in the decomposition half-times is unknown; possibly it is due to the different condition of the inner surface of the bomb in the two runs. In run 2 the wall surface was initially freshly machined stainless steel but in run 3 the wall initially was covered with $HCrO_2$ and some chromium dioxide from the preceding run. Another possible influence is the higher oxygen pressure throughout run 3. The data of run 4 at 325° appear to be best fitted by $r = 1^1/_2$ instead of $r = 1$. Hence no attempt was made to calculate the activation energy for the decomposition reaction.

Properties of the Solid Phases

Chromium Dioxide.—Chromium dioxide, CrO_2, has been assigned the cassiterite (SnO_2) structure, space group $P4_2/mnm$ (D_{4h}^{14}), but the single variable parameter has not been determined.[13] In the present study X-ray pure material was obtained, consisting of opaque, black, strongly magnetic, anhedral crystalline aggregates. The crystals show distinct {110} cleavage. The cell dimensions (from powder pattern, Table II) are a_0 = 4.421 ± 0.002 Å., c_0 = 2.916 ± 0.001 Å.; cell volume 56.99 Å.^{3}; c/a = 0.6596. (Michel and Benard[13] gave a_0 = 4.41 Å., c_0 = 2.86 Å. from powder patterns of very impure material.) The density calculated from cell dimensions (two formular units per cell; formular weight 84.01; weight of unit atomic weight 1.6602 × 10^{-24} g.) is 4.89 g. per cc.

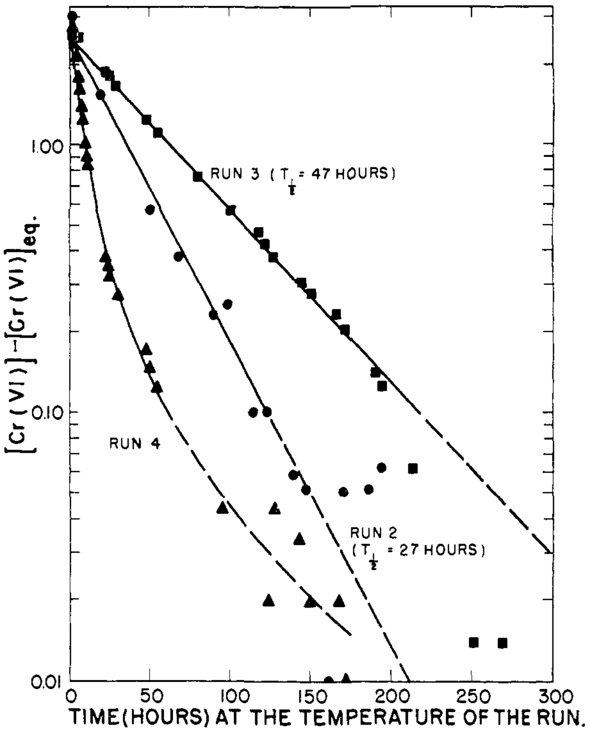

Fig. 2.—Representative kinetics data: ●, run 2 at 300°; ■, run 3 at 300°; ▲, run 4 at 325°.

$HCrO_2$.—Fine-grained crystalline material of the composition $HCrO_2$ has been encountered previously in chromium oxide–water systems. Uninterpreted powder X-ray diffraction patterns, differential thermal analyses, a measured density and an approximate refractive index have been reported.[6,14,15] In the present study drusy aggregates of crystals up to several tenths of a millimeter across were obtained. Quantitative chemical analysis gave, by weight, 61.0% chromium (61.18% calculated) and, by the Penfield method, 9% water (10.60% calculated). On ignition green chromium sesquioxide (Cr_2O_3, identified by powder X-ray diffraction photographs) was formed, with a maximum observed weight loss of 9.5%. Spectrographic analysis revealed small amounts of iron, nickel, cobalt and molybdenum.

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(14) A. Simon, O. Fischer and T. Schmidt, *Z. anorg. u. allgem. Chem.*, **185**, 107 (1930).

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TABLE II

POWDER X-RAY DIFFRACTION PATTERN OF CHROMIUM DIOXIDE

hkl	*d*, Å., calcd.	*d*, Å., obsd.[a]	I/I_1[b]
110	3.126	3.114	100
101	2.434	2.424	60
200	2.211	2.207	10
111	2.132	2.128	20
210	1.977	1.976	10
211	1.636	1.634	75
220	1.563	1.562	25
002	1.458	1.457	15
310	1.398	1.398	15
102	1.385	...	..
221	1.378	...	..
112	1.321	1.322	10
301	1.315	1.316	25
311	1.261	...	..
320	1.226	...	..
202	1.217	1.219	<5
212	1.173	...	..
321	1.130	1.130	10
400	1.105	1.104	5
410	1.072	...	..
222	1.066	1.067	10
330	1.042	1.042	5
312	1.009	1.008	20
411	1.006	...	..
420	0.9886	0.9889	<5
331	.9813	....	..
103	.9493	.9501	<5
322	.9384	....	..
421	.9362	....	..
113	.9282	....	..
430	.8842	....	..
402	.8808	.8812	<5
213	.8723	.8718	10
510	.8670	....	..
412	.8638	....	..
332	.8478	.8479	5
431, 501	.8461	.8460	15
511	.8311	....	..
223	.8254	....	..
520	.8209	....	..
422	.8182	.8183	<5
303	.8114	.8113	5
313	.7981	....	..
521	.7902	.7901	10

[a] Philips 114.6 mm. diameter powder camera, Straumanis mounting; λ(Cu Kα) = 1.5418 Å. [b] Relative peak intensities above background from densitometer measurements.

Calibrated Weissenberg and precession photographs indicate diffraction symbol $\bar{3}mR$ --- and give rhombohedral cell dimensions a_0 = 4.787 ± 0.005 Å., α = 36.3 ± 0.1°; cell volume 34.44 Å.^{3}. (Dimensions of the corresponding triply primitive hexagonal cell are a_0 = 2.984 ± 0.003 Å., c_0 = 13.40 ± 0.01 Å.; cell volume 103.3 Å.^{3}; c/a = 4.49.) The density measured with the Berman balance was 4.11 g. per cc. (Laubengayer and McCune[15] reported a measured density of 4.12 g. per cc.); the density calculated assuming one formular unit per rhombohedral cell (formular weight 85.02; weight of unit atomic weight 1.6602 × 10^{-24} g.) is 4.10 g. per cc. No piezoelectric effect was detected with a Giebe–Scheibe-type apparatus. A crystal structure has been found based on space group $R\bar{3}m$ (D^5_{3d}).[16] The powder pattern is given in Table III.

TABLE III

POWDER X-RAY DIFFRACTION PATTERN OF $HCrO_2$

hkl	*d*, Å., calcd.	*d*, Å., obsd.[a]	I/I_1[b]
111	4.466	4.44	100
100	2.536	2.529	5
110	2.410	2.407	30
222	2.233	2.227	5
211	2.045	2.042	5
221	1.860	1.858	25
322	1.538	1.536	10
$10\bar{1}$	1.491	1.490	15
333	1.489		
210	1.414	1.414	10
332	1.405	1.404	5
$11\bar{1}$	1.285	1.284	<5
200	1.268	1.266	5
321	1.240	1.239	<5
220	1.205	...	..
433	1.189	1.188	5
311	1.163	1.163	5
444	1.117	1.115	<5
443	1.102	...	..
331	1.071	1.071	<5
432	1.054	1.053	<5
422	1.023	...	..
$20\bar{1}$	0.9736	...	..
$21\bar{1}$	.9660	0.9663	<5
544	.9573	....	..
310	.9372	....	..
442	.9298	.9295	<5
320	.9172	.9179	5
554	.8975	....	..
543	.8938	8937	5
555	.8933		
533	.8861	....	..
421	.8696	.8698	5
$2\bar{1}\bar{1}$	.8609	.8612	<5
$22\bar{1}$, 300	.8454	.8454	5

[a] Philips 114.6 mm. diameter powder camera, Straumanis mounting; λ(Cu $K\alpha$) = 1.5418 Å. [b] Relative peak intensities above background from densitometer measurements. The arcs indicate appreciable preferred orientation of the crystals in the powder, arising from the prominent {111} cleavage.

The crystals exhibit rhombohedron {101} and its complementary form {411}, unit rhombohedron {100}, prominent {111} cleavage, and twinning with {122} as twin plane. The crystals are dark brownish red in color, and are optically uniaxial negative with refractive indices for sodium light 2.155 for the ordinary ray, 1.975 for the extraordinary ray (geometric mean 2.093); Lorentz–Lorenz refraction 11.0 cc. (Shafer and Roy[6] gave an approximate refractive index 2.0 ± 0.1.)

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[16] R. M. Douglass, *Acta Cryst.*, in preparation.