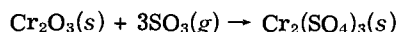


Stability of Chromium (III) Sulfate in Atmospheres Containing Oxygen and Sulfur

K. T. JACOB, D. BHOGESWARA RAO, AND HOWARD G. NELSON

The stability of chromium (III) sulfate in the temperature range from 880 to 1040 K was determined by employing a dynamic gas-solid equilibration technique. The solid chromium sulfate was equilibrated in a gas stream of controlled SO_3 potential. Thermogravimetric and differential thermal analyses were used to follow the decomposition of chromium sulfate. Over the temperature range studied, the change in the Gibbs' free energy of formation of chromium sulfate



can be expressed as

$$\Delta G^\circ = -143,078 + 129.6 T (\pm 300) \text{ cal mole}^{-1}$$

$$\Delta G^\circ = -598,350 + 542 T (\pm 1250) \text{ J mole}^{-1}.$$

X-ray diffraction analysis indicated that the decomposition product was crystalline Cr_2O_3 and that the mutual solubility between $\text{Cr}_2(\text{SO}_4)_3$ and Cr_2O_3 was negligible. Over the temperature range investigated, the decomposition pressures were significantly high so that chromium sulfate is not expected to form on commercial alloys containing chromium when exposed to gaseous environments containing oxygen and sulfur (such as those encountered in coal gasification).

THE corrosion of alloys exposed to environments containing oxygen and sulfur can be analyzed with the aid of chemical potential diagrams. Such diagrams are either plots of 1) the logarithm of the partial pressure of sulfur as a function of $n_A/(n_A + n_B)$, the mole fraction of the metallic component A, for a quaternary system A-B-S-O at a constant temperature and oxygen potential, or 2) the logarithm of the partial pressure of oxygen as a function of $n_A/(n_A + n_B)$ at a constant temperature and sulfur potential. In the case of the five-component system, A-B-C-S-O, the composition of metallic components A, B, and C can be represented on a Gibbs' triangle with the partial pressure of oxygen plotted perpendicular to the plane of the triangle.

To construct such chemical potential plots, reliable thermodynamic data are needed for all the phases involved. Unfortunately, thermodynamic data for some of the binary and ternary oxide and sulfide phases are not available in the literature. Some of the missing data can be estimated with acceptable accuracy using current models and recently established correlations. Using such techniques, sulfur potential plots were developed to explain the sulfidation behavior of SAE 310 stainless steel.¹ However, these correlations are not well established for compounds containing both oxygen and sulfur (such as oxysulfides and sul-

fates). Consequently, the only way of obtaining the information for oxysulfides and sulfates is by conducting proper experiments.

As a part of a program on the corrosion of the internal components of gasifiers it became necessary to develop the chemical potential diagrams for industrial alloys in multicomponent gaseous environments. It was found that no thermodynamic data for chromium (III) sulfate were reported in the literature and hence these experimental studies were undertaken. This communication reports the measured free energies of formation of chromium (III) sulfate.

EXPERIMENTAL MATERIALS

Anhydrous chromium sulfate, $\text{Cr}_2(\text{SO}_4)_3$, was prepared by three different methods. 1) Commercially available, water-soluble violet chromium sulfate, $(\text{Cr}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O})$, with 99.9 pct purity was procured from J. T. Baker Chemical Company. The water molecules were removed by slow heating under a reduced pressure of 10 Nm^{-2} . The weight loss of the sample indicated that dehydration takes place in three stages. The violet 18 hydrate first changed to the 9 hydrate with no color change. Further dehydration yielded a green 3 hydrate and finally a peach-blossom-colored anhydrous chromium (III) sulfate. The last three molecules of water were evolved continuously over a temperature range from 375 to 500 K. The resulting chromium (III) sulfate was insoluble in water. 2) The violet-hydrated sulfate was synthesized in the laboratory by dissolving chromium hydroxide in a calculated quantity of warm sulfuric acid and allowing the resulting green solution to stand for one week. When the violet crystals of chromium sulfate started to settle, these crystals were dehydrated as described above. 3) The anhydrous chromium (III) sulfate was prepared by heating ammonium chromium sulfate with boiling concentrated sulfuric acid.

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APPARATUS AND PROCEDURE

A) Thermogravimetry

A schematic diagram of the thermogravimetric apparatus employed in this study is shown in Fig. 1. The reaction tube and the crucible containing anhydrous $\text{Cr}_2(\text{SO}_4)_3$ were made of silica. A platinum basket containing the silica crucible was suspended on a silica rod and attached to one arm of a Cahn thermobalance through a platinum wire. A reaction mixture containing $\text{Ar} + \text{SO}_2 + \text{O}_2$ was admitted into the reaction tube from the lower end. This gas swept past the radiation baffles supported on a thermocouple sheath and blocks of platinum-on-asbestos, which served as a catalyst. The catalyst helped to achieve the equilibrium between SO_3 , SO_2 , and O_2 rapidly. The equilibrium composition of SO_3 is dependent on the inlet gas composition and reaction temperature. To avoid any reaction with the balance parts, the balance was always flushed with argon gas. The reaction tube was surrounded by a furnace with global heating elements. The furnace gave a constant temperature zone (± 2 K) of 4.5 cm. The temperature of the furnace was controlled within 2 K by a stepless current proportionating controller. The crucible containing $\text{Cr}_2(\text{SO}_4)_3$ and the tip of the thermocouple were placed in a constant temperature zone. The actual temperature of the crucible was recorded during the run by placing a Pt-Pt 13 pct Rh thermocouple im-

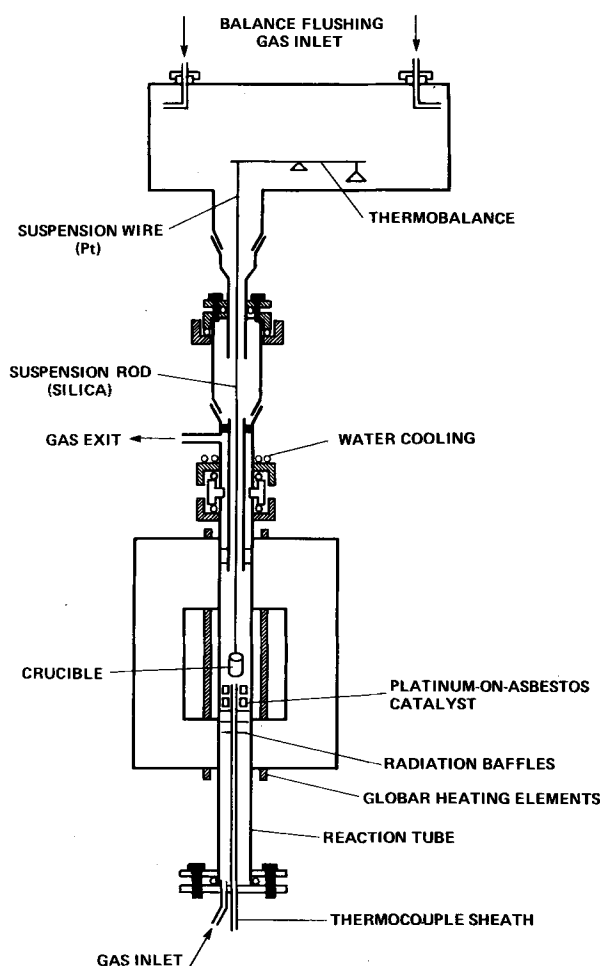


Fig. 1—Schematic diagram of the thermogravimetric apparatus.

mediately below the crucible. Separate experiments were conducted by placing a thermocouple inside the crucible; a good agreement between the actual temperature of the crucible and the sensing thermocouple was observed. In all experiments, the temperature immediately below the sample remained constant within the uncertainties specified above. The output from the thermobalance and the thermocouple were fed to a two-channel potentiometric recorder so that the temperature corresponding to the onset of decomposition could be easily identified.

Gases with 99.9 pct purity were used in this study. The gases were further dried by passing through purification trains. The reactive gas mixtures containing $\text{Ar} + \text{SO}_2 + \text{O}_2$ were prepared by mixing the purified individual gases. The flow rate of each gas was monitored by calibrated rotometers. Gases were mixed in a tower packed with glass beads.

The furnace was rapidly heated to 650 K after flushing the reaction tube with the selected gas mixture at a flow rate of 250 ml min^{-1} (STP) for 3 h. The temperature was then increased at a rate of approximately 2 K min^{-1} in the initial experiments. The approximate decomposition temperature was noted when a significant weight change was detected. In subsequent experiments, using the same gas mixture, the furnace was rapidly heated to a temperature 30 K below the approximate decomposition temperature obtained in the preliminary experiments; the furnace temperature was then increased at a rate of 0.2 K min^{-1} until the decomposition of the sulfate was detected. The decomposition temperature was then determined as a function of the inlet gas composition. The decomposition temperature was discovered to be independent of the method of preparation of the sulfate. After complete decomposition of the sulfate, the temperature was lowered at a controlled rate of 0.2 K min^{-1} . The reformation of $\text{Cr}_2(\text{SO}_4)_3$ on slow cooling was so sluggish that the temperature corresponding to the reformation cannot be accurately determined by this technique. This finding is useful in designing sulfation-resistant alloys containing chromium. The product of decomposition was quenched to room temperature and was identified as Cr_2O_3 by X-ray analysis.

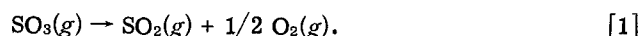
B) Differential Thermal Analysis

The apparatus used for differential thermal analysis was similar to that used by Dewing and Richardson.² The anhydrous chromium sulfate was contained in a thin-walled silica boat placed in a horizontal furnace under a stream of gas of controlled composition flowing at the rate of 100 to 250 ml min^{-1} . The gas mixtures were prepared as described earlier. One leg of the differential thermocouple was immersed in the sulfate (filled to a depth of 2 to 3 mm in the silica boat) and the other leg was placed above the boat to measure the furnace temperature. A separate thermocouple immersed in the sulfate was used to record the temperature of the sample. The output of the differential thermocouple was fed through a dc amplifier to a potentiometric recorder. The furnace was rapidly heated to a temperature 25 K below the decomposition temperature obtained from thermogravimetric studies. Thereafter, the temperature was increased at 0.2 K

min⁻¹ and the variation of the sample temperature was continuously recorded. The decomposition temperature corresponding to each gas composition was indicated by a nonzero value from the differential thermocouple. Since the decomposition reaction is endothermic, the temperature of the sample lagged behind the increasing furnace temperature. The decomposition temperature was independent of the total flow rate of the gases in the range 100 to 250 ml min⁻¹. Heating the sample further produced no evidence of additional reactions with significant heat effects. It could, therefore, be concluded that the decomposition proceeded directly to the oxide without any intermediate phase.

RESULTS AND DISCUSSION

The condensed phases remaining in the crucible after the experiment were analyzed by taking X-ray diffraction patterns. The experimental *d* values were identical to those given in the ASTM index for Cr₂O₃ and Cr₂(SO₄)₃. This indicates that there was no significant solid solubility between Cr₂O₃ and Cr₂(SO₄)₃; hence, the activities of the condensed phases can be taken as unity. The gas phase consists of a mixture of SO₃, SO₂, and O₂. The composition of the gas at the decomposition temperature is different from that of the inlet gas composition because of the reaction between SO₂ and O₂ to form SO₃. The partial pressure of SO₃ can be calculated according to the equation

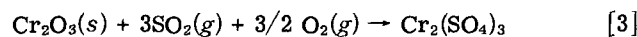


A significant change has recently been introduced in the value for the heat of formation of gaseous SO₃ at 298 K.³ This new value for the heat of formation of SO₃ when used in conjunction with the heat capacity and entropy data given in JANAF Thermochemical Tables⁴ gives the free energy change for reaction [1] as

$$\Delta G_1^0 = 97,780 - 92.78 T (\pm 300) \text{ J mole}^{-1}. \quad [2]$$

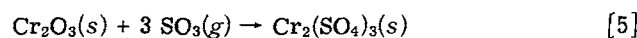
The partial pressures of SO₃, SO₂, and O₂, calculated at the decomposition temperatures from the free energy values and the composition of the inlet gases (using a digital computer and an iterative procedure given in the Appendix), are shown in Table I. From these data

the standard free energy changes for the following reactions were calculated:



$$\Delta G^0 = -RT \ln K = RT \ln (P_{\text{SO}_2}^3 \cdot P_{\text{O}_2}^{3/2})$$

$$\Delta G^0 = -891,690 + 820 T (\pm 1250) \text{ J mole}^{-1} \quad [4]$$



$$\Delta G^0 = -RT \ln K = RT \ln P_{\text{SO}_3}^3$$

$$\Delta G^0 = -598,350 + 542 T (\pm 1250) \text{ J mole}^{-1}. \quad [6]$$

The experimentally obtained free energies of formation of Cr₂(SO₄)₃ according to reaction [5] (using both thermogravimetric and differential thermal analysis (DTA)) are given in Table I and are also plotted as a function of temperature in Fig. 2. The results obtained by both techniques are in mutual agreement. At the lower temperatures the free energies calculated from DTA measurements are about 300 J higher than those obtained by thermogravimetry. In DTA experiments the temperatures were measured by a thermocouple embedded in the sample, while in the thermogravimetric studies the thermocouple was placed immediately below the sample. Since the decomposition was endothermic, the sample was probably at a slightly lower temperature (~3 K) than the furnace atmosphere. The decomposition temperature and the stability of the sulfate measured by DTA would then be lower than that obtained by thermogravimetry at lower temperatures where radiative heat transfer between the furnace and the sample would be slower. Since the differences in the decomposition temperatures are small (~3 K), a least-squares regression analysis giving equal weight to all data points was used to obtain Eq. [6]. At temperatures near 1000 K, the chromium sulfate is only marginally stable with respect to chromium oxide and gaseous sulfur trioxide. This is encouraging for the use of chromium-containing alloys in environments rich in oxygen and sulfur. The integrity of chromium oxide containing protective scales will not be affected by the formation of chromium sulfate. In coal-gasification reactors using Synthane, Battelle, BCR Bi-Gas, or IGT

Table I. Gas Composition, Decomposition Temperatures, and Standard Free Energy Changes for the Dissociation of Cr₂(SO₄)₃ Obtained by Thermogravimetry

Composition of Inlet Gas (Ar + SO ₂ + O ₂), Vol Pct			Decomposition Temperature, K	Composition of Gas at Decomposition Temperature, (Ar + SO ₂ + SO ₃ + O ₂), Vol Pct				ΔG^0 ,* KJ
Ar	SO ₂	O ₂		Ar	SO ₂	SO ₃	O ₂	
2.11	67.60	30.30	1040	2.40	49.99	26.54	21.00	34.41
22.23	62.70	15.07	1024	24.29	50.00	18.50	7.21	43.08
47.55	42.10	10.35	1006	50.44	32.50	12.16	4.90	52.86
71.4	22.90	5.70	980	73.70	17.20	6.46	2.65	66.96
83.28	9.88	6.84	961	84.93	6.10	3.98	4.99	77.25
85.93	4.95	9.12	944	87.00	2.47	2.54	7.97	86.46
89.90	4.10	6.01	935	90.78	2.15	1.99	5.08	91.35
93.78	3.43	2.79	923	94.45	2.03	1.425	2.10	97.86
96.42	2.05	1.53	904	96.82	1.23	0.825	1.125	108.15
98.16	1.36	0.478	882	98.37	0.94	0.426	0.267	120.09

*For the reaction Cr₂(SO₄)₃(s) → Cr₂O₃(s) + 3SO₃(g).

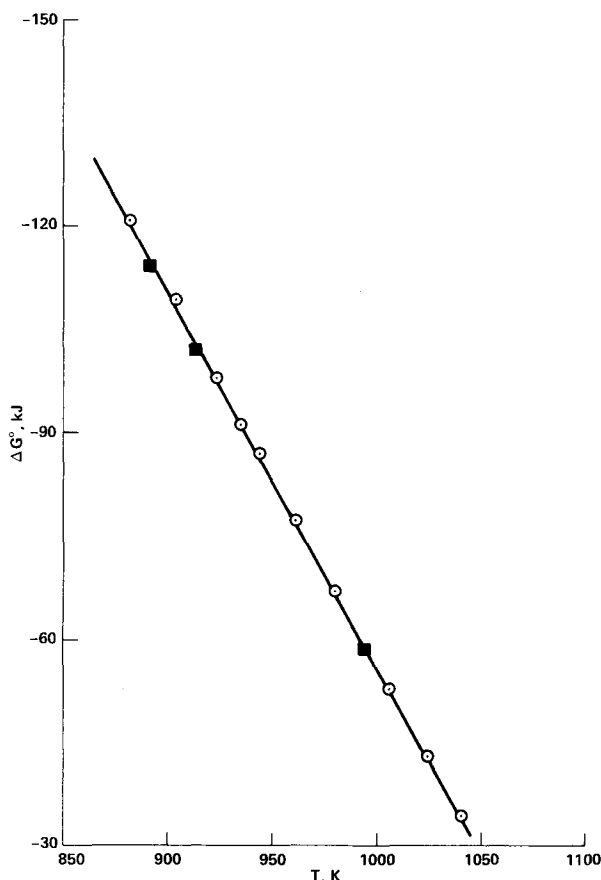


Fig. 2—Free energy of formation of chromium sulfate according to the reaction $\text{Cr}_2\text{O}_3(s) + 3\text{SO}_3(g) \rightarrow \text{Cr}_2(\text{SO}_4)_3(s)$ in kJ per mole; ○, results from thermogravimetry; ■ results from differential thermal analysis.

Hygas processes, the partial pressure of SO_3 ranges between 10^{-22} atm at 900 K to 10^{-15} atm at 1200 K. Clearly, the chromium sulfate phase is unstable under these conditions.

The measured entropy of formation of chromium (III) sulfate (given in Eq. [4]) is compared with the literature values for similar sulfates containing trivalent cations in Table II. The experimental results show that the temperature range over which the free energies of formation of the sulfate could be obtained by these methods was restricted to 160 K. The composition of the gas mixtures prepared by mixing metered streams of component gases cannot be accurately controlled when the concentration of one component is less than 0.5 vol pct, thus restricting the temperature range of this study. Despite this limitation, Table II shows fair agreement between the entropy values of various sulfates. Since the uncertainties in the entropies of formation are at least $\pm 15 \text{ JK}^{-1} \text{ mol}^{-1}$, the results suggest that the entropy changes for reactions involving similar chemical species have approximately constant values ($-812 \pm 25 \text{ JK}^{-1} \text{ mol}^{-1}$). In the absence of reliable calorimetric data, this approximate value may be used to estimate the temperature dependence of the free energies of formation of uninvestigated sulfates containing trivalent ions. This value can be critically assessed only when calorimetric studies are conducted on the heat of formation and low- and high-tempera-

ture heat capacities of sulfates containing trivalent ions.

Both thermogravimetry and differential thermal analysis are essentially nonisothermal techniques that give relatively little information concerning the kinetics of the decomposition. Additionally, the geometry of the sample and the container in the reaction tube and the gas flow pattern around the sample are not amenable to rigorous kinetic analysis. However, approximate values for the rate constant, $k = 8 \times 10^{-4} \text{ Kg M}^{-2} \text{ s}^{-1}$ at 1000 K, and activation energy (Arrhenius) for thermal dissociation, $E_a = 200 \pm 30 \text{ kJ}$, can be obtained from the weight loss curves. The degree of decomposition was found to approximate a linear function of time. This implies that the decomposition is not autocatalytic.

APPENDIX

It can readily be shown from the thermodynamic data⁴ that the partial pressures of sulfur monoxide and monomeric and polymeric sulfur species are negligibly small in the gas mixtures at the temperatures employed in this study. Therefore, one needs to consider only Eq. [1] to calculate the high-temperature gas composition. The corresponding equilibrium constant is

$$K = \exp(-\Delta G_1^\circ/RT) = P_{\text{SO}_2} P_{\text{O}_2}^{1/2} / P_{\text{SO}_3} \quad [\text{A1}]$$

where ΔG_1° is the standard free energy change for reaction [1], R is the gas constant, T is the absolute temperature and the partial pressures are taken at equilibrium. Consider an initial volume of gas containing 1 mole of sulfur dioxide, $n_{\text{O}_2}^0$ moles of oxygen, and n_{Ar}^0 moles of argon at a total pressure of 1 atm. If α moles of SO_3 are formed to reach equilibrium, there remain $(1 - \alpha)$ moles of SO_2 and $(n_{\text{O}_2}^0 - \alpha/2)$ moles of O_2 . The total number of moles of gas becomes $(1 + n_{\text{O}_2}^0 + n_{\text{Ar}}^0 - \alpha/2)$ and the equilibrium pressures are:

$$P_{\text{SO}_2} = (1 - \alpha) / (1 + n_{\text{O}_2}^0 + n_{\text{Ar}}^0 - \alpha/2) \quad [\text{A2}]$$

$$P_{\text{SO}_3} = \alpha / (1 + n_{\text{O}_2}^0 + n_{\text{Ar}}^0 - \alpha/2) \quad [\text{A3}]$$

$$P_{\text{O}_2} = (n_{\text{O}_2}^0 - \alpha/2) / (1 + n_{\text{O}_2}^0 + n_{\text{Ar}}^0 - \alpha/2). \quad [\text{A4}]$$

Equation [A1] then becomes

$$K_\alpha (1 + n_{\text{O}_2}^0 + n_{\text{Ar}}^0 - \alpha/2)^{1/2} = (1 - \alpha)(n_{\text{O}_2}^0 - \alpha/2)^{1/2} \quad [\text{A5}]$$

by replacing the equilibrium partial pressures by

Table II. Comparison of the Entropies of Formation of Sulfates Containing Trivalent Cations

Compound†	$\Delta S^\circ, \text{ JK}^{-1} \text{ mole}^{-1}$
$\text{Fe}_2(\text{SO}_4)_3$	-776 (Ref. 5)
$\text{Al}_2(\text{SO}_4)_3$	-812 (Ref. 6)
$\text{In}_2(\text{SO}_4)_3$	-812 (Ref. 7)
$\text{Sc}_2(\text{SO}_4)_3$	-840 (Ref. 6)
$\text{Cr}_2(\text{SO}_4)_3$	-820 (This work)

*For the reaction $X_2\text{O}_3(s) + 3\text{SO}_2(g) + 3/2\text{O}_2(g) \rightarrow X_2(\text{SO}_4)_3(s)$.

†These compounds have the same hexagonal (rhombohedral) lattice symmetry.

their respective values. Squaring the above expression gives,

$$K^2 \alpha^2 (1 + n_{O_2}^0 + n_{Ar}^0 - \alpha/2) - (1 - \alpha)^2 (n_{O_2}^0 - \alpha/2) = 0. \quad [A6]$$

With the aid of a digital computer, the value of α is determined for input composition (given by n_{Ar}^0 and $n_{O_2}^0$) by using the Newton method on the function, $y = K^2 \alpha^2 (1 + n_{O_2}^0 + n_{Ar}^0 - \alpha/2) - (1 - \alpha)^2 (n_{O_2}^0 - \alpha/2)$, with $\alpha = 0.5$ as the starting point.

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