

The standard Gibbs energies of formation of ACrO_4 (A = Ca, Sr or Ba) from EMF measurements

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Abstract

The thermodynamic stabilities of CaCrO_4 , BaCrO_4 and SrCrO_4 are of interest to materials scientists and also in nuclear technology because these are the possible compounds of fission product-cladding chemical interaction under conditions of accident in fast nuclear reactors. Though there are some reports on the thermodynamic stabilities of CaCrO_4 and BaCrO_4 obtained by the fluoride electrolyte EMF method, there is no reliable thermodynamic information on SrCrO_4 . Hence the EMF of the galvanic cells $\text{Pt, O}_2(\text{g})/\text{CaO, CaF}_2/\text{CaF}_2/\text{AF}_2, \text{ACrO}_4, \text{Cr}_2\text{O}_3/\text{Pt, O}_2(\text{g})$ were studied under an atmosphere of pure oxygen at a pressure of 0.1 MPa over the ranges 788–1070, 851–1116 and 850–1168 K where A is Ca, Sr and Ba respectively.

From the cell EMF data, the standard Gibbs energies of formation ΔG_f^\ominus of the chromates, according to the reaction $\text{AO}(\text{s}) + \frac{1}{2}\text{Cr}_2\text{O}_3(\text{s}) + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{ACrO}_4(\text{s})$ were derived to be $\Delta G_f^\ominus(\text{CaCrO}_4) = -1356.6 + 0.31641T (\pm 0.63) \text{ kJ mol}^{-1}$, $\Delta G_f^\ominus(\text{SrCrO}_4) = -1359.1 + 0.32998T (\pm 0.30) \text{ kJ mol}^{-1}$, $\Delta G_f^\ominus(\text{BaCrO}_4) = -1323.7 + 0.31159T (\pm 0.34) \text{ kJ mol}^{-1}$.

INTRODUCTION

A systematic study of the thermodynamic properties of the ternary compounds between alkaline earth metal oxides AO and chromium sesquioxide are of considerable interest in solid state chemistry from the point of view of the application of alkaline earth metal-substituted lanthanum chromite, $\text{La}_{1-x}\text{A}_x\text{CrO}_3$ as electrode materials in advanced energy production devices [1,2]. Besides this, Sr and Ba are also among the predominant fission products in fast breeder reactors (FBRs) and the products of chemical interaction of SrO and BaO with chromium oxide are of considerable importance for ultimate thermodynamic analysis of the fuel under conditions of reactor accident. However, in oxygen rich atmospheres, the alkaline earth metal chromates ACrO_4 (A = Ca, Sr and Ba) are more

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stable than chromates of the type A_2CrO_4 into which the former decompose on heating to temperatures beyond about 1100 K [3].

Prasad and Abraham [4] have reported the standard Gibbs energy change for the formation of calcium chromate from CaO and Cr_2O_3 at three temperatures, namely 873, 973 and 1073 K, making use of a CaF_2 -based EMF technique (under an atmosphere of oxygen at unit fugacity) with CaO/CaF_2 as the reference electrode. Prasad [5] had determined the standard enthalpy of formation of calcium chromate by solution calorimetry. Deo and Tare [6] have reported the Gibbs energy data on barium chromate in the temperature range 935 – 1187 K, using a similar EMF technique and barium hexaferrite/ferric oxide as the reference electrode. However, while in the thermodynamic data reported by Prasad and Abraham [4] the scatter was rather large, the standard entropy of reaction for the formation of $BaCrO_4$ from BaO and Cr_2O_3 was a small positive quantity ($+3.2 \text{ J K}^{-1} \text{ mol}^{-1}$) and the standard entropy of formation of $BaCrO_4$ was quite low, in the measurements of Deo and Tare [6].

Recently Azad et al. [7,8] have determined the standard Gibbs energies of formation, $\Delta G_{f,ox}^\ominus$ of $LaCrO_3$ and $LaGaO_3$ from the constituent sesquioxides, measuring fluorine potentials in appropriate phase mixtures under oxygen at $1.01 \times 10^5 \text{ Pa}$. Since the precision in these measurements was better, it was decided to redetermine the ΔG_f^\ominus of calcium and barium chromates, which would also possibly help to corroborate the earlier data and fill in the gap in the data on $SrCrO_4$ which have not yet been reported.

EXPERIMENTAL

Materials

Calcium chromate, $CaCrO_4$ was prepared by precipitation from an aqueous solution of $CaCl_2$ and chromic acid in a slightly alkaline medium (pH 8.0) [9]. The precipitate was washed repeatedly with distilled water until the filtrate did not show any turbidity with fresh aliquots of $CaCl_2$. Strontium and barium chromates were prepared by precipitation from aqueous solutions of reagent grade strontium and barium carbonates respectively, in dilute HCl and reagent grade potassium chromate [10]. These precipitates were dried overnight in an air oven at 323 K. The X-ray powder diffractions of these conformed to those of $CaCrO_4$, $SrCrO_4$ and $BaCrO_4$ within the 5 mass% limit of detection of impurity phases by the XRD technique. No peak corresponding to the starting materials was observed.

The test electrode pellets were made by thoroughly mixing the individual chromate with Cr_2O_3 and the corresponding alkaline earth metal difluo-

ride, approximately in equal weight ratio and cold-compacting into cylindrical discs of 10 mm diameter and 3 mm thickness, under a pressure of 100 MPa. Reference electrodes consisted of equal weight ratio mixture of CaO and CaF₂, made into pellets as described above. Single crystal CaF₂, 10 mm in diameter and 3 mm thick (Harshaw/Filtrol, USA) was used as the solid electrolyte in these measurements.

Cell operation

The following isothermal galvanic cells have been employed for the EMF measurements.



An open-cell stacked-pellet assembly was used for the EMF measurements. The cell assembly was held in the constant temperature zone of a vertical furnace. A calibrated Pt–10% Rh/Pt thermocouple, located in the vicinity of the stacked-pellet assembly, was used to monitor the cell temperature. High purity oxygen (IOL, India, purity better than 99.99%) flowing at a rate of about 1 dm³ h⁻¹ and a pressure of 1.01 × 10⁵ Pa was used as the gas atmosphere over the cell. Prior to admission in the cell, the oxygen was passed through drierite (anhydrous CaCl₂) traps for the removal of moisture present in the cylinder gas. The temperature of the furnace was regulated by a proportional power controller to better than ±1 K. The reproducibility of the EMF data was verified by thermal cycling and varying the weight ratio of different constituents of the test electrodes. Other experimental details were identical to those reported elsewhere [11–13].

RESULTS

The results of the EMF measurements on cells I–III shown in Fig. 1, could be represented by the least-squares expressions

$$E_{\text{I}} = 862.5 - 0.45709T (\pm 3.3) \text{ mV} \quad (1)$$

$$E_{\text{II}} = 923.8 - 0.52555T (\pm 1.5) \text{ mV} \quad (2)$$

$$E_{\text{III}} = 775.4 - 0.44136T (\pm 2.5) \text{ mV} \quad (3)$$

valid over the ranges 788–1070, 851–1116 and 850–1168 K respectively. It should be noted that at least three independent series of measurements on different pairs of electrode pellets were made for each of the above

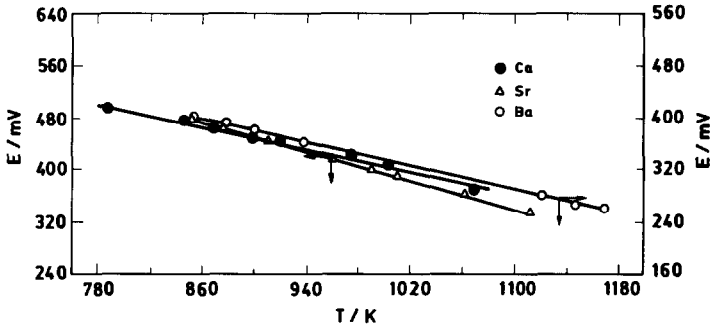
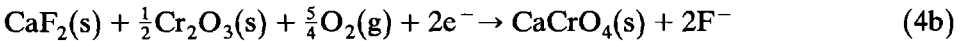
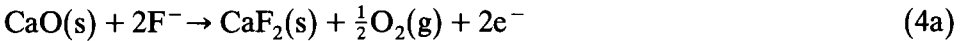


Fig. 1. Temperature dependence of EMF of cells I, II and III.

galvanic cells. However, for the sake of clarity, only one symbol was used for each type of cell I–III to designate the EMF points.

DISCUSSION

The two half-cell reactions for the passage of two faradays of electricity in cell I, could be written as



The overall virtual cell reaction (4c) is obtained by the algebraic addition of (4a) and (4b)



for which the standard Gibbs energy change, ΔG_R^\ominus , was calculated by combining eqn. (1) with the Nernst equation

$$\Delta G^\ominus = -2 \cdot F \cdot E \quad (5)$$

This is shown in Table 1 under S. No. 1.

The EMF results of an identical galvanic cell measurement on CaCrO_4 were reported by Prasad and Abraham [4] at three temperatures 873, 973 and 1073 K. Using these values, a least-squares expression was derived which yielded ΔG_R^\ominus for the same reaction (designated as S. No. 2 in Table 1). At an overlapping temperature of 973 K, the values of $\Delta G_{R(4c)}^\ominus$ are found to be $-80.6 (\pm 0.6)$ from this work, $-92.6 (\pm 1.9)$ from the EMF results of Prasad and Abraham [4] and $-82.0 (\pm 15.9)$ kJ from calorimetry [5]. As could be seen from this comparison, the agreement among the three sets of investigation is not good, considering in particular the large uncertainty in the calorimetric work. The discrepancy in the identical work by Prasad and Abraham [4] could partly be due to the method of preparation adopted by the latter worker who employed solid state reaction route between CaCO_3 and CrO_3 ; this could have given rise to interference by

TABLE 1

Standard Gibbs energy change (kJ) for the formation of $\text{ACrO}_4(\text{s})$ from $\text{AO}(\text{s})$ and $\text{Cr}_2\text{O}_3(\text{s})$

S. No.	Reaction	$\Delta G_{\text{R}}^{\ominus} = A + BT$ (K)	Reference
1	$\text{CaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{CaCrO}_4$	$-166.44 + 0.088206 T$	This work
2	$\text{CaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{CaCrO}_4$	$-176.59 + 0.085856 T$	Prasad and Abraham [4]
3	$\text{CaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \text{SrF}_2 + \frac{3}{4}\text{O}_2$ $\rightarrow \text{SrCrO}_4 + \text{CaF}_2$	$-178.26 + 0.101419 T$	This work
4	$\text{SrO} + \text{CaF}_2 \rightarrow \text{SrF}_2 + \text{CaO}$	$-34.78 + 0.005485 T$	JANAF tables [15]
5	$\text{SrO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{SrCrO}_4$	$-213.05 + 0.106904 T$	This work (from refs. 3 and 4)
6	$\text{CaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \text{BaF}_2 + \frac{3}{4}\text{O}_2(\text{g})$ $\rightarrow \text{BaCrO}_4 + \text{CaF}_2$	$-149.63 + 0.085171 T$	This work
7	$\text{BaO} + \text{CaF}_2 \rightarrow \text{BaF}_2 + \text{CaO}$	$-70.11 + 0.006967 T$	JANAF tables [15]
8	$\text{BaO} \cdot 6\text{Fe}_2\text{O}_3 + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g})$ $\rightarrow \text{BaCrO}_4 + 6\text{Fe}_2\text{O}_3$	$8.23 - 0.014550 T$	Deo and Tare [6]
9	$\text{BaO} + 6\text{Fe}_2\text{O}_3 \rightarrow \text{BaO} \cdot 6\text{Fe}_2\text{O}_3$	$-89.23 + 0.011390 T$	Deo et al. [14]
10	$\text{BaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{BaCrO}_4$	$-219.74 + 0.092138 T$	This work (from refs. 6 and 7)
11	$\text{BaO} + \frac{1}{2}\text{Cr}_2\text{O}_3 + \frac{3}{4}\text{O}_2(\text{g}) \rightarrow \text{BaCrO}_4$	$-81.01 - 0.00316 T$	Deo and Tare [6] (from refs. 8 and 9)

impurity phases such as CaCr_2O_4 . As was mentioned in the section headed Experimental, the synthesis of CaCrO_4 resorted to in the present investigation was through precipitation route to eliminate the occurrence of impurity phases.

The overall cell reaction in the galvanic cell II for the passage of two faradays of electricity is given as S. No. 3 in Table 1. This was combined with the $\Delta G_{\text{f}}^{\ominus}$ data of the binary fluorides and oxides of Ca and Sr to yield the standard Gibbs' energy change for the formation of $\text{SrCrO}_4(\text{s})$ from $\text{SrO}(\text{s})$ and $\text{Cr}_2\text{O}_3(\text{s})$ (S. No. 5). Typically at 973 K, a value of -109.0 kJ was obtained for $\Delta G_{\text{R}(\text{S})}^{\ominus}$. No reliable thermodynamic data are available on SrCrO_4 to make a comparison with the present results. Likewise, the standard Gibbs energy change for the formation of $\text{BaCrO}_4(\text{s})$ from $\text{BaO}(\text{s})$ and $\text{Cr}_2\text{O}_3(\text{s})$ was computed from the cell reaction given in S. No. 6, by using the EMF data represented by eqn. (3), in conjunction with the thermochemical data on fluorides and oxides of Ca and Ba. The resultant Gibbs energy expression is given in S. No. 10. Deo and Tare [6] had reported EMF measurements on the galvanic cell using the same test electrode as in cell III but with $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3 / \text{Fe}_2\text{O}_3 / \text{BaF}_2$ as the reference electrode. Making use of the $\Delta G_{\text{f,ox}}^{\ominus}$ value reported by Deo et al. [14] for the formation of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ from the constituent binary oxides, another numerical expression as given in S. No. 11 was derived, for the formation of $\text{BaCrO}_4(\text{s})$ from $\text{BaO}(\text{s})$ and $\text{Cr}_2\text{O}_3(\text{s})$. At 973 K, values of

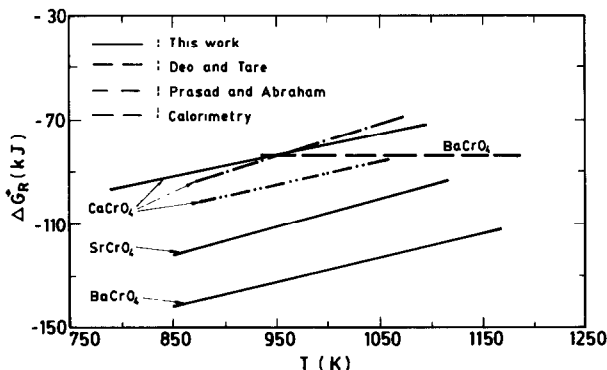


Fig. 2. Comparison of the standard Gibbs energy change for the formation of $ACrO_4$ ($A = Ca, Sr$ and Ba) from AO and Cr_2O_3 .

-130.1 and -84.1 kJ are obtained, corresponding to this work and that reported by Deo et al. [14] respectively. It should be noted that in the work of Deo and Tare [6], there is a marginal increase in the entropy of reaction shown by S. No. 11, which is somewhat surprising in view of the fact that this reaction involves the disappearance of $3/4$ mole of oxygen gas from the left hand side of the reaction to form $BaCrO_4$; in fact such a reaction would be expected to be attended by a considerable decrease in the entropy (mainly translational entropy of the gaseous reactant involved), to the extent of about $120 \text{ J K}^{-1} \text{ mol}^{-1}$. It should also be mentioned that Deo and Tare [6] have ascribed the Gibbs energy expression in S. No. 11 as that for the standard Gibbs energy of formation of $BaCrO_4$; it in fact corresponds to the standard Gibbs energy change for the formation of $BaCrO_4(s)$ from $BaO(s)$, $Cr_2O_3(s)$ and oxygen gas.

For the purpose of comparison, the ΔG_R^{\ominus} for the reactions indicated by S. Nos. 1, 5 and 10 in Table 1 are plotted over the temperature ranges of their measurement, along with those by Prasad and Abraham [4] and calorimetry [5] for $CaCrO_4$ and by Deo and Tare [6] for $BaCrO_4$ in Fig. 2. It should be noted that in these measurements, the lower temperature range is dictated by the ease of attainment of facile equilibrium and possible oxidation of Cr_2O_3 to CrO_3 which would complicate the measurements. However, the upper temperature limit is dictated more by stability of the chromate under study. For instance, $CaCrO_4$ and $BaCrO_4$ have been reported to decompose into a mixture of $CaCr_2O_4/9CaO \cdot 4Cr_2O_3 \cdot CrO_3$ (941 phase) and $BaCr_2O_4/9BaO \cdot 4Cr_2O_3 \cdot CrO_3$ beyond 1073 and 1173 K respectively, according to the phase diagrams of $CaO \cdot Cr_2O_3$ and $BaO \cdot Cr_2O_3$ systems [3]. Though no phase diagram was reported on the $Sr-Cr-O$ system, similar behaviour could be anticipated beyond the upper limit of temperature of measurement (1116 K); in the present work on $SrCrO_4$ no break was observed in the EMF versus temperature linear plot. The possible reason as to why this compound had not been thermodynamically

TABLE 2

Auxiliary thermodynamic data used for the computation of ΔG_R^\ominus and ΔG_f^\ominus of $\text{ACrO}_4(\text{s})$

Compound	ΔG_f^\ominus (kJ mol ⁻¹)	Temperature range (K)	Reference
CaO	$-634.664 + 0.104521T$	298–1200	15
SrO	$-591.061 + 0.099476T$	298–1200	15
BaO	$-548.960 + 0.095853T$	298–1200	15
CaF ₂	$-1222.93 + 0.165796T$	298–1200	15
SrF ₂	$-1214.11 + 0.166236T$	298–1200	15
BaF ₂	$-1207.34 + 0.164095T$	298–1200	15
Cr ₂ O ₃	$-1109.94 + 0.247200T$	1173–1523	16

characterized in the literature, could be due to the difficulties encountered in its synthesis by usual routes, using chromic acid as precursor at a controlled pH. However, precipitation from SrCl_2 by the addition of aqueous K_2CrO_4 was found to yield SrCrO_4 [10]. Since there appears to be no other report on the thermodynamic stability of SrCrO_4 , no comparison of $\Delta G_{R(5)}^\ominus$ for this compound with the literature could be made in Fig. 2.

The reactions and the corresponding thermodynamic data shown in S. Nos. 1, 5 and 10 in Table 1 were also used to derive the standard Gibbs energies of formation of ACrO_4 from AO and Cr_2O_3 . For this purpose, the ΔG_f^\ominus for the fluorides and oxides of Ca, Sr and Ba were taken from JANAF thermochemical tables [15], whereas the data on Cr_2O_3 were those assessed by Sreedharan and Mallika [16]. These data are listed in Table 2. The following least squares expressions were thus derived for ΔG_f^\ominus of CaCrO_4 , SrCrO_4 and BaCrO_4 according to the reaction



$$\Delta G_f^\ominus(\text{CaCrO}_4) = -1356.6 + 0.31641T (\pm 0.63) \text{ kJ mol}^{-1} \quad (788\text{--}1070 \text{ K}) \quad (7)$$

$$\Delta G_f^\ominus(\text{SrCrO}_4) = -1359.1 + 0.32998T (\pm 0.30) \text{ kJ mol}^{-1} \quad (851\text{--}1116 \text{ K}) \quad (8)$$

$$\Delta G_f^\ominus(\text{BaCrO}_4) = -1323.7 + 0.31159T (\pm 0.34) \text{ kJ mol}^{-1} \quad (850\text{--}1168 \text{ K}) \quad (9)$$

Because the relevant comparison had already been made for ΔG_R^\ominus for their formation justifying the discrepancy, a similar exercise was not carried out for ΔG_f^\ominus data to avoid redundancy. It could be seen from eqns. (7)–(9) that there is a systematic trend in the thermodynamic stability of these alkaline earth metal chromates; the stability decreases as one goes down the group from Ca to Ba in the temperature range of this study.

CONCLUSION

The CaF_2 electrolyte-based EMF method is a promising tool for the generation of reliable Gibbs energy data for compounds stable under high oxygen pressures. However, much caution is needed to eliminate interference by parasitic impurity phases by adopting foolproof methods of synthesis of pure compounds as evidenced in the present study of ACrO_4 (A = Ca, Sr or Ba).

REFERENCES

- 1 J. Mizusaki, M. Yoshihiro, S. Yamaguchi and K. Fueki, *J. Solid State Chem.*, 58 (1985) 257.
- 2 N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya and T. Iwata, *J. Mater. Sci.*, 25 (1990) 4531.
- 3 L.L.Y. Chang, M.G. Scroger and B. Philips, in E.M. Levin, C.R. Robbins and H.F. McMurdie (Eds.), *Phase Diagrams for Ceramicists*, American Ceramic Society, 1964, p. 48; 1975, p. 99.
- 4 K.K. Prasad and K.P. Abraham, *Proc. Symp. Mater. Sci.*, BARC-NAL, Bangalore, India, 1969.
- 5 K.K. Prasad, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1972.
- 6 Brahma Deo and V.B. Tare, *Mater. Res. Bull.*, 11 (1976) 469.
- 7 A.M. Azad, R. Sudha and O.M. Sreedharan, *J. Less-Common Met.*, 166 (1990) 57.
- 8 A.M. Azad, R. Sudha and O.M. Sreedharan, *Bull. Mater. Res.*, 25 (1990) 12.
- 9 F. Cotton and G. Wilkinson, *Comprehensive Inorganic Chemistry*, 3rd Edn., Wiley-Eastern, New Delhi, 1975, p. 841.
- 10 C.W.F.T. Pistorius and M.C. Pistorius, *Z. Kristallogr.*, 117 (1962) 259.
- 11 A.M. Azad and O.M. Sreedharan, *J. Appl. Electrochem.*, 17 (1987) 949.
- 12 A.M. Azad, O.M. Sreedharan and J.B. Gnanamoorthy, *J. Nucl. Mater.*, 144 (1987) 94.
- 13 A.M. Azad, Ph.D. Thesis, University of Madras, India, 1989.
- 14 Brahma Deo, J.S. Kachchawaha and V.B. Tare, *Metall. Trans. B*, 7 (1976) 405.
- 15 M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Furip, R.A. McDonald and A.N. Syverud (Eds.), *JANAF Thermochemical Tables*, 3rd Edn., American Chemical Society and American Institute for Physics, New York, 1986.
- 16 O.M. Sreedharan and C. Mallika, Indhira Gandhi Centre for Atomic Research, Kalpakkam, TN, India, RRC-69, 1984.