



# Thermodynamic stabilities of $\text{Cs}_2\text{CrO}_4(\beta)$ , $\text{Cs}_3\text{CrO}_4$ and $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})$ (where $\text{M} = \text{Na}, \text{K}$ or $\text{Cs}$ ) by solid electrolyte emf method

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## Abstract

The emf of the galvanic cells with  $\text{Pt}, \text{Cs}_2\text{CrO}_4 (\alpha \text{ or } \beta) | \text{Cr}_2\text{O}_3 | \text{Cs}_3\text{CrO}_4$  (cell I) and  $\text{Pt}, \text{s}_2\text{CrO}_4(\beta) | \text{Cr}_2\text{O}_3 | \text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  (cell II) against air|Pt reference electrode using 15 mol% calcia stabilized zirconia as the electrolyte were measured to be  $E_{\text{I(a)}}(\text{mV}) = (1345.88 \pm 3.68) - (0.53174 \pm 0.03376)T(\text{K})$ ; (860–967 K)  $E_{\text{I(b)}}(\text{mV}) = (1266.47 \pm 1.50) - (0.45345 \pm 0.04351)T(\text{K})$ ; (1052–1097 K)  $E_{\text{II}}(\text{mV}) = (344.42 \pm 1.84) - (0.25715 \pm 0.0079)T(\text{K})$ ; (1025–1189 K). Using the literature data for the standard Gibbs energies of formation of  $\alpha\text{-Cs}_2\text{CrO}_4$  and  $\text{Cr}_2\text{O}_3$  together with the above numerical expressions for the emf values of cell I, the transition temperature and the standard enthalpy of  $\alpha$ -to- $\beta$  phase transformation in  $\text{Cs}_2\text{CrO}_4$  were found to be 1014 K and 12.8  $\text{kJ mol}^{-1}$ . In addition, the  $\Delta G_f^0(\text{Cs}_3\text{CrO}_4)$  was derived to be as follows:  $(\Delta G_f^0(\text{Cs}_3\text{CrO}_4) \pm 2.0) (\text{kJ mol}^{-1}) = -1531.72 + 0.38044 T(\text{K})$ . The emf results from cell II led to the expression  $(\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7, \text{l}) \pm 3.35) (\text{kJ mol}^{-1}) = -2066.47 + 0.55062 T(\text{K})$ . By making emf measurements on galvanic cells with  $\text{Pt}, \text{M}_2\text{Cr}_2\text{O}_7(\beta) | \text{Cr}_2\text{O}_3 | \text{M}_2\text{Cr}_2\text{O}_7(\text{l})$  (where  $\text{M} = \text{Na}$  or  $\text{K}$ ) against air|Pt as the reference electrode in a cell configuration identical with cell II, the following expressions for  $\Delta G_f^0$  of  $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})$  were derived.  $(\Delta G_f^0(\text{Na}_2\text{Cr}_2\text{O}_7, \text{l}) \pm 2.0) (\text{kJ mol}^{-1}) = -1942.68 + 0.51289 T(\text{K})$ ,  $(\Delta G_f^0(\text{K}_2\text{Cr}_2\text{O}_7, \text{l}) \pm 2.5) (\text{kJ mol}^{-1}) = -2037.35 + 0.5406 T(\text{K})$ . The third law treatment of the emf data on cells I and II yielded the values of  $-1549.8 \pm 1.4 \text{ kJ mol}^{-1}$  and  $-2108 \pm 4 \text{ kJ mol}^{-1}$  for the standard enthalpies of formation,  $\Delta H_{f,298}^0$  of  $\text{Cs}_3\text{CrO}_4(\text{s})$  and  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{s})$ . © 1997 Elsevier Science B.V.

## 1. Introduction

Cesium is one of the major fission products in FBRs [1,2]. The formation of ternary oxides of cesium and chromium as a result of fuel cladding chemical interaction in irradiated oxide fuels had been extensively reported in the literature [3–9]. The type of oxides formed depend not only on the cesium vapor pressure but also on the oxygen potential of the fuel; this in turn depends on the O/M ratio which would tend to increase with burn-up to lower values of hypostoichiometry and also on the Pu content of the fuel [10,11]. Hence for an assessment of the integrity of irradiated fuel pins in FBRs and for a detailed thermodynamic analysis, precise and accurate thermodynamic data for all cesium chromium ternary oxides and the related

phase equilibria at high temperatures are required. Ternary oxides namely,  $\text{Cs}_x\text{CrO}_4$  ( $x = 2$  to  $5$ ),  $\text{CsCr}_3\text{O}_8$  and  $\text{Cs}_2\text{O} \cdot m\text{Cr}_2\text{O}_3$  ( $m = 2$  to  $4$ ) were reported to be present in the Cs–Cr–O system [5,10,11]. According to Fee et al. [10], the oxide  $\text{Cs}_3\text{CrO}_4$  was considered to be the most significant corrosion product formed by interaction between cesium and the stainless steel cladding for the slightly hypostoichiometric  $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2-x}$  fuel. Hence, its thermodynamic stability was studied by Knights and Phillips [12] by employing suitable emf as well as Knudsen cell measurements and by Kim et al. [13] using calorimetry. However, there is considerable disagreement between these two sets of data warranting an independent redetermination of the standard Gibbs energy of formation,  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$  as a function of temperature over the range 700 to 1100 K. In order to determine the high temperature stability of this compound,  $\text{Cs}_3\text{CrO}_4$ , reliable thermodynamic data on the co-existing oxide  $\text{Cs}_2\text{Cr}_2\text{O}_7$  was needed. Such data were

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listed in the thermochemical tables by Knacke et al. [14]. Nevertheless, the tabulated data indicated neither the transition temperature nor the enthalpy of transition for the phase change from  $\alpha$ -to- $\beta$   $\text{Cs}_2\text{CrO}_4$  despite an earlier report characterizing this transition by drop calorimetry by Fredrickson et al. [15]. Therefore, it became necessary to make an independent study of this transition using the emf method. Knights and Phillips et al. [12] reported Gibbs energy data on  $\text{Cs}_4\text{CrO}_4$  from the values of oxygen potentials in the three phase mixtures  $\text{Cs}_3\text{CrO}_4|\text{Cs}_4\text{CrO}_4|\text{Cr}_2\text{O}_3$  and  $\text{Cs}|\text{Cs}_4\text{CrO}_4|\text{Cr}_2\text{O}_3$ . However, the second one could not be an equilibrium mixture as could be seen from the phase diagram by Fee et al. [10] and also from the discussion in a later section of this paper. The compound  $\text{Cs}_5\text{CrO}_4$  was predicted but could not be isolated by Fee et al. Its existence was not confirmed and hence this phase was omitted in the phase diagram proposed by Lindemer et al. [2]. All the higher oxides except  $\text{Cs}_2\text{Cr}_2\text{O}_7$  (s or l), namely  $\text{CsCr}_3\text{O}_8$ ,  $\text{Cs}_2\text{Cr}_3\text{O}_{10}$  and  $\text{Cs}_2\text{Cr}_4\text{O}_{13}$  were reported to be unstable above 770 K, the temperature at which attack of the cladding begins [7]. The oxygen potential of the system  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})|\text{Cs}_2\text{CrO}_4(\alpha)|\text{Cr}_2\text{O}_3$  was reported over a narrow range from 797 to 874 K by Venugopal et al. [16] along with the molar enthalpies of fusion and transition using calorimetry. In addition, low temperature heat capacity data using adiabatic calorimetry were reported by Lyon et al. [17] for  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{s})$  and its  $\Delta H_{f,298}^0$  was reported by O'Hare et al. [18] using acid solution calorimetry. In the present investigation, the transition temperature and the standard enthalpy change for: the  $\alpha$ -to- $\beta$  transition in  $\text{Cs}_2\text{CrO}_4$ ,  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$  over 860 to 1097 K and that of  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  over the range 1025 to 1189 K are reported. By making use of similar oxygen potential measurements on  $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})|\text{M}_2\text{CrO}_4|\text{Cr}_2\text{O}_3$  (where M = Na or K), standard Gibbs energy data on liquid sodium and potassium dichromates have also been measured for the first time using the emf technique and the values are compared with those for Rb and Cs.

## 2. Experimental

### 2.1. Materials

Reagent grade  $\text{Cs}_2\text{CO}_3$  (Alpha Products, USA),  $\text{CsCl}$  (Loba-Chemie, India),  $\text{Na}_2\text{CrO}_4$ ,  $\text{K}_2\text{CrO}_4$  and  $\text{Cr}_2\text{O}_3$  (Johnson and Matthey, U.K.),  $\text{Na}_2\text{Cr}_2\text{O}_7$  as well as  $\text{K}_2\text{Cr}_2\text{O}_7$  (E-Merck, Germany) each of purity 99.9% or better were used as the starting materials. The ternary oxides  $\text{Cs}_2\text{CrO}_4$  and  $\text{Cs}_3\text{CrO}_4$  were synthesized by solid state reaction between  $\text{Cs}_2\text{CO}_3$  and  $\text{Cr}_2\text{O}_3$  in the mole ratios 2:1 and 3:1 respectively after intimate mixing and compacting into cylindrical pellets of 10 mm diameter and 2–3 mm thickness at a pressure of 100 MPa in a hydraulic

press. After compaction, the 2:1 mixture was heated in a stream of dry oxygen at 973 K for about 12 h, whereas the 3:1 mixture was heated in an atmosphere of purified argon at a flow rate of 4 dm<sup>3</sup> per hour at 973 K for 20 h. These procedures were repeated 2–3 times to ensure completion of reactions. The compound  $\text{Cs}_2\text{Cr}_2\text{O}_7$  was made by reacting  $\text{CsCl}$  and  $\text{Na}_2\text{Cr}_2\text{O}_7$  in aqueous solution exploiting the differences in the solubilities of sodium and cesium dichromates [19]. The steps of displacement reaction and the crystallization were repeated thrice to ensure the purity of  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{s})$ . The purity of the compounds synthesized as mentioned above was ascertained by powder X-ray diffraction (XRD) analysis within the 5 mass percent limit of detection of the impurity phases.

### 2.2. Phase equilibrium studies

The co-existence of phases  $\text{Cs}_2\text{CrO}_4|\text{Cs}_3\text{CrO}_4|\text{Cr}_2\text{O}_3$  and  $\text{M}_2\text{CrO}_4|\text{M}_2\text{Cr}_2\text{O}_7|\text{Cr}_2\text{O}_3$  (M = Na, K or Cs) was ascertained by mixing and compacting (as mentioned earlier) the component oxides in equimolar proportions followed by equilibration at 900 K in flowing argon atmosphere for 24 h. The products obtained were examined by XRD to confirm the absence of any other new phase.

### 2.3. EMF method

Two batches of electrode pellets (designated as runs A and B) were made from the above pre-equilibrated equimolar mixtures, one by adding 10% of  $\text{M}_2\text{CrO}_4$  and the other by adding 10% excess of  $\text{Cr}_2\text{O}_3$ . These batches of mixtures were compacted into pellets as described

Table 1  
Temperature dependence of emf of cell I: Pt,  $\text{Cs}_3\text{CrO}_4$ ,  $\text{Cs}_2\text{CrO}_4$  ( $\alpha$  or  $\beta$ ),  $\text{Cr}_2\text{O}_3(\text{s})|15 \text{ CSZ}|\text{air}$  ( $p_{\text{O}_2} = 0.21 \text{ atm}$ ), Pt

(a) Temperature range of $\alpha$ - $\text{Cs}_2\text{CrO}_4$					
Serial <sup>a</sup> no.	T (K)	E (mV)	Serial <sup>a</sup> No.	T (K)	E (mV)
A-1	859.55	893.0	B-1	891.35	870.5
A-2	875.15	881.6	B-2	935.45	846.7
A-3	907.15	858.7	B-3	950.45	840.3
A-4	940.15	841.6	B-4	967.15	836.3
A-5	957.75	839.2			
(b) Temperature range of $\beta$ - $\text{Cs}_2\text{CrO}_4$					
Serial no.	T (K)	E (mV)			
A-1	1052.15	788.5			
A-2	1060.55	785.7			
A-3	1077.15	779.7			
A-4	1097.15	768.0			

<sup>a</sup> A and B are different runs of measurement based on different pellets with marginal (10%) variation in the equimass composition of three phases in order to ascertain the equilibrium nature of the emf values.

Table 2

Temperature dependence of emf of cell II: Pt, Cs<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), Cs<sub>2</sub>CrO<sub>4</sub>(β), Cr<sub>2</sub>O<sub>3</sub>|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt

Serial no. <sup>a</sup>	T (K)	E (mV)	Serial no. <sup>a</sup>	T (K)	E (mV)
A-1	1065.65	67.9	B-1	1024.95	82.9
A-2	1086.35	62.3	B-2	1039.25	78.4
A-3	1110.15	56.5	B-3	1072.55	71.4
A-4	1133.25	51.3	B-4	1095.95	64.8
A-5	1157.05	45.6	B-5	1118.75	58.5
A-6	1181.75	40.2	B-6	1143.45	52.4
A-7	1033.05	80.8	B-7	1029.15	79.4
A-8	1054.35	73.3	B-8	1052.15	73.2
A-9	1076.65	66.7	B-9	1070.95	67.7
A-10	1166.25	45.9	B-10	1093.95	61.3
A-11	1189.15	41.2	B-11	1118.75	55.5
			B-12	1140.95	50.1

<sup>a</sup> As in Table 1.

earlier. This nominal variation in composition was resorted to, for verifying the attainment of true equilibrium. The emf measurements were made on the following galvanic cells:

Pt, Cs<sub>3</sub>CrO<sub>4</sub>(s), Cs<sub>2</sub>CrO<sub>4</sub>(α or β),Cr<sub>2</sub>O<sub>3</sub>(s)|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt (I)Pt, Cs<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), Cs<sub>2</sub>CrO<sub>4</sub>(β),Cr<sub>2</sub>O<sub>3</sub>(s)|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt (II)Pt, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), Na<sub>2</sub>CrO<sub>4</sub>(β),Cr<sub>2</sub>O<sub>3</sub>(s)|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt (III)Pt, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), K<sub>2</sub>CrO<sub>4</sub>(β),Cr<sub>2</sub>O<sub>3</sub>(s)|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt (IV)

where '15 CSZ' represents a 15 mol% calcia stabilized zirconia electrolyte. The one-end closed solid electrolyte tube used was of the dimensions, 12 mm outer diameter, 1.5 mm wall thickness, and 300 mm long with the closed

Table 3

Temperature dependence of emf of cell III: Pt, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), Na<sub>2</sub>CrO<sub>4</sub>(β), Cr<sub>2</sub>O<sub>3</sub>|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt

Serial no. <sup>a</sup>	T (K)	E (mV)	Serial no. <sup>a</sup>	T (K)	E (mV)
A-1	960.15	42.5	B-1	968.55	40.0
A-2	978.45	38.6	B-2	981.15	35.6
A-3	1003.55	30.1	B-3	988.95	36.7
A-4	1024.35	25.8	B-4	1069.35	18.1
A-5	1046.55	21.7			

<sup>a</sup> As in Table 1.

Table 4

Temperature dependence of emf of cell IV: Pt, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>(l), K<sub>2</sub>CrO<sub>4</sub>(β), Cr<sub>2</sub>O<sub>3</sub>|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt

Serial no. <sup>a</sup>	T (K)	E (mV)	Serial no. <sup>a</sup>	T (K)	E (mV)
A-1	978.45	67.9	B-1	999.15	65.7
A-2	1014.75	58.5	B-2	1022.05	61.6
A-3	1054.65	51.9	B-3	1034.45	60.0
A-4	1078.75	45.6	B-4	1044.55	56.9
A-5	1101.25	39.7	B-5	1065.65	50.4
A-6	1118.75	33.9	B-6	1087.65	44.1
A-7	1124.85	32.1	B-7	1112.65	40.2
A-8	1148.15	25.7	B-8	1133.15	35.1

<sup>a</sup> As in Table 1.

end being flat. A nearly static atmosphere of purified argon was provided for the test electrode compartment. The temperature was measured using a Pt–10% Rh/Pt thermocouple (which was calibrated at the freezing points of ultrapure Sn, Zn, Sb and Ag as per IPTS 68) whose junction was located near the flat end of the electrolyte tube in the air reference electrode compartment. The reversibility of the emf readings was ascertained by their reproducibility in thermal cycling. The absence of asymmetric potentials was verified by measuring null emf using the same cell assembly with air in both the electrode chambers over the experimental temperature range.

### 3. Results

The emf results on cells (I) to (IV) are given in Tables 1–4 and plotted in Figs. 1–4 respectively. These results could be represented by the following least squares expres-

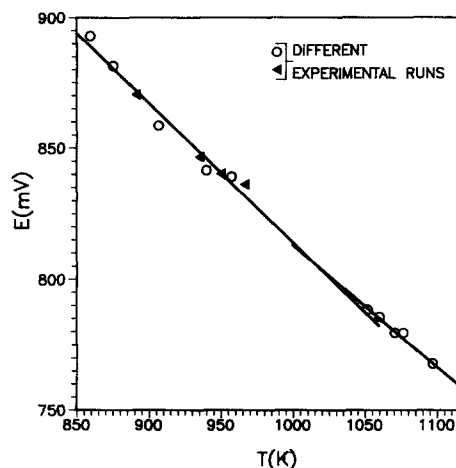


Fig. 1. Temperature dependence of emf of cell I: Pt, Cs<sub>3</sub>CrO<sub>4</sub>(s), Cs<sub>2</sub>CrO<sub>4</sub>(α or β), Cr<sub>2</sub>O<sub>3</sub>(s)|15 CSZ|air (p<sub>O<sub>2</sub></sub> = 0.21 atm), Pt.

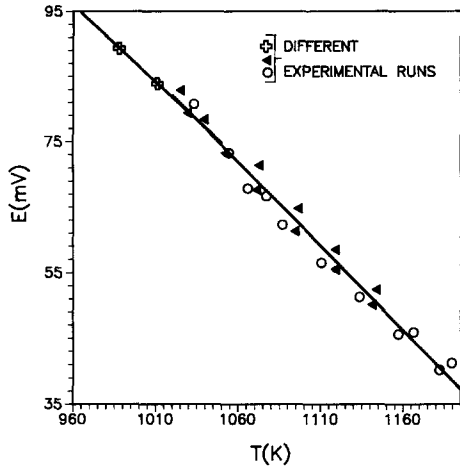


Fig. 2. Temperature dependence of emf of cell II: Pt,  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$ ,  $\text{Cs}_2\text{CrO}_4(\beta)$ ,  $\text{Cr}_2\text{O}_3(\text{s})$ |15 CSZ|air ( $p_{\text{O}_2} = 0.21$  atm), Pt.

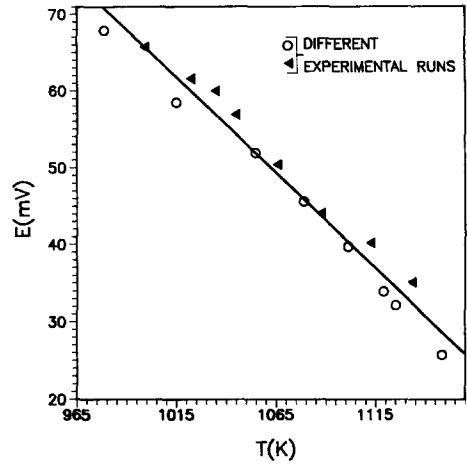


Fig. 4. Temperature dependence of emf of cell IV: Pt,  $\text{K}_2\text{Cr}_2\text{O}_7(\text{l})$ ,  $\text{K}_2\text{CrO}_4(\beta)$ ,  $\text{Cr}_2\text{O}_3(\text{s})$ |15 CSZ|air ( $p_{\text{O}_2} = 0.21$  atm), Pt.

sions valid over the ranges of temperatures indicated within parentheses after each expression:

$$E_{\text{I(a)}}(\text{mV}) = (1345.88 \pm 3.68) - (0.53174 \pm 0.03376)T(\text{K}) \quad (860\text{--}967 \text{ K}), \quad (1)$$

$$E_{\text{I(b)}}(\text{mV}) = (1266.47 \pm 1.50) - (0.45345 \pm 0.04351)T(\text{K}) \quad (1052\text{--}1097 \text{ K}), \quad (2)$$

$$E_{\text{II}}(\text{mV}) = (344.42 \pm 1.84) - (0.25715 \pm 0.0079)T(\text{K}) \quad (1025\text{--}1189 \text{ K}), \quad (3)$$

$$E_{\text{III}}(\text{mV}) = (262.11 \pm 1.32) - (0.22944 \pm 0.01258)T(\text{K}) \quad (960\text{--}1069 \text{ K}), \quad (4)$$

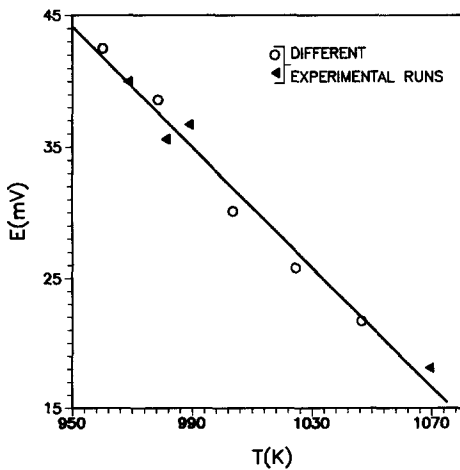


Fig. 3. Temperature dependence of emf of cell III: Pt,  $\text{Na}_2\text{Cr}_2\text{O}_7(\text{l})$ ,  $\text{Na}_2\text{CrO}_4(\beta)$ ,  $\text{Cr}_2\text{O}_3(\text{s})$ |15 CSZ|air ( $p_{\text{O}_2} = 0.21$  atm), Pt.

$$E_{\text{IV}}(\text{mV}) = (313.79 \pm 2.29) - (0.24834 \pm 0.0115)T(\text{K}) \quad (978\text{--}1148 \text{ K}). \quad (5)$$

#### 4. Discussion

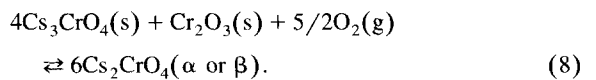
##### 4.1. $\alpha$ -to- $\beta$ phase transition in $\text{Cs}_2\text{CrO}_4$

The emf expressions (1) and (2) were corrected for the standard state of oxygen in the air/Pt reference electrode to yield the following expressions:

$$E_{\text{corrected}}(\text{mV}) = (1345.88 \pm 3.68) - (0.49804 \pm 0.03376)T(\text{K}), \quad (6)$$

$$E_{\text{corrected}}(\text{mV}) = (1266.47 \pm 1.50) - (0.41976 \pm 0.04351)T(\text{K}). \quad (7)$$

For the passage of 10 faraday of electricity, the overall cell reaction could be represented as



The standard Gibbs energy changes,  $\Delta G_{\text{R}}^0(\alpha)$  and  $\Delta G_{\text{R}}^0(\beta)$  for the Eq. (8) were calculated using the Nernst equation and are given below:

$$\Delta G_{\text{R}}^0(\alpha \text{ or } \beta) = 6\Delta G_{\text{f}}^0(\text{Cs}_2\text{CrO}_4, \alpha \text{ or } \beta) - 4\Delta G_{\text{f}}^0(\text{Cs}_3\text{CrO}_4) - \Delta G_{\text{f}}^0(\text{Cr}_2\text{O}_3), \quad (9)$$

$$\Delta G_{\text{R}(\alpha)}^0(\text{kJ mol}^{-1}) = (-1298.60 \pm 3.55) + (0.48054 \pm 0.03257)T(\text{K}), \quad (10)$$

$$\Delta G_{R(\beta)}^0(\text{kJ mol}^{-1}) = (-1221.98 \pm 1.45) + (0.40501 \pm 0.04198)T(\text{K}). \quad (11)$$

These Eqs. (10) and (11) are valid for the  $\alpha$  and  $\beta$  forms of  $\text{Cs}_2\text{CrO}_4$  in the temperature ranges indicated in Eqs. (1) and (2). Since there is no phase transition in  $\text{Cs}_3\text{CrO}_4$  and  $\text{Cr}_2\text{O}_3$  in the range 800–1100 K, the difference in  $\Delta G_R^0$  calculated from Eqs. (10) and (11) would correspond to the standard Gibbs energy change,  $\Delta G_{(\alpha-\beta)}^0$  for the  $\alpha$ -to- $\beta$  transition in  $\text{Cs}_2\text{CrO}_4$ . Thus by solving Eqs. (10) and (11) one obtains

$$\Delta G_{(\alpha-\beta)}^0(\text{Cs}_2\text{CrO}_4)(\text{kJ mol}^{-1}) = (12.77 \pm 0.83) - (0.01259 \pm 0.01243)T(\text{K}). \quad (12)$$

This leads to values of 1014 K and 12.8 kJ mol<sup>-1</sup> for  $T_{\text{trans}}$  and standard enthalpy of transition,  $\Delta H_{\text{trans}}^0$  for  $\text{Cs}_2\text{CrO}_4$ . This value of 1014 K is in fair agreement with that of 1023 K cited by Levin et al. [20], 1028 K by Belyaev et al. [21] and 1031 K by Fredrickson et al. [15] but is considerably lower than 1043 K by Samuseva et al. [22] and 1073 K reported by Erdey et al. [23]. However, this  $\alpha$ -to- $\beta$  transition in  $\text{Cs}_2\text{CrO}_4$  is missing in the thermochemical tables compiled by Knacke et al. [14]. Hence, it may be worthwhile to compare the values of  $T_{\text{trans}}$  and  $\Delta H_{\text{trans}}^0$  for the solid-state transition in  $\text{Cs}_2\text{CrO}_4$  with those of the other alkali metal monochromates  $\text{M}_2\text{CrO}_4$  from the literature. Such a comparison is made in Table 5 which shows a monotonic increase in the  $T_{\text{trans}}$  of  $\text{M}_2\text{CrO}_4$  where M varies from Na to Cs. However, the values of  $\Delta H_{\text{trans}}^0$  for  $\alpha$ -to- $\beta$  transition are more or less constant and are of the order of 10 kJ mol<sup>-1</sup> for all the alkali monochromates. The reasons for the low values of  $\Delta H_{\text{trans}}^0$  for Cs and Rb monochromates, namely, 2.9 and 5.5 kJ mol<sup>-1</sup> respectively (cf. Table 5), obtained by drop calorimetry [15,24] are not quite clear. Efforts were also made to cross check the values of  $T_{\text{trans}}$  and  $\Delta H_{\text{trans}}^0$  for this phase change in  $\text{Cs}_2\text{CrO}_4(\text{s})$  by making measurements of emf of cell II at

lower temperatures. It was found that no reproducible emf measurement could be made on cell II at temperatures lower than 988 K. Thus from the emf results at just two temperatures namely 988 and 1011 K (cf. Fig. 2), only qualitative values of 1037 K and 7 kJ mol<sup>-1</sup> could be derived for  $T_{\text{trans}}$  and  $\Delta H_{\text{trans}}^0$ . It is obvious that not much weight could be given for such data on phase change derived from just two emf readings separated by a narrow span of 23 K. Hence the fair agreement between the value of  $T_{\text{trans}}$  in  $\text{Cs}_2\text{CrO}_4$  from the present investigation and those from the literature may not be merely fortuitous owing to the larger number of data points. However, uncertainty limits for  $T_{\text{trans}}$  and  $\Delta H_{\text{trans}}^0$  from emf can not be readily given in view of the unreliability of the emf technique in identifying the slopes and intercepts with the entropy and enthalpy terms in the Gibbs energy expressions [25].

It may be observed that the emf measurements on cells I and II (for the determination of  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$  and  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$ ) were conducted in the temperature regions encompassing  $T_{\text{trans}}$ . Therefore, it was necessary to compute  $\Delta G_f^0$ , ( $\alpha$ - $\text{Cs}_2\text{CrO}_4$ ) using the following expression calculated from the values compiled by Knacke et al. [14] valid for the range 800 to 1000 K:

$$\Delta G_f^0(\alpha - \text{Cs}_2\text{CrO}_4)(\text{kJ mol}^{-1}) = -1424.57 + 0.37492T(\text{K}). \quad (13)$$

Combining Eqs. (12) and (13),  $\Delta G_f^0$ , ( $\beta$ - $\text{Cs}_2\text{CrO}_4$ ) was calculated to be

$$\Delta G_f^0(\beta - \text{Cs}_2\text{CrO}_4)(\text{kJ mol}^{-1}) = -1411.8 + 0.36233T(\text{K}). \quad (14)$$

This expression for the  $\beta$ -form should be taken as valid at least for a narrow range of temperature of about 100° above  $T_{\text{trans}}$  since the  $\Delta C_p$  terms were neglected.

The uncertainty in the  $\Delta G_f^0$ , of the  $\alpha$ -form was of the order of  $\pm 4$  kJ mol<sup>-1</sup>. Therefore, the uncertainty in  $\Delta G_f^0$  of the  $\beta$ -form could be of the order of  $\pm 5$  kJ mol<sup>-1</sup>.

#### 4.2. $\Delta G_f^0(\text{Cs}_3\text{CrO}_4)$

Substituting (in Eq. (9)) the numerical expressions (11) and (14) as well as that for the critically assessed data for  $\Delta G_f^0(\text{Cr}_2\text{O}_3)$  from the literature [26–28], the  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$  was calculated and is given as follows:

$$\Delta G_f^0(\text{Cs}_3\text{CrO}_4 \pm 2.0)(\text{kJ mol}^{-1}) = -1531.72 + 0.38044T(\text{K}). \quad (15)$$

Eq. (15) is valid over the experimental temperature range of 860 to 1098 K which is fortuitously coinciding with 870 to 1100 K over which range Knights and Phillips [12] had made similar oxygen potential measurements by emf technique on the system  $\text{Cs}_2\text{CrO}_4|\text{Cs}_3\text{CrO}_4|\text{Cr}_2\text{O}_3$ . The  $RT \ln p_{\text{O}_2}$  values thus reported by them agreed well with

Table 5  
 $T_{\text{trans}}$  and  $\Delta H_{\text{trans}}^0$  in  $\text{M}_2\text{CrO}_4$  (M = Na, K, Rb or Cs)

M	$T_{\text{trans}}$ (K)	$\Delta H_{\text{trans}}^0$ (kJ mol <sup>-1</sup> )	Ref.
Na	694	9.6	[14]
K	939	10.0	[14]
Rb	978	8.0	[31]
	998	5.5	[24]
	973	–	[20]
Cs	1031	2.9	[15]
	1014	12.8	this work
	1023	–	[20]
	1028	–	[21]
	1043	–	[22]
	1073	–	[23]

Table 6  
Comparison of  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$

Serial no.	$\Delta G_f^0$ ( $\text{kJ mol}^{-1}$ ) = $A + BT(\text{K})$		$\Delta G_f^0$ ( $\text{kJ mol}^{-1}$ ) at 973 K	Ref. and remarks
	A	B		
1.	-1510.0	0.43	-1092	from table 2 in Ref. [12]
2.	-1533.50	0.38183	-1162	recalculated <sup>a</sup> from Ref. [12]
3.	-1566.85	0.4253	-1153	[13]
4.	-1531.72	0.38044	-1162	this work

<sup>a</sup> The  $\Delta G_f^0$  data for  $\alpha\text{-Cs}_2\text{CrO}_4$  and  $\text{Cr}_2\text{O}_3$  used in this work was combined with  $RT \ln p_{\text{O}_2}$  data from table 1 of Ref. [12] in this calculation.

the present work whereas the  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$  calculated by them differed widely from Eq. (15) owing to their use of rather old reference data for  $\text{Cr}_2\text{O}_3$  and  $\text{Cs}_2\text{CrO}_4$ .

Hence, using the values reported by Knights and Phillips [12] for  $RT \ln p_{\text{O}_2}$  in conjunction with the set of critically assessed data in the present work, the  $\Delta G_f^0$  of  $\text{Cs}_3\text{CrO}_4$

Table 7  
(a) Gibbs energy data used for computing  $\Delta G_f^0$  ( $\text{Cs}_3\text{CrO}_4$ ) at each experimental temperature

Serial no.	T (K)	$\Delta G_R^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0(\alpha\text{-Cs}_2\text{CrO}_4)$ ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0$ ( $\text{Cr}_2\text{O}_3$ ) ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0$ ( $\text{Cs}_3\text{CrO}_4$ ) ( $\text{kJ mol}^{-1}$ )
1.	859.55	-889.58	-1102.31	-897.44	-1206.71
2.	875.15	-879.08	-1096.46	-893.59	-1201.52
3.	891.35	-868.90	-1090.39	-889.58	-1195.97
4.	907.15	-858.03	-1084.46	-885.67	-1190.77
5.	940.15	-842.60	-1072.09	-877.52	-1178.11
6.	957.75	-840.87	-1065.49	-873.17	-1169.73
7.	935.45	-847.37	-1073.85	-878.68	-1179.26
8.	950.45	-841.69	-1068.23	-874.97	-1173.18
9.	967.15	-838.37	-1061.97	-870.84	-1165.65

Serial no.	T (K)	$\Delta G_R^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0(\beta\text{-Cs}_2\text{CrO}_4)$ ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0$ ( $\text{Cr}_2\text{O}_3$ ) ( $\text{kJ mol}^{-1}$ )	$\Delta G_f^0$ ( $\text{Cs}_3\text{CrO}_4$ ) ( $\text{kJ mol}^{-1}$ )
1.	1052.15	-792.12	-1029.92	-849.83	-1134.37
2.	1060.55	-792.58	-1026.87	-847.75	-1130.22
3.	1077.15	-787.33	-1020.85	-843.65	-1123.53
4.	1097.15	-776.69	-1013.59	-838.70	-1116.54

(b) Third-law computation of  $\Delta H_{f,298}^0$  ( $\text{Cs}_3\text{CrO}_4$ )

Serial no.	T (K)	$\Delta G_f^0$ ( $\text{Cs}_3\text{CrO}_4$ ) ( $\text{kJ mol}^{-1}$ )	$\Delta \text{fef}$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$\Delta H_{f,298}^0$ ( $\text{kJ mol}^{-1}$ )
1.	859.55	-1206.71	399.08	-1549.74
2.	875.15	-1201.52	398.69	-1550.43
3.	891.35	-1195.97	398.28	-1550.98
4.	907.15	-1190.77	397.89	-1551.71
5.	940.15	-1178.11	397.06	-1551.41
6.	957.75	-1169.73	396.63	-1549.60
7.	935.45	-1179.26	397.18	-1550.80
8.	950.45	-1173.18	396.81	-1550.33
9.	967.15	-1165.65	396.39	-1549.02
10.	1052.15	-1134.37	394.27	-1549.20
11.	1060.55	-1130.22	394.06	-1548.14
12.	1077.15	-1123.53	393.64	-1547.54
13.	1097.15	-1116.54	393.14	-1547.88

Mean value:  $\Delta H_{f,298}^0 = -1549.8 \pm 1.4 \text{ kJ mol}^{-1}$ .

was also recalculated and is compared in Table 6. It could be seen from this table that the Gibbs energy data reported in the present work shows excellent agreement with those recalculated from the work by Knights and Phillips [12]. Nevertheless, the agreement is only fair with the calorimetric data by Kim et al. [13]. It should be noted that an  $\alpha$ -to- $\beta$  phase transition was reported in  $\text{Cs}_3\text{CrO}_4$  at 774 K by Kim et al. [13] using calorimetry. But this  $T_{\text{trans}}$  lies well below the temperature range of emf studies reported in this work. To assess the temperature dependent errors in the emf measurements and their consistency with the calorimetric data, it was necessary to carry out the third-law analysis. For this purpose, the values of free energy functions for  $\text{Cs}_3\text{CrO}_4$  in the range 800 to 1000 K tabulated by Kim et al. [13] were combined with the corresponding values for the elements  $\text{Cs}(\text{l})$ ,  $\text{Cr}(\text{s})$  and  $\text{O}_2(\text{g})$  from Hultgren et al. [29] and with the  $\Delta G_{\text{R}}^0$  values calculated from each emf value from Table 1 in order to derive those for  $\Delta H_{\text{f},298}^0$  at different experimental temperatures. The details of the computations are given in Table 7(a) and (b).

A third-law plot of  $\Delta H_{\text{f},298}^0$  is shown in Fig. 5. The mean value of  $\Delta H_{\text{f},298}^0$  was found to be  $-1549.8 \pm 1.4$  kJ mol $^{-1}$ . The almost random scatter of values of  $\Delta H_{\text{f},298}^0$  around its mean value in this plot indicates the absence of significant temperature dependent errors in the emf measurements. This value is also found to be in good agreement with  $-1545.4$  kJ mol $^{-1}$  reported by Kim et al. [13].

Lindemer et al. [2] had estimated values of  $\Delta H_{\text{f},298}^0$  for all the alkali chromates of the general formula  $\text{M}_3\text{CrO}_4$  in their review article. Since the experimental data are now reliably known for a couple of such chromates, it is possible to make a comparison of these data. The value of  $\Delta H_{\text{f},298}^0$  of  $\text{Cs}_3\text{CrO}_4$  is seen to be of the same magnitude as that of  $-1548$  kJ mol $^{-1}$  for  $\text{K}_3\text{CrO}_4$  reported by Johnson et al. [30]. Pankajavalli et al. [31] had reported a value of  $-1538$  kJ mol $^{-1}$  for  $\Delta H_{\text{f}}^0$  of  $\text{Rb}_3\text{CrO}_4$  at a mean temperature of their emf measurements namely at 993 K.

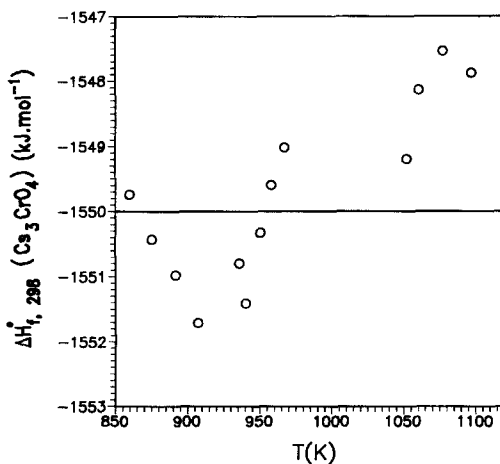


Fig. 5. Third-law plot of  $\Delta H_{\text{f},298}^0$  of  $\text{Cs}_3\text{CrO}_4$ .

Assuming the value of  $\Delta H_{\text{f},993}^0 - \Delta H_{\text{f},298}^0$  for  $\text{Rb}_3\text{CrO}_4$  to be of the same magnitude as for the Cs analog, the  $\Delta H_{\text{f},298}^0$  for  $\text{Rb}_3\text{CrO}_4$  could be estimated to be  $-1554$  kJ mol $^{-1}$ .

Knights and Phillips [12] had reported an expression for  $RT \ln p_{\text{Cs}}$  for the phase mixture  $\text{Cs}_3\text{CrO}_4|\text{Cs}_4\text{CrO}_4|\text{Cr}_2\text{O}_3$  over the range 500 to 680 K using Knudsen cell technique. Combining this, with the equilibrium vapor pressure data for  $\text{Cs}(\text{l})$  from the literature [32] and with Eq. (15), the following expression could be derived for  $\Delta G_{\text{f}}^0$  of  $\text{Cs}_4\text{CrO}_4$ :

$$\Delta G_{\text{f}}^0(\text{Cs}_4\text{CrO}_4)(\text{kJ mol}^{-1}) = -1572.4 + 0.39497T(\text{K}). \quad (16)$$

The Gibbs energy expressions (Eqs. (15) and (16)) could be used to check the consistency with the phase diagram for Cs–Cr–O system. One of the quadrilateral in the Cs–Cr–O phase diagram is formed by the phases  $\text{Cs}(\text{l})$ ,  $\text{Cr}(\text{s})$ ,  $\text{Cr}_2\text{O}_3(\text{s})$  and  $\text{Cs}_4\text{CrO}_4$ . In the phase diagram reported by Knights and Phillips [12], a tie-line between  $\text{Cs}(\text{l})$  and  $\text{Cr}_2\text{O}_3$  was marked suggesting their possible coexistence with  $\text{Cs}_4\text{CrO}_4$ . However, in the phase diagrams suggested by Fee et al. [10] and Lindemer et al. [2], the tie-line is between  $\text{Cs}_4\text{CrO}_4$  and  $\text{Cr}(\text{s})$ . To ascertain which of these two lines is correct, the  $\Delta G_{\text{R}}^0$  for the following reaction was calculated and is given in Eq. (18):



$$\Delta G_{\text{R}(17)}^0 = -277.44 + 0.19603T(\text{K}). \quad (18)$$

As seen from Eq. (18), the  $\Delta G_{\text{R}}^0$  is substantially negative in the useful temperature range upholding the correctness of the phase diagram by Fee et al. [10] and Lindemer et al. [2]. Using Eqs. (13), (15) and (16) in conjunction with  $p_{\text{Cs}}$  values from the literature [32], the following Eqs. (19) and (20) were calculated for  $\log_{10}(p_{\text{Cs}}/\text{mm Hg})$  for the biphasic regions  $\text{Cs}_2\text{CrO}_4|\text{Cs}_3\text{CrO}_4$  and  $\text{Cs}_3\text{CrO}_4|\text{Cs}_4\text{CrO}_4$  respectively:

$$\begin{aligned} \log_{10}(p_{\text{Cs}})(\text{Cs}_2\text{CrO}_4|\text{Cs}_3\text{CrO}_4)(\text{mm Hg}) \\ = 7.398 - 9908/T(\text{K}), \end{aligned} \quad (19)$$

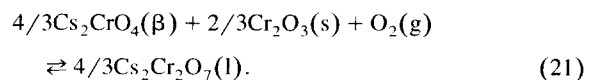
$$\begin{aligned} \log_{10}(p_{\text{Cs}})(\text{Cs}_3\text{CrO}_4|\text{Cs}_4\text{CrO}_4)(\text{mm Hg}) \\ = 6.277 - 5772/T(\text{K}). \end{aligned} \quad (20)$$

These cesium potentials would be helpful in assessing the driving force for the formation of the gaseous  $\text{Cs}_2\text{Te}$  which was reported to be deleterious to the life of the fuel pin [1].

### 4.3. $\Delta G_{\text{f}}^0$ ( $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})$ ) ( $\text{M} = \text{Cs}, \text{Na}$ or $\text{K}$ )

#### 4.3.1. $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$

The overall cell reaction for cell II for the passage of 4 faraday of electricity could be represented by



The standard Gibbs energy change  $\Delta G_R^0$ , for the Eq. (21) would correspond to

$$\Delta G_R^0 = 4/3\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7, \text{l}) - 4/3\Delta G_f^0(\text{Cs}_2\text{CrO}_4, \beta) - 2/3\Delta G_f^0(\text{Cr}_2\text{O}_3). \quad (22)$$

In order to calculate  $\Delta G_R^0$  (Eq. (21)), the emf expression (Eq. (3)) was corrected for the standard state of oxygen in the air reference electrode and was substituted into the Nernst equation to yield the following expression:

$$\Delta G_R^0(\text{kJ mol}^{-1}) = (-132.93 \pm 0.71) + (0.08624 \pm 0.00305)T(\text{K}). \quad (23)$$

By combining Eqs. (14), (22) and (23) with the  $\Delta G_f^0$  of  $\text{Cr}_2\text{O}_3$  from the literature, the  $\Delta G_f^0$  ( $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$ ) was calculated to be

$$\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l}) \pm 4.3)(\text{kJ mol}^{-1}) = -2066.47 + 0.55062T(\text{K}). \quad (24)$$

The above expression is valid over 1025 to 1189 K which was the temperature range of actual emf measurements on cell II. Similar emf measurements were also reported by Venugopal et al. [16] at a somewhat lower temperature range of 797 to 874 K resulting in the expression

$$(E \pm 0.5)(\text{mV}) = 160 - 0.08104T(\text{K}) \quad (25)$$

for cell II using the same air|Pt reference electrode. By making use of the same set of Gibbs energy data for  $\text{Cr}_2\text{O}_3$  and  $\text{Cs}_2\text{CrO}_4(\alpha)$  as in this work, the  $\Delta G_f^0$  of  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  was recalculated from the work by Venugopal et al. to be

$$(\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7, \text{l}) \pm 3.9)(\text{kJ mol}^{-1}) = -2025.28 + 0.51223T(\text{K}). \quad (26)$$

Although the entropy terms in Eqs. (24) and (26) differ considerably, the values of  $-1515$  and  $-1513 \text{ kJ mol}^{-1}$  obtained for  $\Delta G_f^0$  of  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  at 1000 K from the respective equations show an excellent agreement between the two sets of data ignoring the phase change in  $\text{Cs}_2\text{CrO}_4$  by extrapolating Eq. (24) by just  $20^\circ$  below the  $T_{\text{trans}}$ .

#### 4.3.2. $\text{Na}_2\text{Cr}_2\text{O}_7(\text{l})$ and $\text{K}_2\text{Cr}_2\text{O}_7(\text{l})$

The emf results on cells III and IV represented by the least squares expressions (4) and (5) corresponding to the

data in Tables 3 and 4 and Figs. 3 and 4 respectively were processed along similar lines (as in the case of  $\text{Cs}_2\text{Cr}_2\text{O}_7$ ) resulting in the following expressions for  $\Delta G_f^0$  of  $\text{Na}_2\text{Cr}_2\text{O}_7(\text{l})$  and  $\text{K}_2\text{Cr}_2\text{O}_7(\text{l})$ :

$$(\Delta G_f^0(\text{Na}_2\text{Cr}_2\text{O}_7(\text{l})) \pm 2.0)(\text{kJ mol}^{-1}) = -1942.68 + 0.51289T(\text{K}), \quad (27)$$

$$(\Delta G_f^0(\text{K}_2\text{Cr}_2\text{O}_7(\text{l})) \pm 2.5)(\text{kJ mol}^{-1}) = -2037.35 + 0.5406T(\text{K}). \quad (28)$$

In deriving the above expressions, the value of  $\Delta G_f^0$  of the  $\beta$ -form of  $\text{M}_2\text{CrO}_4$  ( $\text{M} = \text{Na}$  or  $\text{K}$ ) calculated from the  $\mu^0$  values listed by Knacke et al. [14] were used. The expression (27) for  $\text{Na}_2\text{Cr}_2\text{O}_7(\text{l})$  is valid over the range 960 to 1069 K while Eq. (28) for  $\text{K}_2\text{Cr}_2\text{O}_7(\text{l})$  is valid for 978 to 1148 K. The values of  $\Delta G_f^0$  of  $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})$  where  $\text{M}$  is  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$  or  $\text{Cs}$  are compared in Table 8. It is found that the  $\Delta G_f^0$  for the dichromates of  $\text{K}$  and  $\text{Rb}$  are about the same magnitude while those of  $\text{Na}$  and  $\text{Cs}$  analogues differ considerably.

To evaluate  $\Delta H_{f,298}^0$  ( $\text{Cs}_2\text{Cr}_2\text{O}_7, \text{s}$ ) the third-law analysis as indicated earlier in Section 4.2, was carried out on the emf data from cell II by making use of the free energy functions for  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  reported by Venugopal et al. [16] for the range 700 to 900 K. This had yielded a value of  $-2108 \pm 4 \text{ kJ mol}^{-1}$  for  $\Delta H_{f,298}^0$  ( $\text{Cs}_2\text{Cr}_2\text{O}_7$ ). The detailed third-law calculations similar to those on  $\text{Cs}_3\text{CrO}_4$  are given in Table 9(a) and (b). However, the third-law analysis revealed the presence of temperature dependent trend in the values of  $\Delta H_{f,298}^0$ . This could be indicative of temperature dependent errors either in the present emf data or in the free energy functions used for computing the enthalpy values. A redetermination of the free energy functions for  $\text{Cs}_2\text{Cr}_2\text{O}_7(\text{l})$  could be helpful in minimizing such errors. This value is compared with those of the other alkali dichromates from the literature along with their Gibbs energy data in Table 8. Due to the lack of reliable data for the free energy functions for dichromates of  $\text{Na}$  or  $\text{K}$ , no third-law analysis was resorted to in deriving  $\Delta H_{f,298}^0$ . However, the values of  $\Delta H_{f,298}^0$  for dichromates of  $\text{K}$  and  $\text{Rb}$  are also similar in contrast to those of  $\text{Na}$  and  $\text{Cs}$ .

Table 8

The  $\Delta H_{f,298}^0$  and  $\Delta G_f^0$  of  $\text{M}_2\text{Cr}_2\text{O}_7$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}$  or  $\text{Cs}$ )

M	$\Delta H_{f,298}^0$ (kJ mol <sup>-1</sup> )	$\Delta G_f^0$ (kJ mol <sup>-1</sup> ) = A + BT (K)		T range (K)	$\Delta G_f^0$ (kJ mol <sup>-1</sup> ) at 1000 K	Ref.
		A	B			
Na	-1982.0 [18]	-1942.68	0.51289	960–1069	-1430	this work
K	-2064.0 [18]	-2037.35	0.5406	978–1148	-1497	this work
Rb	-2058.5 [18]	-2049.89	0.55197	973–1153	-1498	[31]
Cs	-2108.0	-2066.44	0.55122	1025–1189	-1515	this work
	-2100.0	-2025.28	0.51223	797–874	-1513	[16]
	-2091.1 [18]	-	-	-	-	-



Table 9

(a) Gibbs energy data used for computing  $\Delta G_f^0$  of  $\text{Cs}_2\text{Cr}_2\text{O}_7$  at each experimental temperature

Sl. No	$T$ (K)	$\Delta G_R^0$ (kJ mol <sup>-1</sup> )	$\Delta G_f^0(\beta\text{-Cs}_2\text{CrO}_4)$ (kJ mol <sup>-1</sup> )	$\Delta G_f^0(\text{Cr}_2\text{O}_3)$ (kJ mol <sup>-1</sup> )	$\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7)$ (kJ mol <sup>-1</sup> )
1.	1065.65	-40.06	-1025.02	-846.49	-1478.31
2.	1086.35	-38.17	-1017.51	-841.37	-1466.82
3.	1110.15	-36.26	-1008.87	-835.49	-1453.81
4.	1133.25	-34.52	-1000.49	-829.78	-1441.27
5.	1157.05	-32.64	-991.85	-823.89	-1428.28
6.	1181.75	-30.86	-992.88	-817.79	-1424.92
7.	1033.05	-44.61	-1036.85	-854.55	-1497.58
8.	1054.35	-42.01	-1029.12	-849.28	-1485.27
9.	1076.65	-39.75	-1021.03	-843.77	-1472.73
10.	1024.95	-45.31	-1039.79	-856.55	-1502.05
11.	1039.25	-43.77	-1034.60	-853.02	-1493.94
12.	1072.55	-41.51	-1022.52	-844.78	-1476.04
13.	1095.95	-39.26	-1014.02	-838.99	-1462.96
14.	1118.75	-37.11	-1005.75	-833.36	-1450.26
15.	1143.45	-35.08	-996.78	-827.26	-1436.72
16.	1029.15	-44.01	-1038.27	-855.51	-1499.03
17.	1052.15	-41.94	-1029.92	-849.83	-1486.29
18.	1070.95	-40.05	-1023.10	-845.18	-1475.73
19.	1093.95	-37.88	-1014.75	-839.49	-1462.91
20.	1118.75	-35.97	-1005.75	-833.36	-1449.41
21.	1140.95	-34.19	-997.69	-827.87	-1437.27
22.	1166.25	-32.88	-988.51	-821.62	-1423.98
23.	1189.15	-31.38	-980.20	-815.96	-1411.72

(b) Third-law computation of  $\Delta H_{f,298}^0$  of  $\text{Cs}_2\text{Cr}_2\text{O}_7$ 

Sl. No.	$T$ (K)	$\Delta G_f^0(\text{Cs}_2\text{Cr}_2\text{O}_7)$ (kJ mol <sup>-1</sup> )	$\Delta \text{fef}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H_{f,298}^0$ (kJ mol <sup>-1</sup> )
1.	1065.65	-1478.31	592.29	-2109.49
2.	1086.35	-1466.82	589.95	-2107.71
3.	1110.15	-1453.81	587.26	-2105.70
4.	1133.25	-1441.27	584.65	-2103.82
5.	1157.05	-1428.28	581.95	-2101.63
6.	1181.75	-1424.92	579.16	-2109.34
7.	1033.05	-1497.58	595.98	-2113.26
8.	1054.35	-1485.27	593.57	-2111.10
9.	1076.65	-1472.73	591.05	-2109.08
10.	1024.95	-1502.05	596.90	-2113.84
11.	1039.25	-1493.94	595.28	-2112.58
12.	1072.55	-1476.04	591.51	-2110.47
13.	1095.95	-1462.96	588.87	-2108.33
14.	1118.75	-1450.26	586.29	-2106.17
15.	1143.45	-1436.72	583.49	-2103.90
16.	1029.15	-1499.03	596.42	-2112.84
17.	1052.15	-1486.29	593.82	-2111.08
18.	1070.95	-1475.73	591.69	-2109.40
19.	1093.95	-1462.91	589.09	-2107.35
20.	1118.75	-1449.41	586.29	-2105.32
21.	1140.95	-1437.27	583.78	-2103.33
22.	1166.25	-1423.98	580.91	-2101.47
23.	1189.15	-1411.72	578.32	-2099.43

Mean value:  $\Delta H_{f,298}^0 = -2107.7 \pm 3.9$  kJ mol<sup>-1</sup>.

## 5. Conclusion

As  $\text{Cs}_3\text{CrO}_4$  is the most important corrosion compound formed between the fission product Cs (from the fuel) and Cr (from the cladding alloy), the  $\Delta G_f^0$  and  $\Delta H_{f,298}^0$  of this compound were redetermined. The Gibbs energy data so determined were used to calculate those for  $\text{Cs}_4\text{CrO}_4(\text{s})$  using the literature values of cesium potentials for the mixture  $\text{Cs}_3\text{CrO}_4|\text{Cs}_4\text{CrO}_4|\text{Cr}_2\text{O}_3$ . These data in turn had facilitated in resolving the discrepancy in this region of the Cs–Cr–O phase diagram reported in the literature. The  $\alpha$ -to- $\beta$  phase transition in  $\text{Cs}_2\text{CrO}_4$  was also characterized and compared with those in other  $\text{M}_2\text{CrO}_4$  compounds. In addition, the  $\Delta G_f^0$  values of  $\text{M}_2\text{Cr}_2\text{O}_7(\text{l})$  where M is Na, K or Cs were also determined and compared for identifying the existence of any systematic trend, by including the data on  $\text{Rb}_2\text{Cr}_2\text{O}_7(\text{l})$ .

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