

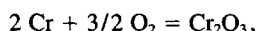


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The Cr-Cr₂O₃ oxygen buffer and the free energy of formation of Cr₂O₃ from high-temperature electrochemical measurements

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Abstract—The free energy of formation of Cr₂O₃, defined by the reaction

has been measured electrochemically using a yttria-doped thoria (YDT) solid electrolyte, in the temperature range from 900 to 1400 K. Fe + “FeO” was used as the reference electrode.

The results have been combined with high temperature heat capacity data from the literature, to give, in J·mol^{−1}

$$\mu_{\text{O}_2}(\pm 170) = -758,585 + 349.718T - 25.5216T \ln T + 0.00935T^2 \quad (600 \text{ K} < T < 1800 \text{ K}).$$

Our results are not in good agreement with the calorimetric data and imply that the currently accepted calorimetric value for the entropy of Cr₂O₃ at 298.15 K may be too low by 4.6 J/K·mol.

INTRODUCTION

Available thermodynamic data show that the Cr-Cr₂O₃ oxygen buffer lies some 5 log-bar units below the Fe-FeO equilibrium at 1600 K in log f_{O_2} – T space. It thus makes a convenient oxygen buffer in experiments concerned with conditions in the solar nebula (e.g., Treiman et al., 1991) or with other situations where an unusually low f_{O_2} is indicated. However, the thermodynamic data are not really that well known: for the calorimetric data, the enthalpy of formation of Cr₂O₃ is quoted by Robie et al. (1979) to have an uncertainty of 8.37 kJ/mol, and indeed the value given in Pankratz (1982) differs by 8.40 kJ/mol, while the standard entropy at 298 K is derived from heat capacity measurements which extend only down to 56 K. Noncalorimetric determinations of the Cr₂O₃-Cr equilibrium disagree both with the calorimetric data and with each other at the level of several kJ/mol. Thermodynamic data for Cr₂O₃ which are considerably more precise than this are also desirable, since Cr₂O₃ provides the standard state reference for the study of the thermodynamic properties of Cr in silicate melts (e.g., Pretorius and Muan, 1992) and the thermodynamic properties and redox behaviour of Cr in subsolidus systems (Li et al., 1995).

The low f_{O_2} of the Cr₂O₃-Cr equilibrium is only accessible to gas mixtures at very high temperatures, at which conditions numerous experimental difficulties make accurate work extraordinarily difficult (e.g., the gas starts to erode alumina muffle tubes, Toker et al., 1991). Also, the f_{O_2} of the Cr₂O₃-Cr equilibrium lies well below the low f_{O_2} limit of ideal ionic conductivity of zirconia-based solid electrolytes. However, the ideal ionic conductivity of thoria-based solid electrolytes extends to much lower f_{O_2} 's than zirconia-based ones and easily encompasses the f_{O_2} of Cr₂O₃-Cr. The present study was made possible by the acquisition of a yttria-doped thoria (YDT) tube. The tube was from old stock; thoria-based ceramics are apparently no longer being commercially manu-

factured, presumably due to occupational safety regulations concerning radioactive materials.

EXPERIMENTAL METHOD

Electrochemical cells of the type:



were constructed as shown in Fig. 1. The design is based on that described in O'Neill and Pownceby (1993), but with modifications necessitated by the dimensions of the YDT tube (12.7 mm OD by 9.53 mm ID by 300 mm long). One of the main sources of error in high temperature electrochemical measurements comes from temperature gradients across the working parts of the cell. In the experimental arrangement of O'Neill and Pownceby (1993) gradients are minimized by using long tubes (400 mm) in a relatively large furnace; here the dimensions of the experiments are constrained by the size of the available YDT tubes, and a different strategy is necessary.

Accordingly, the cells were built to fit into a horizontal muffle tube furnace, the distinguishing feature of which is that it is heated by three independently controlled elements. This enables a constant temperature zone (~0.5°C) to be obtained over an adequate distance (~3 cm), despite the short length of the YDT tubes.

At high oxygen fugacities such as air, YDT absorbs oxygen and becomes a p-type semiconductor. In this state, it has a dark brown colour. This was the condition in which the YDT tube was supplied. It was deoxygenated by annealing for several hours in a stream of forming gas (90% N₂ + 10% H₂); this treatment turns the colour to a pale straw hue, similar to that found in most high quality zirconia-based electrolyte ceramics.

Both the sample electrode (Cr + Cr₂O₃) and the reference electrode (Fe + “FeO”) were prepared by mixing metal and metal oxide powders together in molar ratios of four parts of metal to one part of metal oxide. The pellets weighed 1.5 g (sample electrode, Cr + Cr₂O₃) and 1.2 g (reference electrode, Fe + “FeO”). To eliminate possible contamination of the electrodes from the pellet press, the outer rims of the electrodes were removed by lightly scraping them on emery paper.

EXPERIMENTAL RESULTS

The cell was initially heated to ~1000 K. A steady emf (to within 0.1 mV) was obtained approximately 120 hours after attaining starting temperature. Thereafter, changing the tem-

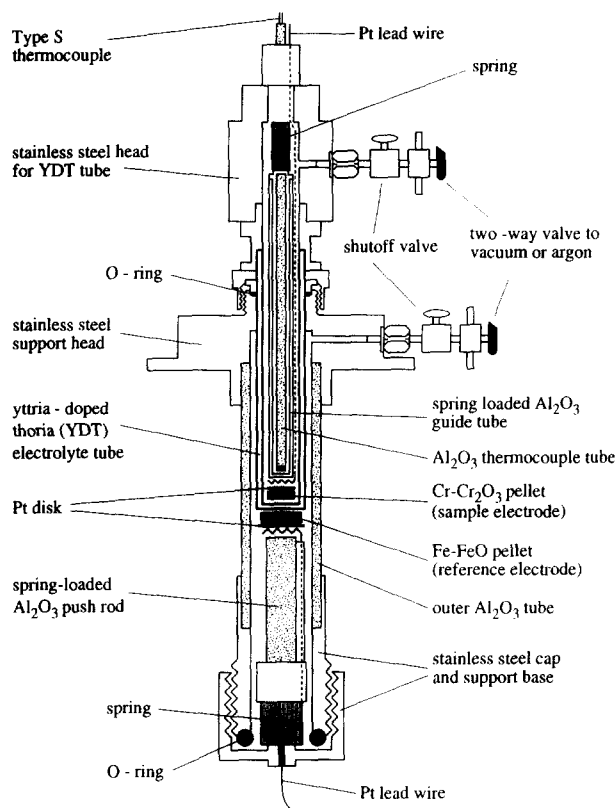


FIG. 1. Schematic diagram of the electrochemical cell. The vertical scale is greatly compressed relative to the horizontal scale. All joints are made with epoxy and are not shown for reasons of clarity.

perature of the cell caused the emf to change smoothly to a new steady value apparently almost immediately. Subsequent analysis of our results, however, shows that this behaviour was deceptive, and that, especially on decreasing temperature, long periods of time (i.e., days at $T < 1100$ K) may be needed to attain true equilibrium. The total length of the experiment reported here was two months.

The experimental results are listed in Table 1. The chemical potential of oxygen of Cr_2O_3 is calculated from the equation:

$$4FE = \mu_{\text{O}_2 \text{ sample}} - \mu_{\text{O}_2 \text{ reference}}, \quad (1)$$

where F is the Faraday constant ($96484.56 \text{ C} \cdot \text{mol}^{-1}$), E is the emf of the cell, and μ_{O_2} is the chemical potential of oxygen of sample electrode ($\text{Cr} + \text{Cr}_2\text{O}_3$) and reference electrode ($\text{Fe} + \text{FeO}$). The reference pressure of O_2 is 1 bar (10^5 Pa). Values of μ_{O_2} for the $\text{Fe} + \text{FeO}$ reference electrode are taken from O'Neill and Pownceby (1993).

Our results are compared to the calorimetric data in Fig. 2, by plotting as a function of temperature the difference in μ_{O_2} between this study and that calculated from the JANAF tables (Chase et al., 1985). Values of $\mu_{\text{O}_{2\text{Cr-Cr}_2\text{O}_3}}$ from the JANAF tables in the temperature range 600–1800 K were fitted to an expression of the form $A + BT + CT \ln T + DT^2$ to give, in $\text{J} \cdot \text{mol}^{-1}$:

$$\begin{aligned} \mu_{\text{O}_{2\text{Cr-Cr}_2\text{O}_3}} &= -765,308 + 352.775T \\ (\text{JANAF}) &- 25.5216T \ln T + 0.00935T^2. \quad (2) \end{aligned}$$

Because of the unexpected sluggishness of the equilibrium, mentioned above, the results need interpreting with extreme care. Most of the data in the temperature range of 900–1300 K (black dots in Fig. 2) present no problem, and we believe these to be sound equilibrium measurements, despite the fact that the nonhorizontal slope defined by these data indicates a disagreement with the calorimetrically determined entropy of Cr or Cr_2O_3 . For the rest of the data (open symbols with the number of the datum attached), we identify three distinct problems:

1) The lowest temperature datum (#7 at 882 K) is clearly anomalous, and, presumably, this temperature is too low for equilibrium to be established.

2) The high temperature data (above 1340 K) deviate from the trend established at 900–1300 K. The deviation is in the direction of a lower emf than expected and is the kind of behaviour expected if the YDT electrolyte develops finite electronic conductivity at high temperature, causing transfer of oxygen from the high μ_{O_2} to the low μ_{O_2} side of the cell. This experimental problem is also found in cells with zirconia-based electrolytes at similar or even lower temperatures (see, for example, the discussion in O'Neill and Pownceby, 1993). In support of this interpretation, examination of the $\text{Cr} + \text{Cr}_2\text{O}_3$ electrode pellet after the run by powder XRD showed that the proportion of Cr metal to oxide had considerably decreased, most of the Cr being oxidized to Cr_2O_3 .

3) Certain data (#s 27 to 32, 54, and 55) seem to have been obtained after insufficient time had been allowed for the cell to reequilibrate after decreasing temperature. The empirical proof of this comes from carefully monitoring the behaviour of the cell after lowering temperature following measurement #32. The emf changed smoothly to a new value almost immediately (that is, as fast as temperature in the cell changes, or about twenty minutes), but then slowly decreased over a period of 300 hours to a value identical with those obtained earlier at the same temperature (#2 and #12). This decrease is given in Table 2, and plotted in Fig. 3. A reasonable explanation of the slower change of emf with time after decreasing temperature could be the formation of an oxide layer coating the metal of the electrode.

Linear regression of the deviations in μ_{O_2} ($\Delta\mu_{\text{O}_2} = \mu_{\text{O}_2, \text{this work}} - \mu_{\text{O}_2, \text{JANAF}}$) of our preferred data (the filled circles in Fig. 2) as a function of temperature gives, in $\text{J} \cdot \text{mol}^{-1}$,

$$\Delta\mu_{\text{O}_2}(\pm 120) = (6723 \pm 119) - (3.057 \pm 0.130)T. \quad (3)$$

Addition of this correction to the calorimetrically derived values of μ_{O_2} from the JANAF tables gives, in $\text{J} \cdot \text{mol}^{-1}$,

$$\begin{aligned} \mu_{\text{O}_{2\text{Cr-Cr}_2\text{O}_3}}(\pm 170) &= -758,585 + 349.718T \\ &- 25.5216T \ln T + 0.00935T^2. \quad (4) \end{aligned}$$

COMPARISON WITH LITERATURE DATA

The difference between our results and the calorimetric data selected by Chase et al. (1985) implies a difference in the enthalpy of formation of Cr_2O_3 of $+10.08 \pm 0.18 \text{ kJ/mol}$. Our value of -1124.6 kJ/mol is thus considerably less than that measured by Mah (1954) of $-1141.7 \pm 1.7 \text{ kJ/mol}$ using bomb calorimetry, but in good agreement with the earlier

Table 1. Experimental results for the electrochemical cell Pt, Cr+Cr₂O₃ | YDT | Fe+"FeO", Pt
The order is that in which the measurements were made.

Nos.	T [K]	EMF [mV]	$\mu(\text{O}_2)$ [kJ/mol]	Nos.	T [K]	EMF [mV]	$\mu(\text{O}_2)$ [kJ/mol]	Nos.	T [K]	EMF [mV]	$\mu(\text{O}_2)$ [kJ/mol]
1	1007.4	458.94	-574.49	26	1128.5	448.64	-554.72	51	1310.8	431.45	-524.13
2	986.7	461.30	-577.96	27	1107.5	450.73	-558.21	52	1249.5	437.38	-534.47
3	965.8	463.56	-581.51	28	1089	452.53	-561.38	53	1189.5	443.12	-544.59
4	945.3	465.70	-585.01	29	1067.7	454.55	-564.90	54	1128.4	449.12	-554.97
5	924.5	467.90	-588.52	30	1047.4	456.65	-568.45	55	1067.7	455.08	-565.11
6	903.1	470.11	-592.04	31	1027.7	458.91	-571.78	56	1169	445.02	-548.02
7	882.3	473.10	-595.79	32	1006.7	460.95	-575.27	57	1269.4	435.42	-531.09
8	903.2	470.26	-592.10	33	986.6	461.13	-577.90	58	1330.6	429.45	-520.75
9	924.5	467.61	-588.41	34	1026.9	457.25	-571.27	59	1370.9	425.45	-514.01
10	945.8	465.25	-584.71	35	1068.2	453.60	-564.53	60	1410.9	421.44	-507.28
11	965.5	463.39	-581.51	36	1109	450.03	-557.81	61	1450.2	416.62	-500.39
12	986.8	461.10	-577.88	37	1148.8	446.35	-551.15	62	1389.5	423.13	-510.72
13	1008	458.96	-574.37	38	1169.6	444.33	-547.62	63	1349.9	427.21	-517.42
14	1027.4	457.18	-571.24	39	1189.4	442.50	-544.35	64	1308.6	431.43	-524.45
15	1048	455.26	-567.78	40	1209.9	440.81	-540.99	65	1265.9	435.71	-531.66
16	1068	453.38	-564.45	41	1229.3	439.04	-537.81	66	1286	433.72	-528.28
17	1089	451.34	-560.92	42	1250.4	437.19	-534.33	67	1326.8	429.64	-521.35
18	1109.4	449.35	-557.48	43	1269.6	435.36	-531.07	68	1348.5	427.39	-517.68
19	1148.9	445.97	-551.01	44	1290.6	433.33	-527.47	69	1367.4	425.32	-514.48
20	1190.3	442.04	-544.11	45	1249.4	437.33	-534.45	70	1388.1	423.16	-510.92
21	1170.2	444.00	-547.50	46	1209.5	441.15	-541.19	71	1408.1	421.00	-507.50
22	1189.4	442.18	-544.23	47	1188.6	443.15	-544.73	72	1430.3	418.51	-503.70
23	1169.1	444.38	-547.77	48	1230.1	439.18	-537.73	73	1447.8	416.50	-500.60
24	1129.3	448.53	-554.61	49	1269.6	435.38	-531.08	74	1427	418.79	-504.19
25	1149.2	446.45	-551.19	50	1290.1	433.40	-527.63				

work of Roth and Wolf (1940), who obtained a value of -1125.8 ± 2.5 kJ/mol.

Assuming that the entropy of Cr metal is correct (see Chase et al., 1985), our results imply that the adopted value of

$S^\circ_{\text{Cr}_2\text{O}_3}$ (298.15 K) in Chase et al. (1985), which is from Anderson (1937), underestimates the true value by 4.6 ± 0.2 J/K·mol. Thus our recommended value for S° (298.15 K) for Cr₂O₃ is 85.74 J/K·mol. The low temperature heat capacity

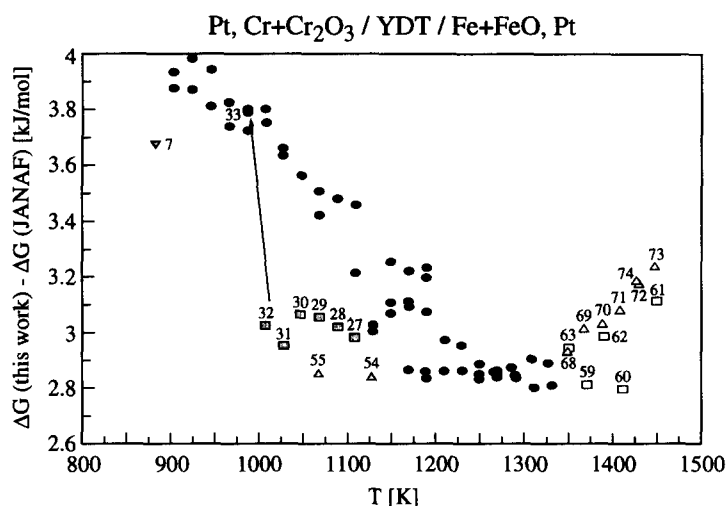


FIG. 2. Results for the free energy of the reaction $2 \text{Cr} + 3/2 \text{O}_2 = \text{Cr}_2\text{O}_3$ from the YDT-cell plotted relative to the calorimetric data from the JANAF tables (Chase et al., 1985). As explained in the text, the black dots represent data thought to have approached closely to equilibrium on either increasing or decreasing temperature, and are therefore the preferred results of this study. Data shown as open symbols, at $T > 1340$ K, are thought to have been affected by oxygen transfer across the YDT electrolyte. Data shown as grey symbols at intermediate temperatures are believed to have not been left for sufficient time to have reached equilibrium. This is demonstrated by the slow adjustment of cell emf in going from datum #32 to #33, which is shown in more detail as a function of time in Fig. 3.

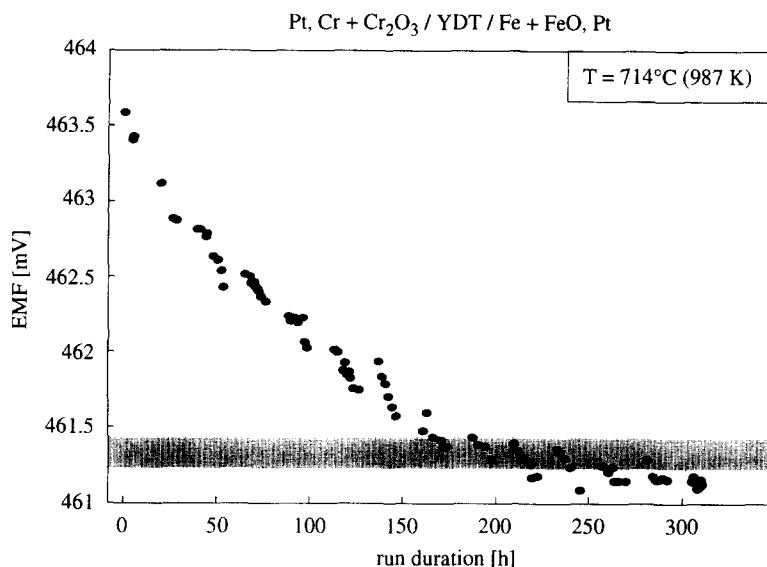


FIG. 3. Change of emf with time after a temperature decrease from 1007 K (step 32) to 987 K (step 33), see arrow in Fig. 2. Shaded area indicates results of previous measurements at 987 K (step 2, 12) after increasing the temperature.

measurements of Anderson (1937) extend down only to 56 K, and it is therefore possible that a significant contribution to the entropy of Cr_2O_3 at low temperatures has been missed. Alternatively, the values measured by Anderson (1937) in the vicinity of the magnetic λ -transition at 307 K may be too low, as indicated by the measurements of Volger (1952) and Bruce and Cannell (1977). Clearly, more low temperature adiabatic heat capacity measurements on Cr_2O_3 are desirable.

In Fig. 4, our results for the free energy of formation of Cr_2O_3 are compared to the previous measurements of Mazandarany and Pehlke (1974) and Jacob (1977), who both employed an emf method with YDT electrolytes and Co-CoO as

the reference electrode. For this comparison, we have recalculated their results using values for the Co-CoO equilibrium from O'Neill and Pownceby (1993). Also shown are the results from the recent very high temperature gas-mixing study of Toker et al. (1991).

Our results are in reasonable agreement with average values from all three studies, discrepancies being of the order of 0–2 kJ/mol. This degree of mutual compatibility could not be obtained if the calorimetrically measured entropy of Cr_2O_3 was accepted.

The free energy of formation of Cr_2O_3 was also measured by Suzuki and Sambongi (1972) with thoria-based solid elec-

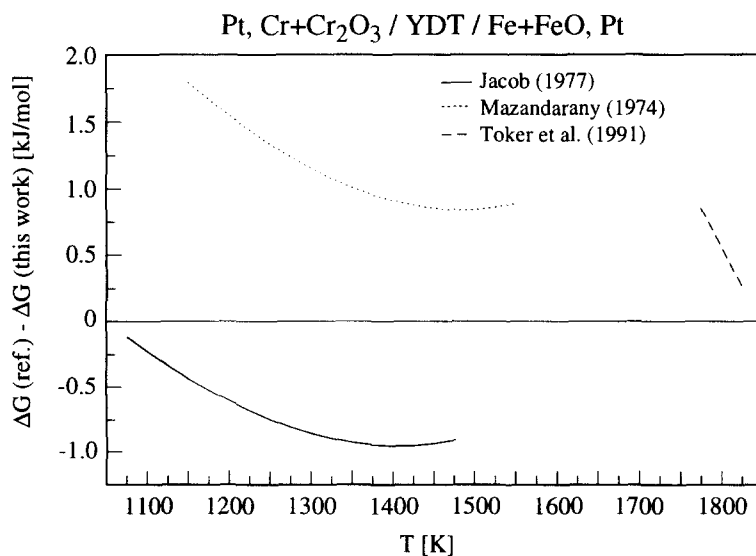


FIG. 4. Comparison of literature data for the free energy of formation of Cr_2O_3 in the temperature ranges in which the measurements were done. Positive deviations indicate a more oxidized result. Both Mazandarany and Pehlke (1974) and Jacob (1977) used the electrochemical method with a YDT electrolyte, as in this study. Toker et al. (1991) used H_2 - CO_2 gas mixing.

Table 2.

Change in emf at 714°C (987 K) after decreasing temperature from 734°C (1007 K)

(No. 33 in Table 1)

time [h]	EMF [mV]	time [h]	EMF [mV]	time [h]	EMF [mV]
	461.30*	97.2	462.07	212.7	461.32
	461.10*	98.5	462.03	214	461.30
0**	463.59	113	462.02	216.5	461.28
4.5	463.41	115	462.00	218.3	461.26
5	463.43	118	462.88	219	461.17
19.5	463.12	118.7	462.93	222	461.18
26.2	462.89	120	461.85	232.5	461.36
28	462.88	121	461.87	234	461.34
39.3	462.82	121.7	461.83	236.5	461.30
40.8	462.82	123.5	461.76	240	461.24
44	462.77	126.3	461.75	245	461.09
44.3	462.79	136.7	461.94	256.7	461.25
48	462.64	138.7	461.84	260	461.21
50.5	462.61	140.7	461.79	262.5	461.24
52	462.54	142.3	461.71	263.5	461.15
53.2	462.43	144	461.64	265.5	461.15
64.7	462.52	146	461.58	269.3	461.15
67.2	462.51	160.7	461.48	280.7	461.29
68.2	462.46	162.7	461.60	284	461.18
69.5	462.47	166	461.44	285.5	461.16
70.2	462.44	170	461.42	287	461.16
71.5	462.42	171.3	461.37	289	461.17
72	462.41	173	461.38	291.5	461.16
73.5	462.37	187	461.44	304.7	461.15
76	462.34	190	461.39	305.7	461.18
88.5	462.24	193.5	461.38	306.7	461.14
89.5	462.21	196.7	461.29	307.7	461.10
91.5	462.23	208.7	461.35	308.7	461.11
93.3	462.20	209	461.40	309.5	461.16
96	462.23	211.3	461.35	310	461.13

Set points of the three temperature zones in the horizontal furnace were 700°C at both ends and 720°C in the middle part of the furnace;

* - previous measurements (Nos. 2 and 12, see Table 1) at T = 714°C (987 K);

** - time interval after changing temperature

trolites and Fe/FeO as the reference electrode. The recalculated values show significant higher free energies compared to this work. The differences vary between +5.4 at 1173 K and +4.5 kJ/mol at 1823 K to +6 at 1450 K.

In summary, we believe that the free energy data for the formation of Cr₂O₃ obtained in this study are more reliable than literature data, and we recommend that these data should be used in thermodynamical calculations.

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