

Solid oxide electrolyte emf cell determination of the standard free energy of Cr_2O_3 and applications to chromium-bearing mineral systems

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Abstract—Emf measurements are reported on cells using a thoria–yttria solid oxide electrolyte. The measured potentials from two cells, $\text{Cr, Cr}_2\text{O}_3|\text{ThO}_2\text{–Y}_2\text{O}_3|\text{Co, CoO}$ and $\text{Cr, Cr}_2\text{O}_3|\text{ThO}_2\text{–Y}_2\text{O}_3|\text{Mn, MnO}$, were used to calculate the standard Gibbs free energy of formation of Cr_2O_3 in the temperature range 875–1275°C. The two separate series of measurements are in good agreement with critically assessed data from the literature based on gas equilibration and calorimetric results.

A summary of solid oxide electrolyte studies on mineral systems is presented with special attention paid to chromium-bearing solutions or compounds. The application of this experimental technique in investigating thermodynamic properties of chromium minerals is discussed.

INTRODUCTION

THE OBJECTIVES of this paper are to show that the solid oxide electrolyte emf technique for determining free energy changes is a precise and reliable method for determining the thermodynamic characteristics of chromium in various minerals; and to review briefly the application of this technique to chromium-bearing mineral systems where thermodynamic measurements have been made and where future work may be focused.

STANDARD FREE ENERGY OF FORMATION OF Cr_2O_3

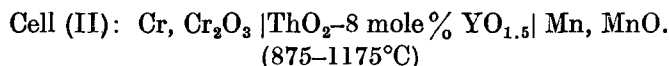
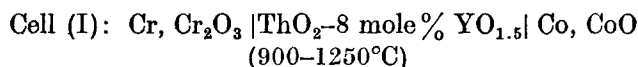
As a base point in examining the thermodynamic behavior of chromium in mineralogical systems, the standard free energy of formation of Cr_2O_3 , the most common and stable form of the oxides of chromium, should be established. A recent investigation employing the solid oxide electrolyte technique (MAZANDARANY, 1972; MAZANDARANY and PEHLKE, 1974) has been used to define the standard Gibbs free energy of formation of Cr_2O_3 .

Thermodynamic functions in the $\text{Cr–Cr}_2\text{O}_3$ system have been the subject of a number of previous investigations, but the results obtained by different techniques have been in relatively poor agreement. JEANNIN *et al.* (1963) investigated the free energy of formation of Cr_2O_3 by equilibrating $\text{Cr–Cr}_2\text{O}_3$ samples with $\text{H}_2/\text{H}_2\text{O}$ mixtures in the temperature range 1040–1300°C. Other investigations of this system (GRUBE and FLAD, 1939; GRANAT, 1936; RAMSEY *et al.*, 1956) using a similar technique gave conflicting results. The investigation of JEANNIN *et al.* (1963) should be

given particularly serious consideration, however, because it provides results that are in agreement with those calculated from calorimetric data.

The solid oxide electrolyte technique also was used for determination of standard free energy of Cr_2O_3 by TRETJAKOW and SCHMALZRIED (1965) and PUGLIESE and FITTERER (1970) in the temperature range 800–1200°C. These investigators used calcia-stabilized zirconia as the electrolyte and the partial pressure of oxygen in air as a reference electrode. Although their data agree reasonably well in the vicinity of 800°C, substantial differences exist at higher temperatures. Furthermore, the results of both of these investigations are in disagreement with the results of JEANNIN *et al.* (1963).

In recent work at the University of Michigan (MAZANDARANY, 1972; MAZANDARANY and PEHLKE, 1974), the standard Gibbs free of Cr_2O_3 has been measured using a solid oxide electrolyte technique with a $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid electrolyte. This work involved measurements on the cells:



EXPERIMENTAL TECHNIQUE FOR MEASUREMENT OF FREE ENERGY RELATIONSHIP

The solid oxide electrolyte galvanic cell used to determine the standard free energy of formation of Cr_2O_3 has been described previously in detail, and is shown schematically in Fig. 1. This solid oxide electrolyte cell incorporates a $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolyte pellet placed between two electrodes. Because the $\text{Cr, Cr}_2\text{O}_3$ electrode has been recognized as a highly non-reversible one (STEELE, 1968), an effort was made to separate the gas phases in contact with the two electrodes. As shown in Fig. 1, a mullite tube was pressed against the surface of the electrolyte to minimize transport of any oxygen-bearing gaseous component between the electrodes. A platinum O-ring was employed to seal the mullite tube and the solid oxide electrolyte. A spring system, as shown schematically in Fig. 1, was utilized to provide some pressure to insure the seal, and to provide secure electrical contact between the electrode lead wires and the electrodes.

The emf of the cells was measured with a Keithley Model 660, high impedance ($10^7 \Omega$) potentiometric voltmeter. A potentiometer was used to measure thermocouple emf's for determination of cell temperatures.

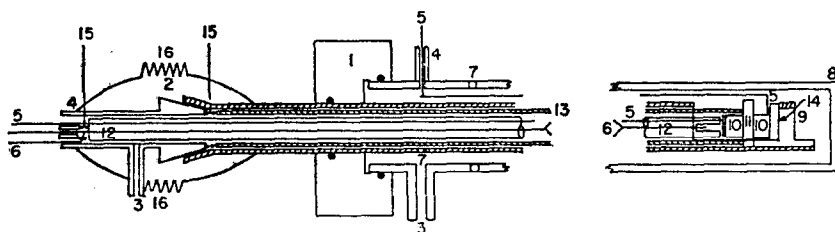


Fig. 1. Schematic drawing of the cell arrangement. 1. O-Ring joint assembly. 2. Ground glass joint. 3. Gas inlet and outlet. 4. Wax seal. 5. Electrode lead wire (Pt-10% Rh). 6. Thermocouple (Pt/Pt-10 Rh). 7. Glass-mullite seal. 8. Mullite tube. 9. Mullite support tube. 10. Electrode. 11. Electrolyte. 12. Alumina push rod. 13. Mullite tube. 14. Zirconia support pellet. 15. Compression springs. 16. Tension spring.

High purity materials were used for the preparation of all cell components. Electrolytes were high temperature sintered pellets made from a mixture of 99.9 per cent pure Y_2O_3 and 99.5 per cent pure ThO_2 starting powders. These powders were pressed and sintered at temperatures exceeding 1950°C for 24 hr in an argon-hydrogen atmosphere. The composition of the electrolyte pellets was 92 mole % ThO_2 -8 mole % $\text{YO}_{1.5}$. The pellets were 2 mm thick and 12 mm in diameter. The electrode pellets were prepared from high purity metal and oxide powders in a 10:1 weight ratio. The pressed pellets were sintered at 900 - 1000°C for 24 hr prior to use. In the case of the manganese oxide electrode, pulverized electrolytic flake manganese was mixed with MnO_2 in a 10:1 weight ratio and sintered at 900 - 1000°C for 24 hr to insure complete conversion of MnO_2 to MnO . In the case of the cobalt-cobalt oxide electrodes, no sintering was necessary after pressing.

The assembled cell was held at temperature in a vertical, platinum-wound resistance furnace. A stagnant cell atmosphere of argon gas was used with a slight positive pressure. To prepare the cell for measurement, the assembly was evacuated and backfilled with argon gas which was purified over Cu_2O catalyst and copper (reduced BTS catalyst). After thermal equilibration, the cell was allowed to come to steady-state conditions over a period of 5-12 hr. The criterion for attainment of an equilibrium measurement was a constant cell potential within ± 0.5 mV over a period of 1 hr, with the only noticeable variations being random, not systematic.

Cell reversibility was indicated by stability of the measured potentials, by the linearity and consistency of cell potential-temperature relationships with temperature cycling, and by reproducibility from run to run. Perturbation of cells by passage of current and subsequent allowance for re-establishment of equilibrium conditions resulted in a steady measured potential within 1 mV of the original measurement.

EXPERIMENTAL RESULTS

The cumulative results of cell I obtained from three independent cell assemblies are listed in Table 1. The data are represented by the following least squares fitted relationship:

$$\text{Cell (I): } E(\text{mV}) = 706.6 - 0.0640T \pm 1.7 \text{ mV} \quad (1173-1523^\circ\text{K}).$$

The standard errors of estimate of the coefficients in this equation are, respectively, ± 2.8 mV and ± 0.0015 mV/ $^\circ\text{K}$. Measurements on cell II also are presented in Table 1. The data from two independent cell assemblies are given by the following relationship:

$$\text{Cell (II): } E(\text{mV}) = 90.67 - 0.0347T \pm 0.8 \text{ mV} \quad (1148-1430^\circ\text{K}).$$

The standard errors of estimate of the coefficients in this equation are, respectively, ± 1.7 mV and ± 0.0008 mV/ $^\circ\text{K}$. These emf-temperature relationships are shown in Figures 2 and 3. A comparison is made in these figures with the data from $\text{H}_2/\text{H}_2\text{O}$ equilibration with chromium and chromium oxide obtained by JEANNIN *et al.* (1963). After the latter results had been adjusted in accordance with solid oxide electrolyte measurements for Co-CoO by KIUKKOLA and WAGNER (1957a) and for the Mn-MnO equilibrium of ALCOCK and ZADOR (1967), it is evident that the results from this study are in close agreement with the earlier gas-solid equilibrium measurements. However, there is substantial disagreement between the results of the present study and those of PUGLIESE and FITTERER (1970) and TRETJAKOW and SCHMALZRIED (1965). The latter authors may have had irreversible conditions because they used a calcia-stabilized zirconia electrolyte with an air reference electrode or

Table 1. Summary of experimental data

Cell (I): Cr, Cr ₂ O ₃ ThO ₂ -YO _{1.5} Co, CoO			Cell (II): Cr, Cr ₂ O ₃ ThO ₂ -YO _{1.5} Mn, MnO		
	Temp. (°C)	Emf (mV)		Temp. (°C)	Emf (mV)
Run 26	1244.9	610.0	Run 29	1100.5	139.6
	1265.8	609.2		1144.2	140.4
	1250.9	608.6		1126.2	139.6
	1249.3	611.5		1100.1	138.5
	1247.1	611.7		1072.8	137.6
	1179.2	615.5		1046.2	136.7
	1181.7	614.7		1046.2	136.7
	1131.6	616.6		1015.5	135.7
	1130.7	618.0		1015.1	135.7
	1079.0	619.8		983.3	134.8
	1084.1	618.6		979.1	134.8
	1034.5	625.7		941.8	133.9
	1038.1	623.5		903.2	132.9
	941.0	628.7		912.6	131.4
	994.5	622.2		967.9	135.1
	989.3	627.5		1019.9	136.4
1035.6	624.2				
Run 27*	1186.0	613.5	Run 30	1074.7	138.0
	1185.7	613.7		1101.3	138.9
	1146.9	614.6		1102.7	138.9
	1052.9	620.5		1145.1	140.1
	1217.5	608.4		1166.2	140.5
	1251.8	606.8		1139.2	139.5
	1272.5	611.1		1115.4	138.4
	1203.3	613.7		1110.3	138.2
	1151.2	614.5		1087.3	137.1
	1151.0	615.9		1058.4	136.0
	1151.2	615.7		1057.9	136.0
				1022.5	134.5
				1022.5	134.5
Run 28	1278.4	604.4		995.2	133.4
	1210.0	611.1		997.4	133.5
	1208.5	610.5		962.9	132.1
	1158.1	618.5		879.1	130.9
	1157.0	615.5		877.4	130.2
	1158.8	613.5		875.1	131.5
	1111.8	618.3		1013.4	134.1
	1112.3	615.3		1012.5	134.1
	906.1	627.8		985.6	133.0
	906.5	631.8		948.4	132.0
	904.7	633.5			
	974.4	629.2			
	1019.1	623.7			
	1121.3	617.3			
	1159.5	615.2			

* Run 27 had to be terminated before any more measurements were made because one electrode lead wire broke.

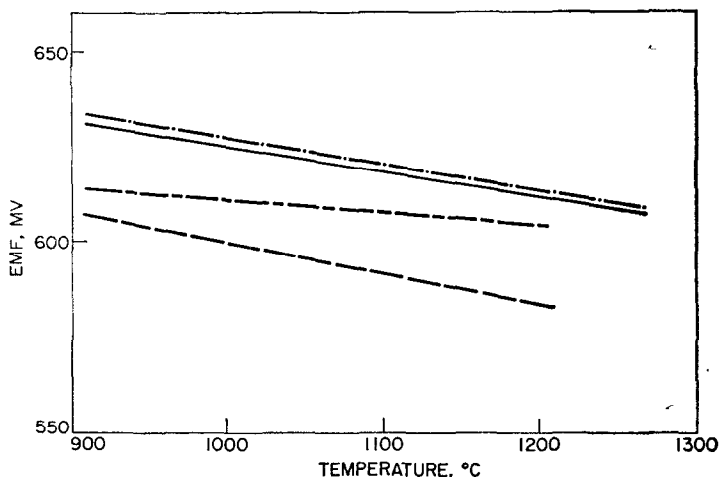


Fig. 2. Cell potential-temperature relationship for Cell (I): $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Co, CoO}$. — This study; $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{CO, CoO}$. — · — Jeannin, Mannerskantz and Richardson; $\text{H}_2\text{-H}_2\text{O}$. Equilibration with $\text{Cr, Cr}_2\text{O}_3$.* — — — Tretjakow and Schmalzried; $\text{Cr, Cr}_2\text{O}_3 | \text{ZrO}_2\text{-CaO} | \text{air}$.* — — — Pugliese and Fitterer; $\text{Cr, Cr}_2\text{O}_3 | \text{ZrO}_2\text{-CaO} | \text{air}$.*

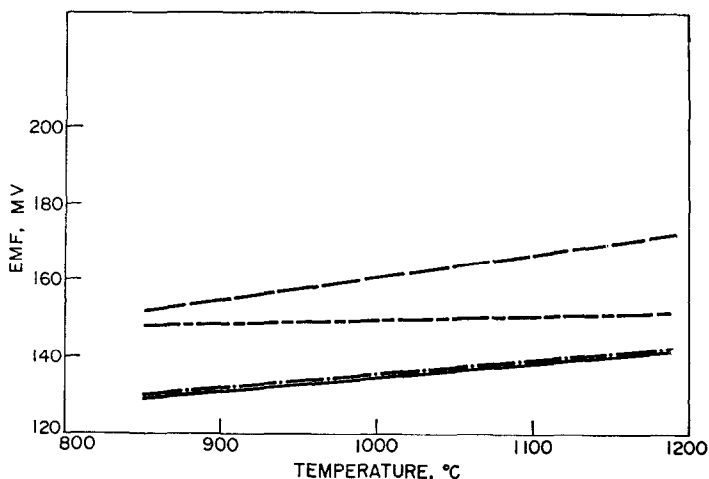


Fig. 3. Cell potential-temperature relationship for Cell (II): $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Mn, MnO}$. — This study; $\text{Cr, Cr}_2\text{O}_3 | \text{ThO}_2\text{-YO}_{1.5} | \text{Mn, MnO}$. — · — Jeannin, Mannerskantz and Richardson; $\text{H}_2\text{-H}_2\text{O}$. Equilibration with $\text{Cr, Cr}_2\text{O}_3$.† — — — Tretjakow and Schmalzried; $\text{Cr, Cr}_2\text{O}_3 | \text{ZrO}_2\text{-CaO} | \text{air}$.† — — — Pugliese and Fitterer; $\text{Cr, Cr}_2\text{O}_3 | \text{ZrO}_2\text{-CaO} | \text{air}$.†

* Adjusted by Mn, MnO data of ALCOCK and ZADOR (1967).

† Adjusted by Co, CoO data of KIUKKOLA and WAGNER (1957).

their electrolyte contained impurity ions. A small amount of electronic conduction in the zirconia electrolyte at low oxygen potentials (for example, the Cr-Cr₂O₃ equilibrium oxygen potential is approximately 10⁻²² atm at 1000°C) could cause transport of oxygen ions from the cathode, air, as used by these latter authors to the Cr, Cr₂O₃ anode. This irreversible effect becomes increasingly larger as the cell potential is increased.

Measured cell potentials for this study from cells I and II are related to the standard Gibbs free energy of formation of Cr₂O₃ by the expression:

$$\Delta G_f^\circ(\text{Cr}_2\text{O}_3) = 3[-2EF + \Delta G_f^\circ(\text{MO})], \quad (1)$$

where E is the measured cell voltage, F is Faraday's constant, and $\Delta G_f^\circ(\text{MO})$ is the standard Gibbs free energy of formation of CoO or MnO for cells I and II, respectively.

Using equation (1) in combination with the cell potential, the standard free energy of formation of Cr₂O₃ was calculated. The data of KIUKKOLA and WAGNER (1967a) for $\Delta G_f^\circ(\text{CoO})$ and those of ALCOCK and ZADOR (1967) for $\Delta G_f^\circ(\text{MnO})$ were used to correct the measured cell potentials to standard conditions. The results of these calculations are as follows:

from Cell (I):

$$\Delta G_f^\circ(\text{Cr}_2\text{O}_3) = -266,990 + 60.15T \pm 250 \text{ cal} \quad (1173-1540^\circ\text{K}),$$

where $\Delta H_f^\circ = -266,990 \pm 400 \text{ cal}$ and $\Delta S_f^\circ = -60.15 \pm 0.21 \text{ cal/}^\circ\text{K}$; and, from Cell (II):

$$\Delta G_f^\circ(\text{Cr}_2\text{O}_3) = -266,270 + 59.55T \pm 100 \text{ cal} \quad (1148-1460^\circ\text{K}),$$

where $\Delta H_f^\circ = -266,270 \pm 240 \text{ cal}$ and $\Delta S_f^\circ = -59.55 \pm 0.11 \text{ cal/}^\circ\text{K}$.

The agreement between these two independent results (approx. $\pm 200 \text{ cal/mole}$) is excellent, and is particularly noteworthy in view of the fact that the uncertainty for the Co, CoO data is $\pm 100 \text{ cal}$, and for the Mn, MnO data $\pm 150 \text{ cal}$.

A comparison in terms of the standard free energy of formation of Cr₂O₃ of the present study with the investigation of JEANNIN *et al.* (1963), TRETJAKOW and SCHMALZRIED (1965), PUGLIESE and FITTERER (1970), and the calorimetric calculations of COUGHLIN (1954) is given in Table 2. The present results agree with those of Jeannin *et al.*, as mentioned above, and are very consistent with the indirect calculations of Coughlin. Agreement of the present results with those of the other reported investigators is much less satisfactory, for the reasons enumerated above relating to the possible irreversibility of the cells employed in those investigations.

In addition to noting the consistency of results between cells I and II, a series of measurements was made specifically to test the reversibility and accuracy of the thoria-yttria electrolyte and Cr, Cr₂O₃ electrode. Reversibility was demonstrated by comparing measurements made on an iron-chromium alloy at 1250°C in a cell of the form, Fe-18 per cent Cr, Cr₂O₃ |ThO₂-YO_{1.5}| Fe-30 per cent Cr, Cr₂O₃ with data calculated from the difference of measured emf's in the cells, Cr, Cr₂O₃ |ThO₂-YO_{1.5}| Fe-18 per cent Cr, Cr₂O₃ and Cr, Cr₂O₃ |ThO₂-YO_{1.5}| Fe-30 per cent Cr, Cr₂O₃. Table 3 shows the results of this comparison. The difference of 1.2 mV is within the anticipated error band relating to the uncertainty of $\pm 0.6 \text{ mV}$ associated with each measured potential and provides further assurance of the accuracy of the present measurements.

Table 2. Standard Gibbs free energy of formation of Cr_2O_3 as reported by various investigators
 ΔG° (cal/mole)

	This study	TRETJAKOW and			COUGHLIN (1964)
		JEANNIN <i>et al.</i> (1963)	SCHMALZRIED (1965)	PUGLIESE and FITTERER (1970)	
	-266,600	-266,700	-258,600		-271,300
T	+ 59.78 T	+ 59.95 T	+ 55.2 T		+ 61.82 T
(°K)	(1173-1523°K)	(1313-1573°K)	(1000-1500°K)	(1000-1500°K)	(298-1823°K)
1173	-196,500	-196,400	-193,800	-193,800	-198,800
1273	-190,500	-190,400	-188,300	-186,900	-192,600
1373	-184,500	-184,400	-182,800	-180,800	-186,400
1448	-180,000	-179,900	-178,700	-175,000	-181,800

Table 3. Comparison of measured and calculated emf for the cell Fe-18Cr,
 Cr_2O_3 | ThO_2 - $\text{YO}_{1.5}$ | Fe-30Cr, Cr_2O_3 at 1250°C

Cell	E (mV)
1. Fe-18Cr, Cr_2O_3 S.O.E.* Cr, Cr_2O_3 ; measured	60.20
2. Cr, Cr_2O_3 S.O.E. Fe-30Cr, Cr_2O_3 ; measured	37.90
3. Fe-18Cr, Cr_2O_3 S.O.E. Fe-30Cr, Cr_2O_3 ; calculated from 1 and 2 above	22.30
4. Fe-18Cr, Cr_2O_3 S.O.E. Fe-30Cr, Cr_2O_3 ; measured	21.10

* Solid oxide electrolyte.

DISCUSSION

The results of this investigation demonstrate the potential of the solid oxide electrolyte technique for thermodynamic studies of systems involving the Cr, Cr_2O_3 equilibrium. One possible application is the measurement of chromium activities in alloy systems. The Cr-Fe, Cr-Ni, and Fe-Ni-Cr systems have been studied using a Cr, Cr_2O_3 reference electrode (MAZANDARANY, 1972). The systems Co-Cr, Mo-Cr, Fe-Cr-Co, Fe-Cr-Mo, Co-Cr-Mo, Ni-Cr-Co and Ni-Cr-Mo are among others that can be studied by this technique. Pure Cr_2O_3 is expected to be the stable oxide in equilibrium with the above alloy systems, although there is reason to believe that Cr_2O_4 may be the stable oxide in systems where iron activity is high (ULMER, 1964; ULMER and WHITE, 1966).

A possible limitation of the technique in the study of alloy thermodynamics is the occurrence of displacement oxide reactions or the dissolution of alloying elements in the more stable oxide, in this case Cr_2O_3 . In point of fact, however, the thermodynamics of such reactions can be studied by this technique. For example, measurements of cell potentials on an electrode of Fe, FeO (in Cr_2O_3) would give the activity of FeO in oxides in the Fe-Cr-O system. Similarly, spinel formation in such a system can be investigated by the solid oxide electrolyte technique. Solid solutions of NiO- Cr_2O_3 and CoO- Cr_2O_3 also can be studied.

The thermodynamic properties of non-stoichiometric oxides can be studied by this technique. Measurements of cell potentials on an $\text{MO}_{x\pm\delta}$ electrode, where δ is fixed by a controlled oxygen potential in the gas phase and measured by such

methods as gravimetric analysis, can provide precise thermodynamic data on the non-stoichiometric oxide, $MO_{x \pm \delta}$.

Finally, one can envision this technique being employed in thermodynamic studies of carbide formation and carbide solid solutions. For example, measurements of cell potentials on electrodes: (Cr, $Cr_{23}C_2$, Cr_2O_3), ($C_{23}C_2$, Cr_7C_3 , Cr_2O_3), (Cr_7C_3 , Cr_3C_2 , Cr_2O_3) and (Cr_2O_3 , Cr_3C_2 , C) might provide precise thermodynamic data on various chromium carbides. Similar measurements in other metal-C-O systems can be made extending the technique to solid solutions of various carbides.

In considering further applications of the solid oxide electrolyte technique to chromium-bearing minerals, it should be noted that a number of studies already have been reported. These investigations are reviewed in the following paragraphs.

SOLID ELECTROLYTES FOR THERMOCHEMICAL MEASUREMENTS IN CHROMIUM-BEARING MINERALS

Over the past ten years the application of solid electrolyte galvanic cells for obtaining high temperature thermodynamic data gradually has been extended from binary compounds to multi-component mineral systems. Research on solid electrolytes has centered on increasing the ionic conductivity, the structural and chemical stability, and the temperature and oxygen pressure ranges of the electrolyte. Attainment of these objectives and refinement of measuring techniques to eliminate undefined emf potentials and to achieve reversible cells should result in increased precision and accuracy and permit the use of the emf method on many mineral systems.

Galvanic cells incorporating solid electrolytes have been discussed from both a theoretical and practical viewpoint by KIUKKOLA and WAGNER (1957a, b). Reviews of the state-of-the-art of solid state electrochemistry and solid electrolyte galvanic cells have been published, respectively, by RALEIGH (1967) and RAPP and SHORES (1970). Comprehensive coverage of solid electrolytes can be found in the two volumes entitled *Physics of Electrolytes* edited by HLADIK (1972). ETSSELL and FLENGAS (1970) reviewed the electrical properties of solid oxide electrolytes and gave reference to an extensive number of investigations of the Gibbs free energy of solid inorganic systems. References to most of the compounds listed in Tables 4 and 5 can be found in their publication. SATO (1971, 1972) has discussed the application of solid electrolyte techniques for measuring oxygen fugacities of natural mineral systems. Although anionic conducting solid electrolytes, especially solid oxide electrolytes, have received the most attention in thermodynamic studies of minerals, cationic conducting solid electrolytes that can operate near room temperature also are available. Beta-alumina (KUMMER, 1972) is a versatile ceramic electrolyte in which Li^+ , Na^+ , Rb^+ , Ca^{2+} and Sr^{2+} ions exhibit high ionic mobility with little electronic conductivity.

An examination of the literature shows that several binary and ternary oxide systems were studied in the 1960's by emf methods and that intensive work is still underway on these systems to corroborate data and to obtain higher accuracies. At present only a small fraction of the minerals studied are chromium-bearing compounds. TRETJAKOW and SCHMALZRIED (1965) studied the thermodynamic properties of chromites, ferrites, and aluminates in the temperature range of 725–1225°C using a calcia-stabilized zirconia solid electrolyte and air as a reference electrode.

Table 4. Phases for which thermodynamic data have been obtained using ZrO₂-based electrolytes. Unless otherwise specified, references to the thermodynamic data for the compounds listed below are given by ETSSELL and FLENGAS (1970)

Oxide solid solutions	Oxides	Ternary compounds
(Mg, Ni)O	Cu ₂ O	MnFe ₂ O ₄
(Mg, Fe)O	Cu ₂ O*	MgMoO ₄
(Fe, Ni)O	CuO	CaWO ₄
(Mn, Fe)O	NiO	SrWO ₄
(Mn, Fe) ₃ O ₄	Fe _x O†	CuCr ₂ O ₄
(Mn, Fe)O-(Mn, Fe) ₃ O ₄	Fe _x O‡-Fe ₃ O ₄	NiCr ₂ O ₄
Ni _y Fe _{3-y} O ₄	Fe ₃ O ₄	FeCr ₂ O ₄
CO _y Fe _{3-y} O ₄	Fe ₃ O ₄ -Fe ₂ O ₂	CoCr ₂ O ₄
Mg _y Fe _{3-y} O ₄	PbO	MgCr ₂ O ₄
WO ₂	PbO*	Cu ₂ Al ₂ O ₄
WO _{2.72}	SnO§	NiAl ₂ O ₄
WO _{2.90}	SnO*§	CoAl ₂ O ₄
WO ₃	In ₂ O ₃	NiTiO ₃
Nb ₂ O ₄ -Nb ₂ O _{5-z}	MnO-Mn ₃ O ₄	FeTiO ₃
ZnO	Mn ₃ O ₄ -Mn ₂ O ₃	Fe ₂ TiO ₄
Cr ₂ O ₃	CoO	CoTiO ₃
SiO ₂	MoO ₂	Co ₂ TiO ₄
V ₅ O ₉ , V ₈ O ₁₅ (VASIL'eva <i>et al.</i> , 1973)		PbSiO ₃
		Pb ₂ SiO ₄
		Pb ₄ SiO ₆
		Ni ₂ SiO ₄
		Fe ₂ SiO ₄
Nonstoichiometric compounds		Sulfides
UO _{2+x}	TiO _{2-x}	PtS, Rh _x S, ZnS,
U _y Th _{1-y} O _{2+x}	LiFe ₅ O _{8-x}	MnS, MoS ₂ , NbS ₂ ,
U _y Zr _{1-y} O _{2+x}	Co _y Fe _{3-y} O _{4-x}	TaS ₂
Ni _{1-x} O	MnFe ₂ O _{4±x}	FeS
Co _{1-x} O	Mn _y Fe _{3-y} O _{4+x}	(ARMYANOVA and FILIPPOV, 1972)
Fe _{1-x} O	MgFe ₂ O _{4-x}	
Fe ₂ O _{3-x}	Mg _y Fe _{3-y} O _{4-x}	
Nb ₂ O _{5-x}	MgFe _{2-y} Cr _y O _{4±x}	

* Liquid.

† Wustite in equilibrium with Fe.

‡ Wustite in equilibrium with Fe₃O₄.§ Probably SnO₂ in equilibrium with Sn.

The Gibbs free energy of formation was calculated for reactions $AO + B_2O_3 = AB_2O_4$, where A is Fe, Ni, Co, Cu, and B is Al, Fe, and Cr. As shown in Table 6, their values for the standard free energies of formation of the Ni, Cu, and Fe chromites are considerably lower than those determined by an emf method utilizing a La₂O₃-doped ThO₂ electrolyte and an Fe, FeO reference electrode (LEVITSKII *et al.*, 1965a, b; REZUKHINA *et al.*, 1965). No credible explanation for the discrepancies in the data for the chromites has been offered and verified. The temperature dependencies of the Gibbs free energy of formation of Fe and Co chromite found by Levitskii *et al.* and Rezukhina *et al.* agree well with data obtained by gas equilibration methods.

TABLE 5. Phases for which thermodynamic data have been obtained using ThO₂-based electrolytes. Unless otherwise specified, references to the thermodynamic data for the compounds listed below are given by ETSSELL and FLENGAS (1970)

Oxides	Oxide solid solutions	Ternary compounds
Cu ₂ O	(Mn, Ni)O	CoMoO ₃
NiO	Silicides	CoMoO ₄
Fe _x O		MgMoO ₃
PbO	TaSi ₂ , Ta _{4.5} Si,	MgMoO ₄
SnO ₂	Ta ₃ Si ₃ , Ta ₂ Si	MgWO ₄
CoO	Carbides	CaWO ₄
MoO ₂		Ca ₂ WO ₆
WO ₂	Cr ₃ C ₂ (MABUCHI <i>et al.</i> , 1971)	SrWO ₄
Cr ₂ O ₃	Nonstoichiometric	BaWO ₄
MnO	compounds	Ba ₃ WO ₆
Ta ₂ O ₅		NiCr ₂ O ₄
NbO	U ₁ Pu _{1-y} O _{2±x}	CoCr ₂ O ₄
Nb ₂ O _{5-x}	TiO _{2-x}	FeCr ₂ O ₄
NbO-NbO ₂	NbO _{2-x}	NiAl ₂ O ₄ *
NbO ₂ -Nb ₂ O _{5-x}	Ti _{0.5} Nb _{0.5} O _{2±x}	CoAl ₂ O ₄ *
Al ₂ O ₃	Ta ₂ O _{5-x} †	FeAl ₂ O ₄
VO _{2x-1}	CeO _{2-x}	CoTiO ₃
(VASIL'EVA <i>et al.</i> , 1971)	PuO _{2-x}	CaTiO ₃
TiO _{2x-1}		
(VASIL'EVA <i>et al.</i> , 1971)		

* Contain excess Al and O in stoichiometric amounts.

† Claimed that this phase existed until $x = 0.46$ which is rather unlikely.

Table 6. Free energy of formation of Fe, Co, and Ni chromites from their respective oxides ΔG° (cal/mole)

Spinel	AO + B ₂ O ₃ = AB ₂ O ₄	Reference
FeCr ₂ O ₄	-13750 + 3.93T (1000-1500°K)	TRETJAKOW and SCHMALZRIED (1965)
	-14885 + 3.75T (1300-1400°K)	REZUKHINA <i>et al.</i> (1965)
CoCr ₂ O ₄	-19360 + 5.77T (1000-1500°K)	TRETJAKOW and SCHMALZRIED (1965)
	-21845 + 6.67T (1273-1473°K)	LEVITSKII <i>et al.</i> (1965)
NiCr ₂ O ₄	-12930 + 5.17T (1000-1500°K)	TRETJAKOW and SCHMALZRIED (1965)
	-17550 - 1.07T (1300-1542°K)	LEVITSKII <i>et al.</i> (1965b)

An investigation of the thermodynamic properties of solid solutions of magnesium ferrite and chromite has been made by an emf method that incorporated a calcia-stabilized zirconia electrolyte with an Fe, FeO reference electrode (GUZEI *et al.*, 1967). Standard free energies of formation were reported for MgFe_{1.415}Cr_{0.632}O_{4.07} and four reduced samples with the compositions MgFe_{1.415}Cr_{0.632}O_n where $n = 4.05, 4.04, 3.95,$ and 3.90 in the temperature range of 900-1000°C. The free energy values were in good agreement with those obtained by an H₂/H₂O gas equilibration method.

TANAKA *et al.* (1971a) measured the standard free energies of formation of CrF_2 and CrF_3 at 600°C by an emf technique in which a single crystal of CaF_2 was used as an electrolyte and Mg , MgF_2 as the reference electrode. The values reported were $\Delta G_f^\circ(\text{CrF}_2) = -156.4$ and $\Delta G_f^\circ(\text{CrF}_3) = -229.1$ kcal/mole.

Several studies of the thermochemistry of chromium carbides have appeared because of the importance of these carbides in steelmaking. The agreement of the temperature dependence of $\Delta G_f^\circ(\text{Cr}_3\text{C}_2)$ was good for two different emf methods, one employing an yttria-doped thoria electrolyte (TANAKA *et al.*, 1971a) and the other a single crystal of CaF_2 (MABUCHI *et al.*, 1971). Another emf method using CaF_2 gave low values for $\Delta G_f^\circ(\text{Cr}_3\text{C}_2)$ (KLEYKAMP, 1969).

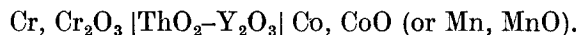
Chromium silicides also have been examined by an emf method in which an NaCl-KCl-CrCl_2 solid electrolyte was employed (EREMENKO, *et al.*, 1971). The standard Gibbs free energies of formation of CrSi_2 and CrSi between 700 – 850°C were reported as $\Delta G_f^\circ(\text{CrSi}_2) = -18600 - 1.17T$ and $\Delta G_f^\circ(\text{CrSi}) = -14300 - 0.56T$.

In a study of the petrogenesis of the Bushveld Complex: pyroxene-spinel-feldspar, FLYNN *et al.* (1972) used a zirconia-yttria solid electrolyte to obtain f_{O_2} - T plots for three coexisting cumulus minerals: bronzite, chromite, and anorthite.

The measurement of thermochemical properties of chromium-bearing silicates such as uvarovite by the emf method has yet to be reported, probably because of the difficulties relating to the sluggish equilibration both in silicate phase mixtures and with respect to the 'reversible' electrode reaction. Interfacial polarization between the electrode and solid electrolyte in such systems possibly can be eliminated by the use of a solid electrolyte in which an ionic conducting halide is incorporated into a non-conducting silicate matrix. Research in this area may make the solid electrolyte galvanic cell method of measuring high temperature thermochemical properties of minerals more useful to mineralogist and petrologists.

SUMMARY

Reversible oxygen potentials in equilibrium with the Cr , Cr_2O_3 electrode were measured with reference to the Co , CoO and Mn , MnO equilibria in solid oxide electrolyte cells of the type:



Based on these measurements the standard Gibbs free energy of formation of Cr_2O_3 was calculated to be:

$$\Delta G_f^\circ(\text{Cr}_2\text{O}_3) = -266,600 + 59.78T(^{\circ}\text{K}) \pm 350 \text{ cal; } (1173\text{--}1523^{\circ}\text{K}).$$

The results are in good agreement with available data in the literature based on $\text{H}_2/\text{H}_2\text{O}$ equilibration and calorimetric measurements. These findings indicate that the Cr , Cr_2O_3 electrode can operate reversibly in oxygen concentration cells involving $\text{ThO}_2\text{-Y}_2\text{O}_3$ electrolytes at high temperatures.

Applications of the solid electrolyte cell technique to various chromium-bearing compounds have been reviewed and systems amenable to future study in this fashion are outlined. It is evident that the method can be employed advantageously in a large number of systems.

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