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# Electrochemical Determination of Thermodynamic Properties of $\text{NiCr}_2\text{O}_4$ and $\text{CoCr}_2\text{O}_4$

By Seth C. Schaefer



UNITED STATES DEPARTMENT OF THE INTERIOR

**Report of Investigations 9043**

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of Thermodynamic Properties  
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**UNITED STATES DEPARTMENT OF THE INTERIOR**  
Donald Paul Hodel, Secretary

**BUREAU OF MINES**  
Robert C. Horton, Director

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UNITS OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere	kcal/mol	kilocalorie per mol
cal	calorie	kPa	kilopascal
cal/mV	calorie per millivolt	min	minute
cm <sup>3</sup> /min	cubic centimeter per minute	mm	millimeter
g	gram	mV	millivolt
h	hour	Pa	pascal
J	joule	wt pct	weight percent
K	kelvin		

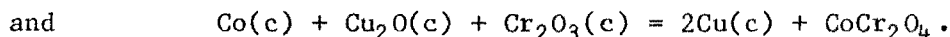
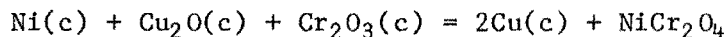
# ELECTROCHEMICAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF $\text{NiCr}_2\text{O}_4$ and $\text{CoCr}_2\text{O}_4$

By Seth C. Schaefer<sup>1</sup>

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## ABSTRACT

The Bureau of Mines investigated the standard Gibbs energies of formation  $\Delta G_f^\circ$ , for  $\text{NiCr}_2\text{O}_4$  (nickel chromite) and  $\text{CoCr}_2\text{O}_4$  (cobalt chromite). High temperature galvanic cells employing stabilized  $\text{ZrO}_2$  (zirconia) as the solid electrolyte were used to measure the open-circuit potentials for the cell reactions



Equilibrium oxygen pressures for the  $\text{Ni}-\text{Cr}_2\text{O}_3-\text{NiCr}_2\text{O}_4-\text{O}_2$  system were determined from the electromotive force (emf) measurements and are expressed as

$$\log p_{\text{O}_2} = -25,164/T + 8.62584; (1,172.8-1,260.0 \text{ K}),$$

where pressure ( $p_{\text{O}_2}$ ) is in atmospheres (1 atm = 101.325 kPa) and temperature (T) is in kelvins. Similarly, equilibrium oxygen pressures for the  $\text{Co}-\text{Cr}_2\text{O}_3-\text{CoCr}_2\text{O}_4-\text{O}_2$  system are expressed as

$$\log p_{\text{O}_2} = -40,877/T + 17.15372; (1,173.5-1,256.3 \text{ K}).$$

Standard Gibbs energies of formation expressed in kilocalories per mol (1 cal = 4.184 J) of  $\text{NiCr}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$  were derived from these measurements and auxiliary data from the literature. The results are expressed as follows:

$$\Delta G_f^\circ(\text{NiCr}_2\text{O}_4) = (-324.171 + 79.51 \times 10^{-3}T) \pm 0.403 \text{ kcal/mol};$$

$$(1,172.8-1,260.0 \text{ K})$$

and 
$$\Delta G_f^\circ(\text{CoCr}_2\text{O}_4) = (-360.119 + 99.02 \times 10^{-3}T) \pm 0.405 \text{ kcal/mol};$$

$$(1,173.5-1,256.3 \text{ K}).$$

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## INTRODUCTION

Thermodynamic properties of  $\text{NiCr}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$  were investigated by the Bureau of Mines as a part of its program to expand the base of scientific information needed to devise innovative technologies. Accurate thermodynamic data of chromites are required for assessment of slag-metal equilibria, refining of metals, metal-refractory interactions, and also to provide a basis for construction of equilibrium phase diagrams. A review of existing data for  $\text{NiCr}_2\text{O}_4$  (1-5)<sup>2</sup> and  $\text{CoCr}_2\text{O}_4$  (1, 4, 6-7) shows considerable disagreement, even in results of investigations that used essentially the same technique to measure the Gibbs energies of formation.

Application of stabilized  $\text{ZrO}_2$  as a selective solid-anion electrolyte has been demonstrated in determination of Gibbs energies for cell reactions involving metal-metal oxide systems at elevated temperatures (8). Within the limitation of the ionic domain of stabilized  $\text{ZrO}_2$ ,

any equilibrium involving oxygen may be investigated by this technique (9). The method is based on the measurement of the difference in the chemical potential of oxygen between a reference electrode of known oxygen potential and an electrode of unknown oxygen potential. The relationship between the open-circuit potential of the cell and the Gibbs energy for the actual cell reaction is

$$\Delta G (\text{reaction}) = -nFE, \quad (1)$$

where  $\Delta G$  is the change in Gibbs energy for the cell reaction,  $n$  is the number of electrochemical equivalents in the reaction,  $F$  is the Faraday constant (23.061 cal/mV equivalent), and  $E$  is the emf in millivolts. The transference number of oxygen is essentially unity in the range of oxygen potential of this investigation (9). The standard states are the saturated coexisting phases.

## EXPERIMENTAL WORK

## MATERIALS

High-purity reagents were obtained from commercial sources and used without further purification. Analyses of these reagents were confirmed and are presented in table 1. Ultra-high-purity argon was passed through  $\text{Mg}(\text{ClO}_4)_2$  (magnesium perchlorate) and purified of residual oxygen by passing over hot titanium-zirconium chips to provide an inert atmosphere in the cell for the electrodes.

## APPARATUS AND PROCEDURE

Internal arrangement of the cell is illustrated in figure 1. The apparatus, potentiometer, and standardized thermocouple have previously been described (10).  $\text{NiCr}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$  were synthesized by heating equimolar mixtures of the component oxides at 1,650 K in air

for 3 days. Repeated cycles of grinding and heating were required to ensure complete reaction. Homogeneity was checked and verified by X-ray diffraction analyses. The electrode mixtures were prepared by blending  $\text{NiCr}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ , and Ni or  $\text{CoCr}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ , and Co in 2:1:1 ratios by weight. These electrode mixtures were heated for 1 day at 1,575 K in an argon atmosphere. X-ray diffraction analyses confirmed the phase composition.

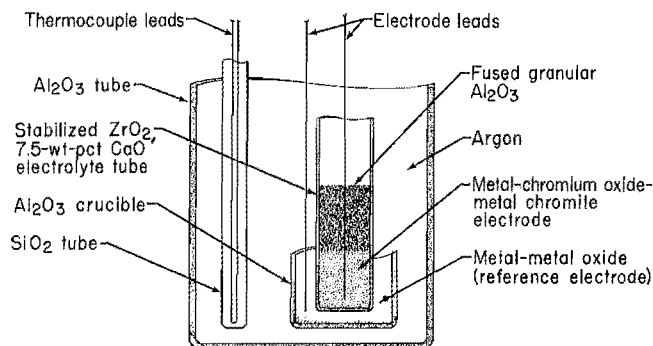


FIGURE 1.—High-temperature galvanic cell.

<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Impurities<sup>1</sup> detected in reagents

Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct
Cu:		Cr <sub>2</sub> O <sub>3</sub> :		CoO:	
Al.....	<0.01	Fe.....	0.006	Al.....	0.29
H.....	.0033	Na.....	.18	Cu.....	.26
O.....	.0913	Pb.....	.05	Pb.....	<.02
Si.....	<.01	V.....	.043	Mg.....	.08
Cu <sub>2</sub> O:		Ni:		Mn.....	.04
B.....	<.003	Co.....	.045	Ni.....	.39
Fe.....	<.01	NiO:		Si.....	.18
Ni.....	<.03	None.....	NAp	Na.....	.62
		Co:			
		Ni.....	.09		

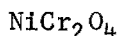
NAp Not applicable.

<sup>1</sup>Impurities not detected by spectrochemical analyses, except as noted in the table, were Ag, Al, As, B, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, Sb, Si, Sn, Ta, Ti, V, W, Y, Zn, and Zr.

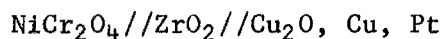
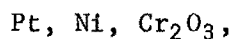
The reference electrode, consisting of 2 to 3 g of a 1:1 mixture of Cu + Cu<sub>2</sub>O, was placed in an Al<sub>2</sub>O<sub>3</sub> crucible surrounding the ZrO<sub>2</sub> electrolyte tube that contained the three-phase chromite electrode. Approximately 100 mm of 60-mesh granular, fused Al<sub>2</sub>O<sub>3</sub> was placed above the three-phase chromite electrode. Preliminary tests showed that this cover improved the cell operation by retaining the equilibrium oxygen pressure generated at the interface of the electrode and the electrolyte. The assembled cell was purged with argon and then evacuated before being backfilled with argon. Cells were operated at a positive pressure of approximately 30 Pa, and argon flow was approximately 15 cm<sup>3</sup>/min. Cells were

heated to 1,173 K and permitted to stabilize for 16 h. Emf measurements were made with a Keithley<sup>3</sup> model 642 high-input-impedance digital electrometer. Approximately 8 to 16 h were required to achieve equilibrium potentials. Reversibility of the cell was checked by approaching equilibrium from above and below a specified temperature. Cell response was slow to achieve equilibrium with decreasing temperatures. After completion of the test, the cell was dismantled and the electrodes were sampled for analyses by X-ray diffraction. Reproducibility was checked by obtaining measurements of several cells for each determination.

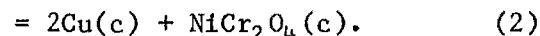
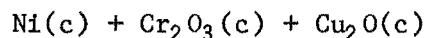
#### RESULTS AND DISCUSSION



The equilibrium oxygen pressure for the Ni-Cr<sub>2</sub>O<sub>3</sub>-NiCr<sub>2</sub>O<sub>4</sub>-O<sub>2</sub> system and standard Gibbs energy of formation of NiCr<sub>2</sub>O<sub>4</sub> were determined by measuring the potentials of the high-temperature galvanic cell



with the overall cell reaction



Potential measurements from five cells that were used for the NiCr<sub>2</sub>O<sub>4</sub> determination are given in table 2. These results may be expressed as a function of temperature by the least squares equation

<sup>3</sup>Reference to specific equipment does not imply endorsement by the Bureau of Mines.



TABLE 2. - Emf (E), of cell Pt, Ni, Cr<sub>2</sub>O<sub>3</sub>, NiCr<sub>2</sub>O<sub>4</sub>//ZrO<sub>2</sub>//Cu<sub>2</sub>O, Cu, Pt

Measure- ment	Tempera- ture, K	Emf (E), mV		Measure- ment	Tempera- ture, K	Emf (E), mV	
		Measured <sup>1</sup>	Calculated <sup>2</sup>			Measured <sup>1</sup>	Calculated <sup>2</sup>
1.....	1,172.8	314.68	314.59	12.....	1,213.7	311.97	312.12
2.....	1,174.7	314.48	314.48	13.....	1,214.9	311.77	312.05
3.....	1,174.8	314.47	314.47	14.....	1,228.8	311.23	311.21
4.....	1,175.0	314.08	314.46	15.....	1,231.6	311.52	311.04
5.....	1,175.2	314.57	314.44	16.....	1,232.3	311.42	311.00
6.....	1,189.8	313.34	313.56	17.....	1,232.7	311.12	310.97
7.....	1,191.6	313.73	313.45	18.....	1,240.9	311.10	310.48
8.....	1,192.1	313.92	313.42	19.....	1,248.7	309.87	310.01
9.....	1,193.2	313.03	313.36	20.....	1,250.1	309.67	309.92
10.....	1,212.2	312.17	312.21	21.....	1,252.8	309.26	309.76
11.....	1,212.8	311.87	312.18	22.....	1,260.0	309.24	309.33

<sup>1</sup>Average of 2 measurements ( $\pm 0.05$  mV) taken at 20-min intervals and corrected for cell calibration.

<sup>2</sup>Calculated from linear equation  $E = (385.389 - 0.060368T) \pm 0.32$ .

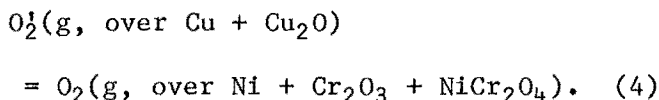
and standard error of estimate as follows:

$$E = (385.389 - 0.060368T) \pm 0.32;$$

$$(1,172.8 - 1,260.0 \text{ K}), \quad (3)$$

where E is the emf expressed in millivolts. Smooth emf data derived from equation 3 are given in columns 4 and 8 of table 2. Representative emf-versus-temperature data are illustrated in figure 2.

The equilibrium oxygen pressure,  $p_{O_2}$ , over Ni + Cr<sub>2</sub>O<sub>3</sub> + NiCr<sub>2</sub>O<sub>4</sub> was determined from the potential measurements for cell reaction 2, which may also be expressed as



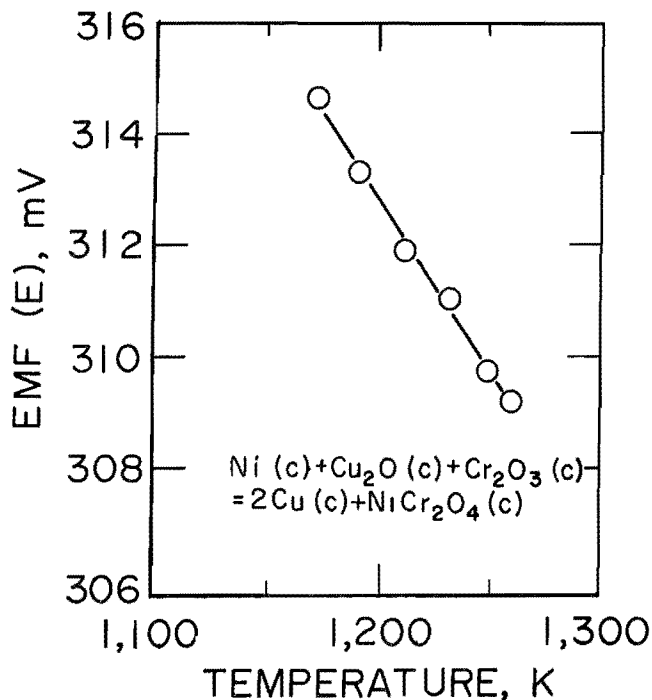
The corresponding standard Gibbs energy change for reaction 4 is

$$\Delta G(\text{reaction 4}) = -nFE \\ = RT \ln p_{O_2} - RT \ln p_{O_2^{\frac{1}{2}}}, \quad (5)$$

where n is 4, F is the Faraday constant, E is the emf from equation 3, and  $p_{O_2^{\frac{1}{2}}}$  is the oxygen pressure over the reference electrode (Cu + Cu<sub>2</sub>O). Pressures are expressed in atmospheres (1 atm = 101.325

kPa). In the temperature range 1,100 to 1,300 K, the standard Gibbs energy of formation of Cu<sub>2</sub>O from a critical analysis of published data (11) is expressed as

$$\Delta G_f^\circ(\text{Cu}_2\text{O}) = (-39.796 + 16.95 \times 10^{-3} T) \\ \pm 0.200 \text{ kcal/mol}, \quad (6)$$

FIGURE 2.—Emf (E) versus temperature for NiCr<sub>2</sub>O<sub>4</sub> cell.

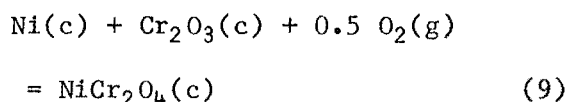
and the dissociation pressure of oxygen,  $pO_2^1$ , over  $Cu + Cu_2O$  in equations 4 and 5 may be expressed as

$$\log pO_2^1 = -17,395/T + 7.40882. \quad (7)$$

Rearranging equation 5 and substituting the value of  $pO_2^1$  from equation 7 and E from equation 3 yields

$$\log pO_2 = -25,164/T + 8.62584. \quad (8)$$

Figure 3 illustrates the thermodynamic stability of the  $Ni-Cr_2O_3-NiCr_2O_4-O_2$  system. Reaction 4 and equation 5 are independent relationships that are applicable to any equilibrium involving oxygen. These values of  $pO_2$  are the key for computing the standard Gibbs energy for the reaction



from the relationship

$$\begin{aligned} \Delta G^\circ(\text{reaction 9}) &= -RT \ln K_9 \\ &= 0.5RT \ln pO_2, \end{aligned} \quad (10)$$

where  $K_9$  is the equilibrium constant for reaction 9, and the condensed phases are

assumed to have unit activity. Resolution of the equilibrium oxygen pressure provides a basis for the construction of equilibrium phase diagrams. The diagrams of the experimental data show the predominance areas of the various phases and the equilibria between them as a function of temperature and equilibrium oxygen pressure.

The lattice parameter of a solid solution generally changes with composition up to the saturation limit and then remains constant beyond that point. Lattice parameters of the components in the equilibrated electrode mixtures showed no major change from the lattice parameters of the reagents that were used to prepare electrode mixtures. Consequently, the intersolubility is negligible, and the foregoing assumption that the condensed phases have unit activity does not introduce any appreciable error in the Gibbs energy of formation of  $NiCr_2O_4$  in the temperature range of this investigation. Linear equations expressing the oxygen pressures and the standard Gibbs energy change for reaction 9 are given in table 3. Results of previous investigators are also presented in table 3.

A standard Gibbs energy of formation of  $NiCr_2O_4$  was determined from the relationship

$$\begin{aligned} \Delta G_f^\circ(NiCr_2O_4) &= \Delta G^\circ(\text{reaction 9}) \\ &+ \Delta G_f^\circ(Cr_2O_3). \end{aligned} \quad (11)$$

Substituting the standard Gibbs energy change for reaction 9 as given in columns 4 and 5 of table 3 and the standard Gibbs energy of formation of  $Cr_2O_3$  (12), expressed as

$$\begin{aligned} \Delta G_f^\circ(Cr_2O_3) &= (-266.600 + 59.78 \times 10^{-3} T) \\ &\pm 0.350 \text{ kcal/mol}, \end{aligned} \quad (12)$$

yields the following standard Gibbs energy of formation of  $NiCr_2O_4$ :

$$\begin{aligned} \Delta G_f^\circ(NiCr_2O_4) &= (-324.171 + 79.51 \times 10^{-3} T) \\ &\pm 0.403 \text{ kcal/mol}; \\ &(1,172.8-1,260.0 \text{ K}). \end{aligned} \quad (13)$$

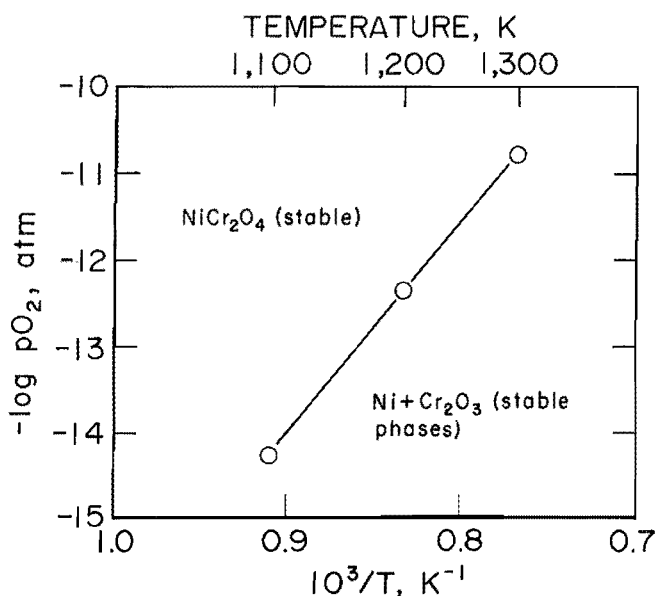


FIGURE 3.—Equilibrium diagram for the  $Ni-Cr_2O_3-NiCr_2O_4$  system.

TABLE 3. - Thermodynamic data for  $\text{Ni(c)} + \text{Cr}_2\text{O}_3(\text{c}) + 0.5 \text{O}_2(\text{g}) = \text{NiCr}_2\text{O}_4(\text{c})$ 

Method	Temperature range, K	log $p_{\text{O}_2}$ , atm	Standard Gibbs energy change, cal <sup>1</sup>		Reference
			$\Delta H^\circ$	$-\Delta S^\circ$	
Emf.....	1,172.8-1,260.0	-25,164/T+ 8.62584	-57,571	19.73	This work.
	1,000 -1,500	-30,061/T+11.12853	-68,774	25.46	Tretjakow (1).
	1,300 -1,540	-32,080/T+ 8.40103	-73,394	19.22	Levitskii (2).
	1,013 -1,253	-29,939/T+11.00614	-68,494	25.18	Kozłowska-Rog (3).
Gas phase equilibration..	1,073 -1,380	-34,936/T+15.30719	-79,926	35.02	Kunmann (4).

$${}^1\Delta G^\circ(\text{reaction}) = 0.5RT \ln p_{\text{O}_2} = \Delta H^\circ - T\Delta S^\circ.$$

TABLE 4. - Standard Gibbs energy of formation ( $-\Delta G^\circ$ ) for  $\text{NiCr}_2\text{O}_4$ , kilocalories per mol

Temperature, K	Tretjakow (1)	Levitskii (2)	Kozłowska-Rog (3)	Kunmann (4)	This work
1,100.....	241.610	ND	241.538	242.246	ND
1,150.....	237.348	ND	237.290	237.506	232.735
1,200.....	233.086	ND	233.042	232.766	228.759
1,250.....	228.824	ND	228.794	228.026	224.784
1,300.....	224.562	237.294	ND	ND	ND
1,350.....	220.300	233.344	ND	ND	ND
1,400.....	216.038	229.394	ND	ND	ND
1,450.....	211.776	225.444	ND	ND	ND
1,500.....	207.514	221.494	ND	ND	ND

ND Not determined.

Results from this investigation together with those of previous investigators (1-4) are given at specified temperatures in table 4 and illustrated in figure 4. As noted in figure 4, the results from this investigation are slightly more positive than those reported by three previous investigators (1, 3-4). Although  $\Delta S^\circ$  for reaction 9 reported by Kunmann, Rogers, and Wold (4) is much larger than that reported by the other two investigators (1, 3), figure 4 shows that the standard Gibbs energies of formation,  $\Delta G_f^\circ$ , of  $\text{NiCr}_2\text{O}_4$  for the three investigations are in good agreement. This is explained by the fact that to generate figure 4 from table 3 involves the standard Gibbs energy of  $\text{Cr}_2\text{O}_3$  as given by equation 12. The difference in  $\Delta S^\circ$  for reaction 9 is largely overwhelmed by the temperature coefficient term of equation 12. Results of another investigation (2) are above the temperature range of this investigation and approximately 13 kcal/mol more

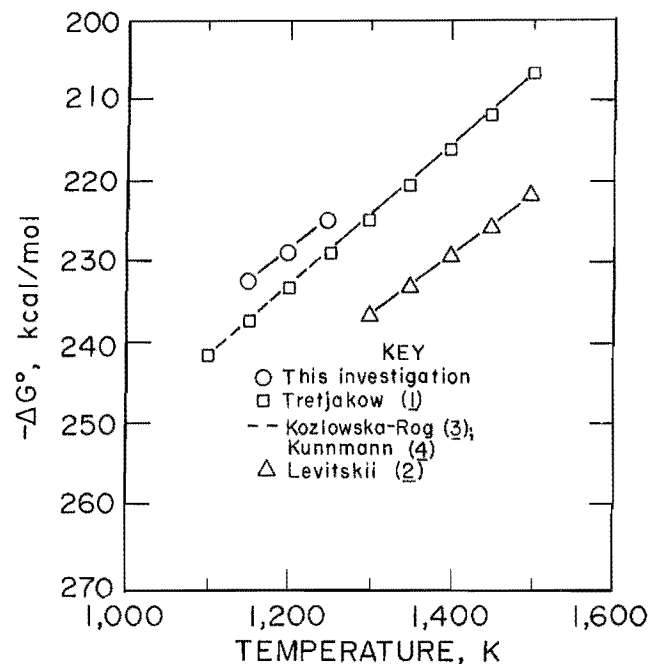


FIGURE 4.—Standard Gibbs energy change for  $\text{Ni(c)} + 2\text{Cr(c)} + 2\text{O}_2(\text{g}) = \text{NiCr}_2\text{O}_4(\text{c})$ .

negative than those of a similar emf investigation (1). Slow diffusion rate in the solid phases and failure to achieve equilibrium are the probable causes for these discrepancies. Precautions taken in this investigation included careful preparation of the electrode mixture, X-ray diffraction analyses of the electrode mixtures before and after experiments, and allowing 8 to 16 h at each temperature to achieve stable equilibrium potential measurements.

A standard Gibbs energy of formation of  $\text{NiCr}_2\text{O}_4$  can also be obtained directly from the cell potentials of reaction 2 and the relationship

$$\Delta G^\circ(\text{reaction 2}) = -nFE = \Delta G_f^\circ(\text{NiCr}_2\text{O}_4) - \Delta G_f^\circ(\text{Cr}_2\text{O}_3) - \Delta G_f^\circ(\text{Cu}_2\text{O}). \quad (14)$$

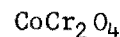
In equation 14,  $n = 2$ . Rearranging equation 14 and substituting the value of  $E$  from equation 3 and the standard Gibbs energies of  $\text{Cu}_2\text{O}$  (11) and  $\text{Cr}_2\text{O}_3$  (12) from equations 6 and 12, respectively, yields

$$\Delta G_f^\circ(\text{NiCr}_2\text{O}_4) = (-324.171 + 79.51 \times 10^{-3}T) \pm 0.403 \text{ kcal/mol};$$

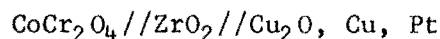
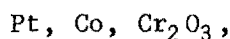
$$(1,172.8 - 1,260.0 \text{ K}). \quad (15)$$

Equations 13 and 15 are identical. This is to be expected because the standard Gibbs energy of formation of  $\text{Cu}_2\text{O}$  is

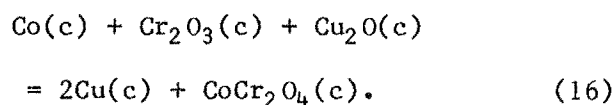
involved in both methods for resolution of the Gibbs energy of formation of  $\text{NiCr}_2\text{O}_4$ .



The equilibrium oxygen pressure of the  $\text{Co-Cr}_2\text{O}_3\text{-CoCr}_2\text{O}_4\text{-O}_2$  system and the standard Gibbs energy of formation of  $\text{CoCr}_2\text{O}_4$  were determined by measuring the potentials of the high-temperature cell



with the overall cell reaction



Potential measurements from four cells that were used for the  $\text{CoCr}_2\text{O}_4$  determination are given in table 5. These results may be expressed as a function of temperature by the linear equation and standard error of estimate.

$$E = (1,164.8053 - 0.483378T) \pm 0.77, \quad (17)$$

where  $E$  is the emf in millivolts. Smooth emf values derived from equation 17 are given in columns 4 and 8 of table 5. Representative emf-versus-temperature data are illustrated in figure 5.

TABLE 5. - Emf ( $E$ ) of cell Pt, Co,  $\text{Cr}_2\text{O}_3$ ,  $\text{CoCr}_2\text{O}_4 // \text{ZrO}_2 // \text{Cu}_2\text{O, Cu, Pt}$

Measurement	Temperature, K	Emf ( $E$ ), mV		Measurement	Temperature, K	Emf ( $E$ ), mV	
		Measured <sup>1</sup>	Calculated <sup>2</sup>			Measured <sup>1</sup>	Calculated <sup>2</sup>
1.....	1,173.5	598.66	597.56	12.....	1,232.4	568.56	569.09
2.....	1,174.7	596.31	596.98	13.....	1,232.7	567.66	568.95
3.....	1,175.0	596.96	596.84	14.....	1,234.0	568.44	568.32
4.....	1,175.3	596.01	596.69	15.....	1,235.4	567.37	567.64
5.....	1,193.7	587.85	587.80	16.....	1,235.7	567.44	567.50
6.....	1,194.0	586.43	587.65	17.....	1,248.8	561.37	561.16
7.....	1,195.5	587.40	586.93	18.....	1,252.2	560.67	559.52
8.....	1,215.5	580.64	577.26	19.....	1,254.9	558.16	558.21
9.....	1,214.5	577.89	577.74	20.....	1,256.2	557.42	557.59
10.....	1,215.7	577.44	577.16	21.....	1,256.3	557.22	557.54
11.....	1,232.0	568.96	569.28				

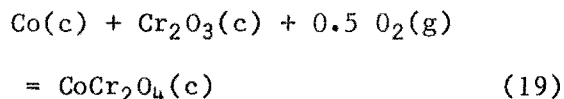
<sup>1</sup>Average of 2 measurements ( $\pm 0.05$  mV) taken at 20-min intervals and corrected for cell calibration.

<sup>2</sup>Calculated from linear equation  $E = (1,164.8053 - 0.483378T) \pm 0.77$ .

The equilibrium oxygen pressure,  $p_{O_2}$ , over  $Co + Cr_2O_3 + CoCr_2O_4$  was obtained by the method previously described for reaction 4. Rearranging equation 5 and substituting values of  $p_{O_2}'$  from equation 7 and  $E$  from equation 17 yields

$$\log p_{O_2} = -40,877/T + 17.15372. \quad (18)$$

Figure 6 illustrates the thermodynamic stability of the  $Co-Cr_2O_3-CoCr_2O_4-O_2$  system. The standard Gibbs energy for the reaction



is obtained from the relationship

$$\begin{aligned} \Delta G^\circ(\text{reaction 19}) &= -RT \ln K_{19} \\ &= 0.5RT \ln p_{O_2}, \end{aligned} \quad (20)$$

where  $K_{19}$  is the equilibrium constant for reaction 19, and the condensed phases are assumed to have unit activity.

Lattice parameter measurements of the electrode components showed no major change from the lattice parameters of the reagents that were used to prepare the electrode mixtures. Consequently, inter-solubility between the electrode components is negligible and the foregoing assumption is justified. Linear equations expressing the oxygen pressures and standard Gibbs energies for reaction 19 from this investigation, together with the results of previous investigators, are given in table 6.

A standard Gibbs energy of formation of  $CoCr_2O_4$  was determined from the relationship

$$\begin{aligned} \Delta G_f^\circ(CoCr_2O_4) &= \Delta G^\circ(\text{reaction 19}) \\ &+ \Delta G_f^\circ(Cr_2O_3). \end{aligned} \quad (21)$$

Substituting the standard Gibbs energy for reaction 19 as given in columns 4 and 5 of table 6 and the standard Gibbs energy of formation of  $Cr_2O_3$  from equation 12 yields

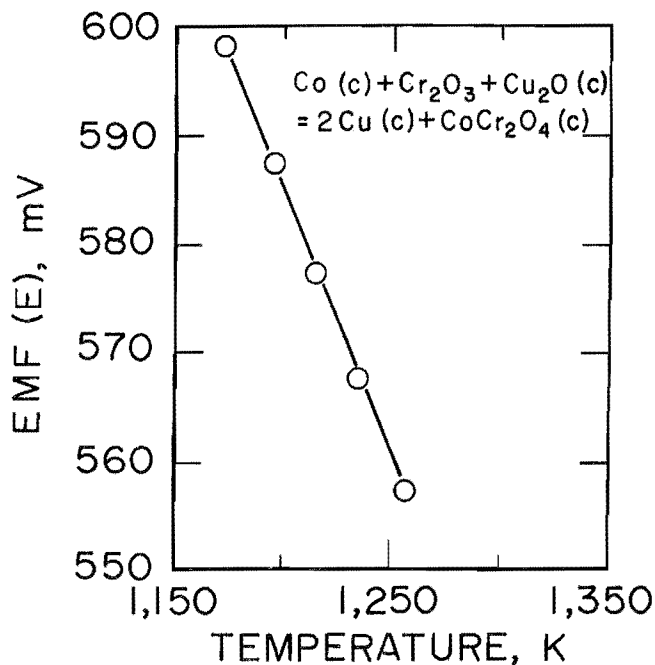


FIGURE 5.—Emf (E) versus temperature for  $CoCr_2O_4$  cell.

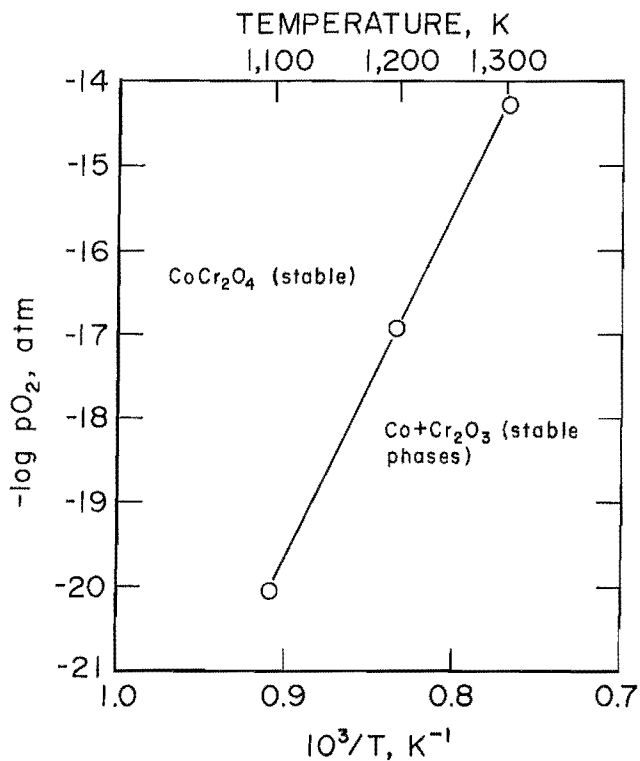


FIGURE 6.—Equilibrium diagram for the  $Co-Cr_2O_3-CoCr_2O_4$  system.

TABLE 6. - Thermodynamic data for  $\text{Co}(c) + \text{Cr}_2\text{O}_3(c) + 0.5 \text{O}_2(g) = \text{CoCr}_2\text{O}_4(c)$ 

Method	Temperature range, K	log $p\text{O}_2$ , atm	Standard Gibbs energy change, cal <sup>1</sup>		Reference
			$\Delta H^\circ$	$-\Delta S^\circ$	
Emf.....	1,173.5-1,256.3	-40,877/T+17.15372	-93,519	39.24	This work.
	1,000 -1,500	-32,813/T+ 9.79538	-75,070	22.40	Tretjakow (1).
	1,270 -1,490	-33,899/T+10.18877	-77,555	23.31	Levitskii (6).
Gas phase equilibration..	1,073 -1,380	-38,214/T+14.02212	-87,427	32.08	Kunmann (4).

$${}^1\Delta G^\circ(\text{reaction}) = 0.5RT \ln p\text{O}_2 = \Delta H^\circ - T\Delta S^\circ.$$

$$\Delta G_f^\circ(\text{CoCr}_2\text{O}_4) = (-360.119 + 99.02 \times 10^{-3}T) \pm 0.405 \text{ kcal/mol};$$

$$(1,173.5-1,256.3 \text{ K}). \quad (22)$$

Standard Gibbs energies of formation of  $\text{CoCr}_2\text{O}_4$  at specified temperatures are presented in table 7 together with the results of previous investigators (1, 4, 6). Figure 7 shows that the results from

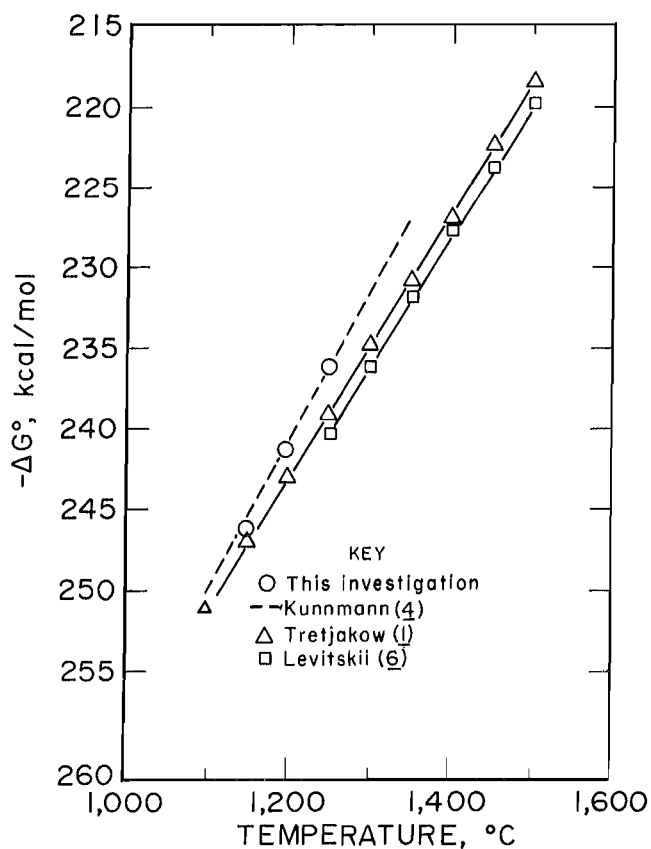


FIGURE 7.—Standard Gibbs energy change for  $\text{Co}(c) + 2\text{Cr}(c) + 2 \text{O}_2(g) = \text{CoCr}_2\text{O}_4(c)$ .

this investigation agree well with those reported in a gas phase equilibration investigation (4), but are more positive than the data obtained by two previous emf investigations (1, 6). These discrepancies are probably caused by the low diffusion rate in the solid-state reaction of the cobalt chromite electrode and failure to achieve equilibrium. Although precautions similar to those mentioned for the  $\text{NiCr}_2\text{O}_4$  determination were taken, some errors may have been introduced by failure to achieve reversible equilibrium potentials. Considerable difficulty was encountered in obtaining reversible measurements with decreasing temperature, even after allowing 16 h to equilibrate; consequently, most of the measurements for  $\text{CoCr}_2\text{O}_4$  were obtained with increasing temperatures.

A standard Gibbs energy of formation can also be derived directly from the cell potentials of reaction 16 and the relationship

$$\Delta G^\circ(\text{reaction 16}) = -nFE = \Delta G_f^\circ(\text{CoCr}_2\text{O}_4) - \Delta G_f^\circ(\text{Cr}_2\text{O}_3) - \Delta G_f^\circ(\text{Cu}_2\text{O}). \quad (23)$$

In equation 23,  $n = 2$ . Rearranging equation 23 and substituting the value of  $E$  from equation 17 and the standard Gibbs energies of formation of  $\text{Cu}_2\text{O}$  and  $\text{Cr}_2\text{O}_3$  from equations 6 and 12, respectively, yields

$$\Delta G_f^\circ(\text{CoCr}_2\text{O}_4) = (-360.119 + 99.02 \times 10^{-3}T) \pm 0.405 \text{ kcal/mol};$$

$$(1,173.5-1,256.3 \text{ K}). \quad (24)$$

TABLE 7. - Standard Gibbs energy of formation ( $-\Delta G_f^\circ$ )  
for  $\text{CoCr}_2\text{O}_4$ , kilocalories per mol

Temperature, K	Tretjakow (1)	Levitskii (6)	Kunnmann (4)	This work
1,100.....	-251.261	ND	-250.408	ND
1,150.....	-247.152	ND	-245.815	-246.246
1,200.....	-243.042	ND	-241.222	-241.295
1,250.....	-238.933	-240.293	-236.629	-236.344
1,300.....	-234.823	-236.138	-232.036	ND
1,350.....	-230.714	-231.984	-227.443	ND
1,400.....	-226.604	-227.829	ND	ND
1,450.....	-222.495	-223.675	ND	ND
1,500.....	-218.385	-219.520	ND	ND

ND Not determined.

Equations 22 and 24 are identical, which is to be expected since the standard Gibbs energy of formation of  $\text{Cu}_2\text{O}$  is

involved in both methods for derivation of the standard Gibbs energy of formation of  $\text{CoCr}_2\text{O}_4$ .

#### SUMMARY AND CONCLUSIONS

Equilibrium oxygen pressures for the  $\text{Ni-Cr}_2\text{O}_3\text{-NiCr}_2\text{O}_4\text{-O}_2$  and  $\text{Co-Cr}_2\text{O}_3\text{-CoCr}_2\text{O}_4\text{-O}_2$  systems were determined by a high-temperature emf measurement method using stabilized  $\text{ZrO}_2$  as the solid

electrolyte. The emf measurements yielded the standard Gibbs energies of formation of  $\text{NiCr}_2\text{O}_4 + \text{CoCr}_2\text{O}_4$  that are expressed as follows:

$$\Delta G_f^\circ(\text{NiCr}_2\text{O}_4) = (-324.171 + 79.51 \times 10^{-3}T) \pm 0.403 \text{ kcal/mol};$$

$$(1,172.8-1,260.0 \text{ K})$$

and

$$\Delta G_f^\circ(\text{CoCr}_2\text{O}_4) = (-360.119 + 99.02 \times 10^{-3}T) \pm 0.405 \text{ kcal/mol};$$

$$(1,173.5-1,256.3 \text{ K}).$$

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