Thermodynamic Properties of the Oxides of Copper and Nickel

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Recent measurements of high-temperature equilibria involving copper and nickel oxides have been critically correlated by second- and third-law methods employing the newly redetermined calorimetric data on Cu_2O and CuO. Excellent consistency was found between the calorimetric and equilibrium data, and selected values of the heat of formation at 298° K. for NiO, Cu_2O, and CuO were calculated to be −57,240 ± 130, −40,760 ± 100, and −37,200 ± 100 cal. per mole, respectively.

THE couples Cu—Cu_2O, Cu_2O—CuO, and Ni—NiO are being used with increasing frequency as oxygen-pressure standards in measurement of high-temperature equilibria by e.m.f. (*2, 12, 14, 17*) and decomposition pressure (*11, 18*) methods. For this purpose, selected values for the thermodynamic properties of these couples are desirable, based on the most reliable modern measurements. It is the purpose of this paper to fulfill this need.

Recent studies of metal-metal oxide equilibria, employing electrolytic cells with a solid electrolyte, have produced high-temperature equilibrium data of improved precision, covering wide ranges of temperature. These data, plus recent calorimetric data on copper and nickel oxides, have been subjected to correlation by second- and third-law methods to yield selected values for the thermodynamic properties of these oxides. All computations have been made with the aid of a digital computer, both to minimize the chance of arithmetic error and to reduce the task to manageable proportions.

The basic relations used in the third-law method are given in Equations 1 to 3.

$$\Delta fef = \frac{\Delta(H_T - H_{298})}{T} - \Delta S^\circ_{298} - \Delta(S_T - S_{298}) \quad (1)$$

$$\Delta fef = A + BT + CT^2 \quad (2)$$

$$\Delta H^\circ_{298} = \Delta F^\circ_T - T\Delta fef = \Delta F^\circ_T - AT - BT^2 - CT^3 \quad (3)$$

Literature values for $H_T - H_{298}$, S°_{298}, and $S_T - S_{298}$ at 100° temperature intervals are used in Equation 1 to calculate the change in free-energy function, Δfef, for the reaction. Next, Δfef is expressed as an empirical function of temperature. The empirical constants of Equation 2 are evaluated for each 200° temperature interval from the known values of Δfef at the middle and each end of the temperature interval. Finally, each pair of experimental values of ΔF°_T and T are used in Equation 3 to evaluate a separate value of ΔH°_{298}. The set of values of ΔH°_{298} is then averaged and the standard deviation from the average computed.

The second-law method employs Equations 4 to 6.

$$\beta = \frac{\Delta(H_T - H_{298})}{T} - \Delta(S_T - S_{298}) \quad (4)$$

$$\beta = A' + B'T + C'T^2 \quad (5)$$

$$\Delta H^\circ_{298} - T\Delta S^\circ_{298} = \Delta F^\circ_T - \beta T = \Delta F^\circ_T - A'T - B'T^2 - C'T^3 = \tau \quad (6)$$

β is evaluated at 100° intervals from literature values of enthalpy and entropy increments and Equation 4. β is expressed as empirical equations, in the same manner as for Δfef, according to Equation 5. Finally, Equation 6 is used with pairs of experimental points to evaluate τ for each experimental point. The least squares straight line for τ *vs.* T is then evaluated to yield the intercept, ΔH°_{298}, the slope, $-\Delta S^\circ_{298}$, and the standard deviation of the points from the straight line.

A fully consistent set of data will yield the same result from both second- and third-law methods. Lack of agreement indicates an inconsistency either in the experimental data points or the basic data used to calculate Δfef and β. Comparison of the two correlating methods is a useful means to diagnose the nature of the inconsistency. In cases where ΔS°_{298} is known with good precision, the third-law method is generally conceded to yield the more trustworthy results (*8*).

Review of Thermodynamic Properties. Table I summarizes the most reliable values of the basic properties for the substances considered here. All standard entropies are known with good precision. The entropy value for Cu_2O(c) is that recently redetermined by Mah *et al.* (*13*), and it differs significantly from the value based on the older work of Hu and Johnston (*6*).

All data for Cu(c) and O_2(g) were taken from the JANAF Tables (*8*) in order that the results derived in this paper may be consistent with that compilation.

$\Delta H^\circ_{f_{298}}$ for NiO(c) is known with good precision from the calorimetric study of Boyle, King, and Conway (*3*). In contrast, values for the heat of formation of the copper oxides have been in doubt for many years, and Table I shows the range of values reported for these data. Mah and coworkers (*13*) have recently reported data on the combustion calorimetry of copper metal to produce mixtures of Cu_2O and CuO. They have used their data, along with older high-temperature equilibrium data, to calculate values for the heat of formation of Cu_2O and CuO. Their results are the most reliable up to this time, but values of greater accuracy and reliability can be obtained from calculations based on the recent high-temperature, solid-electrolyte e.m.f. studies considered herein.

Table I. Literature Values of Thermodynamic Properties[a]

	$\Delta H^\circ_{f_{298}}$, Kcal.	S°_{298}, Cal./° K.	$H_T - H_{298}$, $S_T - S_{298}$
O_2	0.	49.004 ± .01 (*8*)	(*8*)
Cu(c)	0.	7.913 ± .04 (*8*)	(*8*)
Cu_2O(c)	−39.8 (*15*) to −41.8 (*4*)	22.08 ± .1 (*13*)	(*13*)
CuO(c)	−37.1 (*15*) to −38.3 (*4*)	10.183 ± .1 (*8*)	(*13*)
Ni(c)	0.	7.14 ± .02 (*7*)	(*7*)
NiO(c)	−57.30 ± 0.1 (*3*)	9.08 ± .04 (*9*)	(*10*)

[a] Reference numbers are in parenthesis.

The heat functions, $H_T - H_{298}$ and $S_T - S_{298}$, for CuO(c) and Cu_2O(c) have been redetermined recently by Mah (*13*), and the new values are significantly lower than those based on the early measurements of Wohler and Jochum (*19*). These new data successfully resolve the long-standing disagreement between second- and third-law correlating methods for equilibrium data on the copper oxides.

FORMATION OF NICKEL OXIDE

The equilibrium

$$Ni(c) + \tfrac{1}{2}O_2 = NiO(c) \qquad (7)$$

has been studied recently by Rizzo, Bidwell, and Frank (*14*) who measured the e.m.f. of a cell with a solid electrolyte and an air reference-electrode, between 986° and 1273° K. The authors supplied their original data points (43 in number, from three separate experiments), which did not appear in their published paper.

Kiukkola and Wagner (*12*) also report equilibrium data for Reaction 7 (at nine temperatures between 1023° and 1413° K.) determined from the e.m.f. of a cell with solid electrolyte and an iron-wustite reference electrode.

Alcock and Belford (*1*) report the results of measurements by Tomlinson and Young on the gas-solid equilibrium

$$Ni + CO_2 = NiO + CO$$

$$\Delta F^\circ = 11{,}270 - 0.07T$$

between 820° and 1120° K. From this free-energy equation and the JANAF (*8*) values for the free energy of CO and CO_2, the author has calculated the following free-energy equation for Reaction 7.

$$\Delta F^\circ = -56{,}779 + 21.71T - 0.50 \times 10^{-3}T^2$$

Twelve points between 820° and 1120° K. were calculated from this equation to compare with the two cell-e.m.f. studies.

In the correlations which follow, four data points of Rizzo, Bidwell, and Frank and one from Kiukkola and Wagner (at 1123° K.) were discarded because their deviation from the others was excessive. The remaining 59 data points were subjected to second- and third-law correlations, employing values of the entropy and heat functions reviewed in Table I. The results are given in Table II.

The second- and third-law correlations show a remarkable degree of agreement, both with each other and with the calorimetric measurement of ΔH°_{298} reported in Table I. This is the kind of agreement between high-temperature equilibrium measurements and basic thermodynamic constants which is seldom found. Considered separately, the third-law values of ΔH°_{298} were −57,245 for Rizzo's e.m.f. data, −57,288 for Kiukkola's e.m.f. data, and −57,180 for Tomlinson's gas equilibrium data.

In choosing selected values for this reaction, the third-law values are preferred to the second-law values because the entropy of all constituents at 298° K. is known with good precision. Furthermore, Rizzo's data were preferred because of the more direct method of measurement. The uncertainty of the selected value for ΔH°_{298} represents two standard deviations of the experimental points from this value, and it is large enough to include all but three of the 59 data points used in this correlation. Table III gives the values of ΔF°_f and log P_{O_2} at 100° intervals, based on these selected values.

FORMATION OF CUPROUS OXIDE

Rizzo, Bidwell, and Frank (*14*) have also reported solid-electrolyte e.m.f. studies of two cells involving, respectively, the reaction

$$2Cu(c) + \tfrac{1}{2}O_2 = Cu_2O(c) \qquad (8)$$

$$Cu_2O(c) + Ni(c) = NiO(c) + 2Cu(c) \qquad (9)$$

Their original data (31 points from 2 cells, covering the range 983° to 1263° K., for Reaction 8; 81 points from 4 cells, covering the range 873° to 1313° K., for Reaction 9) were supplied by the authors.

Steele and Alcock (*17*) have also reported e.m.f. data for Reaction 9 (seven points from 673° to 1273° K.). Their data agree well with those of Rizzo, Bidwell, and Frank, and the two sets of data were combined to yield 88 points for Reaction 9.

Table II shows the results of correlation of these data. Once again the results of second- and third-law correlations are in good agreement, which establishes that the experimental method is not subject to significant systematic error, and that the free energy functions for the constituents are reliable. The small value of the standard deviation for these reactions illustrates the unusual precision that is typical of many solid-electrolyte e.m.f. studies.

By combining the third-law results for Reactions 7 and 9, an independent value for the heat of formation of Cu_2O(c) is obtained (line 8:2 of Table II). The agreement between the two values is excellent, and the selected value for the heat of formation of Cu_2O(c), −40,760 ± 100 cal., has been chosen to fall between the two values. For comparison,

Table II. Results of Data Correlations[a]

		Second Law		Third Law	
	Reaction and Data Sources	$-\Delta H^\circ_{298}$, cal./mole	$-\Delta S^\circ_{298}$, cal./° K./mole	$-\Delta H^\circ_{298}$ cal./mole	$-\Delta S^\circ_{298}$ cal./° K./mole
(7)	$Ni + \tfrac{1}{2}O_2 = NiO$				
	1. Ref. (*1, 12, 14*)	57,259 ± 65	22.581	57,238 ± 65	22.562
	2. Selected values			57,240 ± 130	22.562
(8)	$2Cu + \tfrac{1}{2}O_2 = Cu_2O$				
	1. Ref (*14*)	40,913 ± 34	18.394	40,744 ± 36	18.248
	2. 7:1 and 9:1, this table			40,776 ± 97	18.248
	3. Selected values			40,760 ± 100	18.248
(9)	$Cu_2O + Ni = NiO + 2Cu$				
	1. Ref (*14, 17*)	16,554 ± 30	4.398	16,462 ± 32	4.314
(10)	$4CuO = 2Cu_2O + O_2$				
	1. Ref. (*2, 5, 16*)	−67,093 ± 42	−52.266	−67,289 ± 46	−52.432
	2. Selected values			−67,280 ± 100	−52.432
(11)	$Cu + \tfrac{1}{2}O_2 = CuO$				
	1. Selected values (from 8:3 and 10:2, this table)			37,200 ± 100	22.232

[a] Uncertainties in ΔH°_{298} represent one standard deviation, except for selected values which are two or more standard deviations.

Table III. Selected Values for Nickel and Copper Oxides[a]

	NiO(c), Reaction 7		Cu_2O(c), Reaction 8		Cu_2O-CuO, Reaction 10		CuO(c), Reaction 11
T., ° K.	$-\Delta F^\circ$, cal./mole	$-\log P_{O_2}$, atm.	$-\Delta F^\circ$, cal./mole	$-\log P_{O_2}$, atm.	$+\Delta F^\circ$, cal./mole	$-\log P_{O_2}$, atm.	$-\Delta F^\circ$, cal./mole
298.15	50513 ± 130	74.054	35320 ± 100	51.781	51648 ± 100	37.859	30572 ± 100
400	48234	52.708	33461	36.564	46376	25.339	28325
500	46042	40.250	31646	27.665	41320	18.061	26153
600	43930	32.003	29846	21.743	36394	13.257	24022
700	41832	26.121	28062	17.523	31554	9.852	21920
800	39752	21.719	26291	14.365	26793	7.319	19844
900	37693	18.306	24547	11.922	22112	5.370	17802
1000	35637	15.577	22808	9.969	17507	3.826	15781
1100	33596	13.350	21088	8.380	12952	2.573	13782
1200	31571	11.500	19372	7.056	8486	1.546	11808
1300	29540	9.932	17695	5.950	3985	0.670	9844
1400	27514	8.590	15822	4.940	(–443)[b]	(–0.069)[b]	7800
1500	25507	7.433	13728	4.000			
1600	23501	6.420					
1700	21510	5.531					

[a] Reference states are Ni(α) to 600°, Ni(β) 700° to 1700°; NiO(α) to 500°, NiO(γ) 600° to 1700°; Cu(c) to 1300°, Cu(l) 1400° to 1500°; Cu_2O(c) and CuO(c) all temperatures . [b] Metastable to liquid oxide above 1350° K.

Mah and coworkers calculate –40,830 ± 300 cal. for the heat of formation of Cu_2O, based on their calorimetric study and older equilibrium data on the decomposition of CuO to Cu_2O. The uncertainty assigned to ΔH°_{298} ±100 cal., represents three standard deviations of the value determined by third-law correlation of data for Reaction 8. Table III gives values of ΔF°_f and log P_{O_2} for formation of Cu_2O(c), based on the selected values.

FORMATION OF CUPRIC OXIDE

Bidwell (*2*) has recently studied the equilibrium

$$4CuO(c) = 2Cu_2O(c) + O_2 \qquad (10)$$

between 973° and 1273° K., by means of a cell with solid electrolyte and an air reference-electrode. He reports values of e.m.f. at seven temperatures, each the average of five or more determinations.

Reaction 10 has also been studied by numerous investigators who employed direct measurement of the equilibrium oxygen pressure. Below 1150° K., where the oxygen partial pressure is less than 1 cm. of Hg, this method often yields erratic results owing to incomplete removal of adsorbed moisture and other gases from the system. At higher temperatures, however, the accuracy is good, and the results of independent investigations are in good agreement. For comparison with the e.m.f. results of Bidwell, the following direct oxygen pressure measurements were used: 12 points from Smyth and Roberts (*16*) between 1189° and 1346° K. (their values at higher temperatures were discarded because they exceed the eutectic temperature, 1350° K. between CuO and Cu_2O); seven points from Foote and Smith (*5*) between 1223° and 1323° K.

Line 10:1 of Table II shows the correlation when all the data for Reaction 10 are combined. For comparison, the third-law results for the individual data sets yield (for ΔH°_{298}) 67,274 for Bidwell, 67,335 for Roberts and Smyth, and 67,271 for Foote and Smith. The agreement is very good between the different data sets and between second- and third-law methods. The selected value for ΔH°_{298} is chosen to favor the third-law results from Bidwell's data.

Combination of the selected values for Reactions 8 and 10 yields, for the formation of CuO(c),

$$Cu(c) + \tfrac{1}{2}O_2 = CuO(c) \qquad (11)$$

$$\Delta H^\circ_{298} = -37{,}200 \pm 100 \text{ cal./mole}$$

An independent value for the heat of formation of CuO(c) may be obtained by combination of the selected value for formation of Cu_2O (Reaction 8) with the calorimetric data of Mah on the combustion of copper metal to mixtures of Cu_2O and CuO. This yields –37,290 ± 260 cal. per mole for the heat of formation of CuO(c). The agreement between the independent values is well within the calculated uncertainties. The selected value for the heat formation of CuO, –37,200 cal. per mole, was chosen to favor the third-law value because of the smaller uncertainty involved. Table III gives values of ΔF°_f for formation of CuO(c), and ΔF° and log P_{O_2} for Reaction 10, based on the selected values.

CONCLUSION

The new calorimetric data of Mah (*13*) on the entropy of Cu_2O(c) and the high temperature heat content of Cu_2O(c) and CuO(c), coupled with recent high-temperature equilibrium data determined by solid-electrolyte e.m.f. studies, yield excellent third-law correlations for reactions involving NiO, Cu_2O, and CuO. All of the data are internally consistent, and the resulting calculated values of ΔF° and log P_{O_2} for the metal-metal oxide couples possess a high degree of reliability.

NOMENCLATURE

C_p = heat capacity at constant pressure, cal. per degree mole
fef = free energy function, reference 298.15° K., for a substance, cal. per degree mole
Δ*fef* = change in free energy function for a reaction, ref. 298.15° K., cal. per degree mole
ΔF° = change in standard free energy for a reaction, cal. per mole
ΔH° = change in enthalpy for a reaction, cal. per mole
ΔH°_f = change in enthalpy of formation from the elements, cal. per mole
$(H_T - H_{298})$ = heat content of a substance at *T*., ° K., relative to 298.15° K., cal. per mole
S°_T = entropy of substance at *T*., ° K., cal. per degree mole
ΔS° = entropy change for a reaction, cal. per degree mole
$(S_T - S_{298})$ = entropy of a substance at *T*., ° K., relative to 298.15° K., cal. per degree mole
T = temperature, ° K.

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Second Virial Coefficients from the Gaussian-Six Intermolecular Potential

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A two-parameter Gaussian-Six intermolecular potential function,

$$E(r) = \frac{e^2}{r}\left[1 + \frac{\operatorname{erf}(2^{-1/2}\beta r) - 2\operatorname{erf}(\beta r)}{1 - \exp(-\beta^2 r^2/2)} - \frac{(2/\pi)^{1/2}\beta r - 4\operatorname{erf}(\beta r/2)}{\exp(\beta^2 r^2/2) - 1}\right] - \frac{C'}{r^6}$$

was used to calculate the reduced second virial coefficients of gases for the following parametric values: $\bar{T}^* = [k\bar{T}/\beta e^2] = 0.0005(0.0005)0.0125$ and $K = [C'\beta^5/e^2] = 1.00(0.05)2.00(0.20)3.00$. The intermolecular potential parameters, β and C'/e^2, were determined from the experimental data on second virial coefficients for argon, krypton, xenon, nitrogen, carbon dioxide, methane, ethane, propane, and ethylene. Comparison with experimental data indicates that the Gaussian-Six potential function is a slight improvement over the Lennard-Jones (6, 12) potential function in the lower temperature range for nonpolar, spherical molecules.

BECAUSE OF THE uncertainties associated with both the inverse power and the exponential forms of the repulsive potential, consideration of other functional forms is desirable, preferably those having theoretical bases. One such expression for the repulsion potential has been developed from quantum mechanics by Jansen (*12*). Jansen's model is based on the following assumptions and simplifications (*12*): Only single interatomic exchange of electron pairs is taken into account. Effects due to exchange of two or more pairs of electrons between the same two atoms are therefore not considered. Contributions due to coupling of inter- and intraatomic exchange are neglected. The electron charge distribution of an atom has spherical symmetry.

Three atoms are considered, and a summation is made over single-exchange effects between all possible pairs of electrons having parallel spin. This total effect is then replaced by exchange between one effective electron on each atom. The charge distribution for the effective electron is expressed in the Gaussian form

$$\rho(r) = (\beta^3\pi^{-3/2})\exp(-\beta^2 r^2) \qquad (1)$$

in which $\rho(r)$ is the charge density at a distance, r, from the nucleus while β is a parameter.

Based on the model just described, Jansen has developed an expression for the triatomic, first-order, many-body interaction. By considering only the two nearest-neighbor atoms, a and b, and ignoring the effect of the third, distant atom, the expression for a pair interaction is simplified to the form

$$(H_{ab})^0/e^2 = \frac{1}{r} - \frac{1}{1 - \Delta_{ab}^2}\left[2G_{au(b)} - 2\Delta_{ab}G_{ab(a)} - A_{abab} + A_{aabb}\right] \qquad (2)$$

where e is the electron charge, or 4.802×10^{-10} statcoulomb. For a Gaussian distribution of electron charge as given by Equation 1, the integrals occurring in Equation 2 for the first-order perturbation Hamiltonian, $(H_{ab})^0$, are listed in Table I as given by Jansen (*12*).

The first-order Hamiltonian is the sum over single-exchange effects between all possible pairs of electrons of two atoms; thus, it can be interpreted as the repulsive energy. Then, the first-order London dispersion force, the inverse sixth-power attraction potential ($-C'r^{-6}$) is superimposed into Jansen's first-order repulsive energy function to constitute the proposed intermolecular potential function. Thus, the Gaussian-Six potential function is given by the form

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