Controversy on the Free Energy of Formation of CaO—Additional Evidence in Support of Thermochemical Data
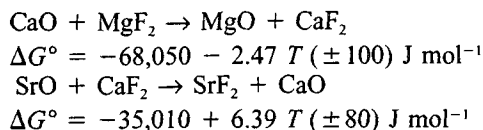
K.T. JACOB and VIJI VARGHESE

The standard free energies of formation of CaO derived from a variety of high-temperature equilibrium measurements made by seven groups of experimentalists are significantly different from those given in the standard compilations of thermodynamic data. Indirect support for the validity of the compiled data comes from new solid-state electrochemical measurements using single-crystal CaF_2 and SrF_2 as electrolytes. The change in free energy for the following reactions are obtained:

$$CaO + MgF_2 \rightarrow MgO + CaF_2$$
$$\Delta G^\circ = -68{,}050 - 2.47\ T\ (\pm 100)\ \text{J mol}^{-1}$$
$$SrO + CaF_2 \rightarrow SrF_2 + CaO$$
$$\Delta G^\circ = -35{,}010 + 6.39\ T\ (\pm 80)\ \text{J mol}^{-1}$$

The standard free energy changes associated with cell reactions agree with data in standard compilations within ± 4 kJ mol^{-1}. The results of this study do not support recent suggestions for a major revision in thermodynamic data for CaO.
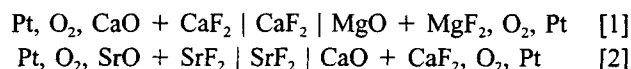
I. INTRODUCTION

CALCIUM oxide is an important constituent of many metallurgical slags and fluxes, and its thermodynamic properties are important in the analysis of equilibrium states in a variety of pyrometallurgical processes. Multinary oxides containing CaO are also important in ceramic technology. The standard free energy of formation of CaO is a key parameter required for the calculation of phase diagrams of interest to high-temperature technology. Values for the standard free energy of formation of CaO given in most compilations of thermodynamic data[1,2,3] are primarily based on closely agreeing combustion[4] and solution[5] calorimetric determinations of the enthalpy of formation and heat capacity measurements at low (4 to 300 K)[6] and high temperatures (564 to 1170 K).[7]

In recent times, the thermochemical values for the Gibbs energy of formation of CaO have been seriously challenged by several researchers.[8,9,10] It is suggested that the Gibbs energy of formation at temperatures above 1600 K is 25 to 35 kJ mol^{-1} more positive than that given in the standard tables.[1,2,3] Since such a major revision has serious implications, additional solid-state galvanic cell measurements which throw new light on the controversy have been conducted. The results of these experiments provide indirect support for the thermochemical data.[1,2,3] A critical assessment of high-temperature equilibrium studies reported in the literature[8–14] is presented.
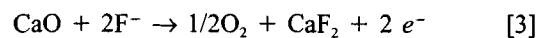
II. GALVANIC CELL MEASUREMENTS
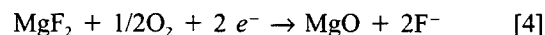
A. Experimental Design

Two solid-state galvanic cells, based on alkaline-earth fluorides as the solid electrolytes, have been designed to test values for the Gibbs energy of formation of CaO. The cells can be represented as

$$\text{Pt, } O_2\text{, CaO} + CaF_2 \mid CaF_2 \mid \text{MgO} + MgF_2\text{, } O_2\text{, Pt} \quad [1]$$
$$\text{Pt, } O_2\text{, SrO} + SrF_2 \mid SrF_2 \mid \text{CaO} + CaF_2\text{, } O_2\text{, Pt} \quad [2]$$

where the right-hand electrodes are positive. Diatomic oxygen gas at pressure of 0.1 MPa is flowed over both electrodes. Transport numbers of the fluoride ion in the CaF_2 and SrF_2 solid electrolytes are greater than 0.99 in the range of temperatures and fluorine chemical potentials encountered in this study. The electromotive force (emf) of the cells is therefore directly related to the standard free energy change for reactions involving CaO. For cell 1, the electrochemical reaction at the left electrode is
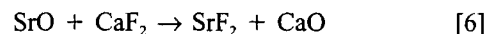
$$CaO + 2F^- \rightarrow 1/2 O_2 + CaF_2 + 2\ e^- \quad [3]$$

At the right electrode,

$$MgF_2 + 1/2 O_2 + 2\ e^- \rightarrow \text{MgO} + 2F^- \quad [4]$$

The virtual cell reaction is

$$CaO + MgF_2 \rightarrow \text{MgO} + CaF_2 \quad [5]$$

Similarly, for cell 2, the virtual cell reaction is

$$SrO + CaF_2 \rightarrow SrF_2 + CaO \quad [6]$$

If the standard free energies of formation of CaO given in standard thermodynamic compilations[1,2,3] are incorrect, then the measured emfs of cells 1 and 2 should be substantially different from those computed from the tabulated data.

In the design of the galvanic cells for measuring thermodynamic properties of oxides, using alkaline-earth fluorides as solid electrolytes, material compatibility at the

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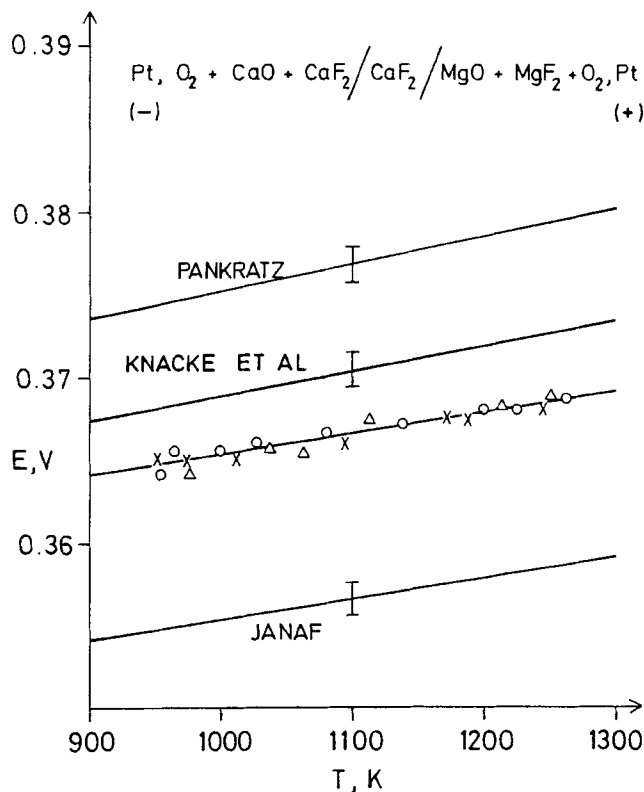Manuscript submitted June 26, 1995.

Fig. 1—Temperature dependence of the emf of cell 1. Experimental data for each experiment are shown by a separate symbol. Values computed from thermodynamic data are shown for comparison.

electrodes should be ensured, as described by Jacob et al.[15] Solid electrolyte CaF$_2$ cannot be used in contact with SrO because of the negative standard free energy change[1,2,3] associated with the exchange reaction:

$$CaF_2 + SrO \rightarrow SrF_2 + CaO \qquad [7]$$
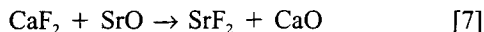
However, CaF$_2$ solid electrolyte is compatible with MgO, and SrF$_2$ is stable in contact with CaO; hence, the choice of single-crystal CaF$_2$ electrolyte for cell 1 and single-crystal SrF$_2$ electrolyte for cell 2.

B. Measurement Technique

The electrodes were prepared from an intimate equimolar mixture of the constituent oxide and fluoride phases. Fine powder of Pt ($\approx$25 mol pct) was added to the mixture and then compacted at a pressure of 25 MPa using a steel die. The role of Pt powder was to catalyze the exchange reaction that generates fluorine chemical potential at the electrodes:

$$1/2O_2 + AF_2 \rightarrow AO + F_2 \qquad [8]$$
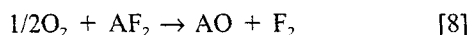
where A = Mg, Ca, or Sr. The compacted pellets were sintered under prepurified oxygen at 1250 K for 8 hours. All the chemicals used in the preparation of the electrodes and the solid electrolytes were of purity higher than 99.99 pct. The oxides were calcined in vacuum (10^{-2} Pa) at 1473 K for 8 hours before use.

The apparatus used in this study for emf measurements was similar to that described elsewhere.[16,17] The electrode pellets were spring loaded on either side of the transparent

single-crystal AF$_2$ (A = Ca or Sr), with a platinum gauze sandwiched between each electrode pellet and the electrolyte. Platinum electrical leads were spotwelded to the gauze. The pellets were held together under pressure by a system of alumina tubes and rods.[16,17] After assembling the cell and raising its temperature to 573 K, the outer alumina tube enclosing the cell was evacuated and then refilled with prepurified oxygen gas. The procedure was repeated three times to remove residual moisture adsorbed on ceramic tubes. The cells were then operated under flowing oxygen. A single stream of purified oxygen flowed over both electrodes at the rate of 2.5 mL s^{-1}. High-purity oxygen gas (99.999 pct) obtained commercially was further purified by passing over CuO at 800 K for converting trace CO and H$_2$ to CO$_2$ and H$_2$O. The CO$_2$ was absorbed by passing the gas over NaOH pellets. The oxygen gas was subsequently dried by passing through silica gel and anhydrous Mg(ClO$_4$)$_2$ and P$_2$O$_5$. Removal of residual moisture from oxygen gas was found to be essential for successful operation of the cells. Interaction of fluoride electrolytes with moisture resulted in an opaque coating of the corresponding oxides on the surface. The alkaline-earth oxides at the electrodes also readily reacted with CO$_2$ and H$_2$O in the gas phase, leading to unsteady emf when cells were operated for several days. Use of the simple stacked-pellet cell configuration was dictated by the nonavailability of long CaF$_2$ tubes. Since partial pressure of fluorine at electrodes was below 10^{-16} Pa at a mean experimental temperature of 1100 K, the transport of fluorine between the electrodes via the gas phase was not significant.

The emfs were measured with a high impedance digital voltmeter in the temperature range 940 to 1260 K. The emfs registered steady values in 3 to 8 hours depending on temperature; longer periods were required at lower temperature. Reversibility of the emf was checked by microcoulometric titration. A small current ($\approx$50 μA) was passed through the cell in either direction for 5 minutes, using an external potential source. After the titration in each direction, the open circuit emf was monitored as a function of time. In every case, the emf was found to return to the original value before the titration. The emf was also found to be reproducible on cycling temperature and was independent of flow rate of argon gas through the cell in the range of 2 to 6 mL s^{-1}. To ensure the absence of thermal gradient across the cell, the emf of a symmetric cell, with CaF$_2$ as solid electrolyte and identical CaO + CaF$_2$ electrodes, was measured as a function of temperature. The cell emf was ±0.2 mV and no systematic trends were observed. At the end of the experiments, electrodes were examined by X-ray diffraction. The phase composition of the electrodes was found to be unaltered during the experiment.

III. RESULTS

Reversible emf of cell 1 is plotted as a function of temperature in Figure 1. Data from each run are shown by a separate symbol. Within the experimental uncertainty (±0.5 mV), the emf is a linear function of temperature. The least-squares regression analysis gives

$$E_1 = 352.6 + 1.28 \times 10^{-2} T (\pm 0.5) \text{ mV} \qquad [9]$$

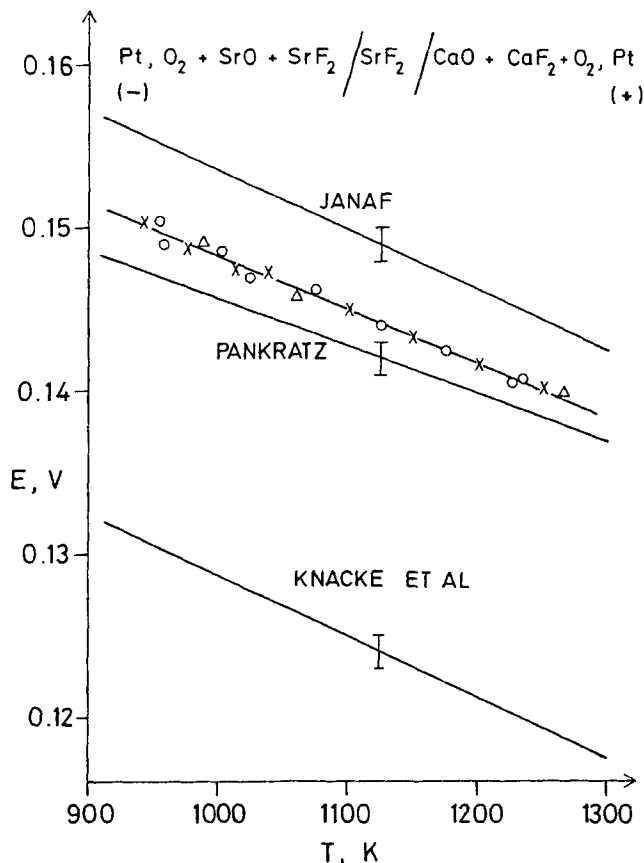The emfs calculated from thermodynamic data in three

Fig. 2—Measured and calculated emf of cell 2 as a function of temperature.

Fig. 3—Comparison of the standard free energies of formation of CaO from different sources.

compilations—Janaf,[1] Pankratz,[2] Knacke et al.[3]—are also displayed in Figure 1 for comparison. The experimental measurements are in good agreement with data from Knacke et al. The maximum difference between the measured and computed emfs is 10 mV, corresponding to a difference of 1.3 kJ mol⁻¹ for the cell reaction. The standard free energy change for Reaction [5] can be computed from the emf of cell 1:

$$\Delta G_5{}^\circ = -\eta F E_1 \qquad [10]$$
$$= -68,050 - 2.47\ T\ (\pm 100)\ \text{J mol}^{-1}$$

where $\eta = 2$ is the number of electrons involved in the electrochemical reactions at each electrode and F is the Faraday constant.

The measured emf of cell 2 is compared with that calculated from thermodynamic data in Figure 2. The measured emfs are reasonably close to values calculated from the compilation of Pankratz[2] and the Janaf tables.[1] The measured emf is approximately 20 mV higher than that computed from the data given by Knacke et al.[3] The least-squares regression analysis of the measured emf gives

$$E_2 = 181.4 - 3.31 \times 10^{-2}\ T\ (\pm 0.4)\ \text{mV} \qquad [11]$$

The corresponding free energy change for Reaction [6] is

$$\Delta G_6{}^\circ = -\eta F E_2 \qquad [12]$$
$$= -35,010 + 6.39\ T\ (\pm 80)\ \text{J mol}^{-1}$$

The emf measurements on cells 1 and 2 are in general agreement with the thermodynamic data given in standard

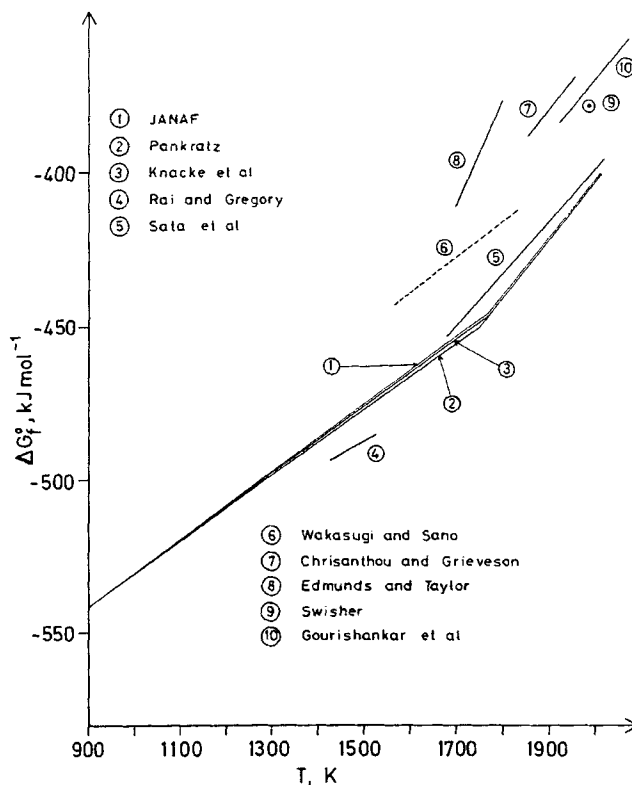compilations,[1,2,3] with maximum deviation of 4 kJ mol⁻¹ in the free energy change corresponding to the cell reaction. The temperature dependence of the measured emfs is also in reasonable agreement with the thermodynamic data. The emfs give values for the free energy change associated with the virtual cell reactions involving CaO. They do not directly give the free energy of formation of CaO. However, if the data for CaO given in standard tables[1,2,3] are in serious error, the results reported in this study would require compensating errors in the free energies of formation of other phases (MgO, SrO, MgF₂, SrF₂, or CaF₂) involved in the cell reactions. This is rather unlikely for two separate reactions. Thus, the present emf measurements do not support a major revision in the thermodynamic data[1,2,3] for CaO.

IV. ANALYSIS OF FREE ENERGY MEASUREMENTS

A. Measurements Involving CaC₂

Information on the free energy of formation of CaO can be deduced from a number of high-temperature studies.[8-14] These are compared with the thermochemical data[1,2,3] in Figure 3. From a study of the graphite solubility in the lime-saturated slags belonging to the system CaO-SiO₂-Al₂O₃, Swisher[2] suggested the formation of CaC₂ from CaO and C above 1983 K when $P_{CO} = 1.01 \times 10^5$ Pa. The free energy of formation of CaO can be deduced from these observations using auxiliary data for CaC₂ and CO from Knacke et al.[3] The derived value is shown in Figure 3.

Edmunds and Taylor[11] studied the reaction between

lime-saturated CaO-CaF$_2$ slags and graphite to form CaC$_2$ and CO in the temperature range 1693 to 1823 K:

$$CaO \text{ (s)} + 3C \text{ (s)} \rightarrow CaC_2 \text{ (s)} + CO \text{ (g)} \qquad [13]$$
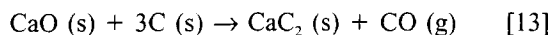
They used a Sievert-type apparatus to measure the partial pressure of CO in equilibrium with CaO, CaC$_2$, and graphite. The flux of calcium vapor from the reaction zone was minimized by enclosing the reactants in a graphite crucible with a tightly fitting lid. From the measured pressure of CO, the free energy of formation of CaO was calculated using auxiliary data for CaC$_2$ and CO. As shown in Figure 3, their data are substantially more positive than those given in thermochemical compilations. CaC$_2$ is known to dissolve in liquid CaF$_2$ at the experimental temperature. Then the activity of CaC$_2$ in the slag is expected to be less than unity, giving raise to a higher pressure of CO during measurement. Hence, the standard free energy of CaO deduced by Edmunds and Taylor[11] is unreliable.

More recently, Chrysanthou and Grieveson[9] studied Reaction [13] under the controlled pressure of CO between 1753 and 1973 K using a Cartesian manostat. The derived free energy of formation of CaO is also shown in Figure 3. Wakasugi and Sano[8] measured the concentration of Ca in liquid Ag, which was equilibrated with a lime-saturated slag held in a graphite crucible under controlled Ar + CO mixture in the temperature range 1570 to 1831 K. The activity of Ca in Ag was independently determined by equilibrating CaC$_2$-saturated slags with Ag in graphite crucibles under an inert atmosphere. Their results also show significant positive deviation from thermochemical data.[1,2,3]

All four of the high-temperature studies described previously[8,9,11,12] use auxiliary data for CaC$_2$ to obtain the free energy of formation for CaO. The uncertainty in the free energy of formation of stoichiometric CaC$_2$ is estimated to be ±15 kJ mol^{-1}. Recently, Ono et al.[18] have reported new measurements on the Gibbs energy of formation of CaC$_2$ in the range 1223 to 1673 K. They equilibrated a mixture of Ca + CaC$_2$ with a thin sheet of iron in a closed iron crucible kept under an inert gas blanket. From the concentration of carbon in iron and known thermodynamics of the iron-carbon system, they computed the standard free energies of formation of CaC$_2$, which are more negative by 5.5 to 12 kJ mol^{-1} than those given in the compilation of Knacke et al.[3] The details of the arrangement of phases inside the iron crucible has not been documented by Ono et al. It is not clear whether the iron sheet was firmly held in contact with CaC$_2$. Was CaC$_2$ present on both sides of the iron sheet? Since carbon cannot be transported through the gas phase under the experimental conditions used, good contact between CaC$_2$ and iron sheet is essential for equilibrium partitioning of carbon between the phases. There is no information in the literature regarding carbon solubility in liquid calcium. As acknowledged by Ono et al., the derived free energy of formation of CaC$_2$ would be more negative if there was significant solubility of carbon in the metal.

The extent of nonstoichiometry of CaC$_2$ in equilibrium with graphite at high temperature is not known. Also, the solid solubility between CaO and CaC$_2$ has not been measured at high temperature, although a eutectic temperature of 2103 (± 10) K is reported.[19] At temperatures above 723 (±20) K, CaC$_2$ has the rock-salt structure, similar to CaO.

The tetragonal-to-cubic transition is associated with orientational disorder of the linear C$_2^{-2}$ ions. Although the lattice parameter of the cubic CaC$_2$ ($a = 0.592$ nm)[20] is approximately 23 pct greater than that of CaO ($a = 0.481$ nm),[21] significant solid solubility is expected at temperatures higher than 1600 K. Among the four separate investigations[8,9,11,12] involving CaC$_2$ as an equilibrium phase, X-ray diffraction was used to characterize CaC$_2$ only in the study by Chrysanthou and Grieveson.[9] Even there, the X-ray diffraction pattern or lattice parameter of CaC$_2$ is not presented, preventing an assessment of the state of CaC$_2$ at equilibrium. Most investigations have relied on the reaction of CaC$_2$ with H$_2$O to form C$_2$H$_2$ as evidence for the presence of the carbide. Unfortunately, this test does not distinguish between pure CaC$_2$ and CaC$_2$ in solid solution. In view of these uncertainties, great reliability cannot be placed on high-temperature measurements involving CaO, CaC$_2$, and C.

B. Measurements Involving Other Phases

Rai and Gregory[13] used the torsion effusion technique to measure equilibrium pressure for the reaction

$$CaO \text{ (s)} + C \text{ (s)} \rightarrow Ca \text{ (s)} + CO \text{ (g)} \qquad [14]$$
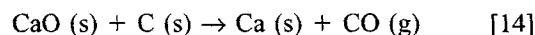
in the temperature interval 1429 to 1525 K. The measured pressure was found to be time dependent. They observed log P to vary linearly with time. They estimated the equilibrium pressure by extrapolating to zero time. The free energy of formation of CaO derived from their measurements, using auxiliary data on gaseous Ca and CO from Knacke et al.[3] is more negative than those given in thermodynamic compilations.[1,2,3]

Sata et al.[14] have measured the vapor pressure of Ca(OH)$_2$ produced by the reaction

$$CaO \text{ (s)} + H_2O \text{ (g)} \rightarrow Ca(OH)_2 \text{ (g)} \qquad [15]$$
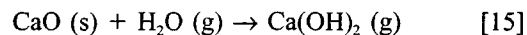
in the temperature range 1678 to 2016 K, using a transpiration technique. Free energy of formation of CaO was calculated using auxiliary data for gaseous Ca(OH)$_2$ and H$_2$O from Janaf.[1] The calculated values shown in Figure 3 are more positive than the thermochemical data by 3 to 7 kJ mol^{-1}. However, considering the uncertainty of ±40 kJ mol^{-1} in the free energy of formation of Ca(OH)$_2$ gas, great reliability cannot be placed on the results obtained from the transpiration study.

Free evaporation experiments were conducted in the temperature ranges 1773 to 2173 K by Sata et al.[14] and 1830 to 2072 K by Gourishankar et al.[10] The partial pressure of Ca over CaO deduced from the measurements of Sata et al.,[4] assuming the evaporization coefficient to be unity, agrees well with the equilibrium pressure calculated from the Janaf data[1] at 1773 K. At higher temperatures, the measured pressure is somewhat lower than that calculated from the Janaf data. In contrast to the results of Sata et al., the Langmuir vaporization studies of Gourishankar et al. indicate that the partial pressure of calcium is more than an order of magnitude higher than that calculated using the Janaf data. Sata et al. used a tungsten heater and measured the temperature using a W-5 pct Re/W-26 pct Re thermocouple calibrated against the melting points of pure Pt, Pd, and Rh. Gourishankar et al. used an induction furnace and

a graphite susceptor to heat the sample. The temperature was measured by an optical pyrometer calibrated against the melting point of Nb_2O_5 and a W-5 pct Rh/W-26 pct Rh thermocouple, which are not very reliable standards for temperature measurement. The compositions of both limbs of the thermocouple fall in the two-phase region, $W_{ss} + \varepsilon$, of the phase diagram for the system W-Rh.[22]

There are two possible reasons for the high rates of mass loss of CaO samples under free vaporization observed by Gourishankar et al.[10] First, the partial pressure of CaO species in the gas may be higher than that assumed by the authors, who have used the Janaf data[1] for gaseous CaO. The Janaf data is primarily based on mass spectrometric measurement of the dissociation energy of CaO gas ($D_0^0 = 380.7$ (± 21) kJ mol^{-1}) by Drowart[23] and Colin et al.[24] The large uncertainty associated with the free energy of formation of gaseous CaO indicates the possibility of a larger contribution to the mass loss from CaO vapor species. A second cause for the higher mass loss arises from the possible reduction of CaO by carbon. Since their graphite susceptor was probably at a much higher temperature than the CaO sample, it is quite likely that gaseous carbon atoms, molecules, or ions emitted by the susceptor would have directly impinged on their sample, forming CO. However, the second explanation cannot account for their results for MgO, unless an evaporation coefficient considerably less than unity is assigned. They found that the mass loss for MgO under the free evaporation condition was much less than that anticipated on the basis of established thermodynamic data.[1,2,3] Gourishankar et al. suggested values for the standard free energy of formation that were 33 kJ mol^{-1} more positive than Janaf for CaO and 34 kJ mol^{-1} more negative than Janaf for MgO. The difference between the free energies of MgO and CaO is thus altered by 67 kJ mol^{-1}. Our measurements on cell 1 directly contradict this result.

More recent evidence in support of thermochemical values for the Gibbs energy of formation of CaO comes from the study of the physical chemistry of the reduction of CaO by aluminum in vacuum[25,26] and alloy-oxide phase equilibria in the system Ca-Al-O at 1373 K.[27] The measured partial pressure of Ca for the reduction reaction and alloy oxide equilibria are consistent with the thermochemical data for CaO and Al_2O_3[1] within ± 4 kJ mol^{-1}.

V. SUMMARY

The emf measurements in the temperature range 940 to 1260 K using two solid-state cells based on single crystals of CaF_2 and SrF_2 as solid electrolytes provide indirect sup-

port for the free energy of formation of CaO deduced from calorimetric data. Many high-temperature free energy measurements show substantial deviations from the calorimetric data.[1,2,3] A critical assessment of the high-temperature measurements reveals several sources of uncertainty.

REFERENCES

1. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Fruip, R.A. Mc Donald, and A.N. Syverud: Janaf Thermochemical Tables, 3rd ed., J. Phy. Chem. Ref. Data, 1985, vol. 14, suppls. 1-2, pp. 1-1856.
2. L.B. Pankratz: Thermodynamic Properties of Elements and Oxides, U.S. Bureau of Mines Bull. 672, U.S. Department of the Interior, U.S. Government Printing Office, Washington, DC, 1982.
3. O. Knacke, O. Kubaschewski, and K. Hesselmann: Thermochemical Properties of Inorganic Substances, 2nd ed., Springer-Verlag, Berlin, 1991.
4. E.J. Huber, Jr. and C.E. Holley, Jr.: J. Phys. Chem., 1956, vol. 60, pp. 498-99.
5. F.D. Rossini, D.D. Wagman, W.H. Evans, S. Levine, and I. Jaffee: Selected Values of Chemical Thermodynamic Properties, U.S. National Bureau of Standards Circ. 500, 1952.
6. E. Gmelin: Z. Naturforsch. A, 1969, vol. 24, pp. 1794-1800.
7. J.J. Lander: J. Am. Chem. Soc., 1969, vol. 73, pp. 5794-97.
8. T. Wakasugi and N. Sano: Metall. Trans. B, 1989, vol. 20B, pp. 431-33.
9. A. Chrysanthou and P. Grieveson: Scand. J. Metall., 1991, vol. 20, pp. 165-67.
10. K.V. Gourishankar, M.K. Ranjbar, and G.R. St. Pierre: J. Phase Equilibria, 1993, vol. 14, pp. 601-11.
11. D.M. Edmunds and J. Taylor: J. Iron Steel Inst., 1972, vol. 210, pp. 280-83.
12. J.H. Swisher: Trans. TMS-AIME, 1968, vol. 242, pp. 2033-37.
13. J.H. Rai and N.W. Gregory: J. Phys. Chem., 1970, vol. 74, pp. 529-34.
14. T. Sata, T. Sasamoto, and K. Matsumoto: High Temp. High Press., 1982, vol. 14, pp. 399-408.
15. K.T. Jacob, K. Swaminathan, and O.M. Sreedharan: Solid State Ionics, 1989, vol. 34, pp. 167-73.
16. K.T. Jacob and J.P. Hajra: Bull. Mater. Sci., 1987, vol. 9, pp. 37-46.
17. K.T. Jacob, K.P. Abraham, and S. Ramachandran: Metall. Trans. B, 1990, vol. 21B, pp. 521-27.
18. H. Ono, A. Kobayashi, F. Tsukihashi, and N. Sano: Metall. Trans. B, 1992, vol. 23B, pp. 313-16.
19. V.R. Juza and H.U. Schuster: Z. Anorg. Allg. Chem., 1961, vol. 311, pp. 62-75.
20. M.A. Bredig: J. Phys. Chem., 1942, vol. 46, pp. 801-19.
21. H. McMurdie: Powder Diffraction J., 1986, vol. 1, p. 266.
22. F.A. Shunk: Constitution of Binary Alloys, 2nd suppl., McGraw-Hill Book Co., New York, NY, 1969, p. 648.
23. J. Drowart: Bull. Soc. Chim. Belges., 1964, vol. 73, pp. 451-58.
24. R. Colin, P. Goldfinger, and M. Jeunehomme: Trans. Faraday Soc., 1964, vol. 60, pp. 306-16.
25. K.T. Jacob and S. Srikanth: High Temp. Mater. Processes, 1990, vol. 9, pp. 77-92.
26. K.T. Jacob and S. Srikanth: Trans. Ind. Inst. Met., 1991, vol. 44, pp. 369-73.
27. S. Srikanth, V.S. Srinivasan, K.T. Jacob, and M. Allibert: Rev. Int. Hautes Temper. Refract., 1991, vol. 27, pp. 131-39.