Theoretical Estimations of $\Delta H^\circ_{f,T}$, $\Delta S^\circ_{f,T}$, and $\Delta G^\circ_{f,T}$ for Ca(O$_2$)$_2$

PASUPATI SADHUKHAN* AND ALEXIS T. BELL

Chemical Engineering Department, University of California, Berkeley, California 94720

Theoretical calculations have been made to predict the standard heat, entropy, and free energy of formation of Ca(O$_2$)$_2$. It is concluded that while the free energy of formation of Ca(O$_2$)$_2$ is strongly negative over the temperature range 100 to 550°K, the compound is thermodynamically unstable relative to CaO and CaO$_2$.

Introduction

Attempts to synthesize calcium superoxide, Ca(O$_2$)$_2$, have failed to yield a pure product (*1–4*) and it has been suggested (*3*) that in those cases where Ca(O$_2$)$_2$ is reported the O$_2^-$ anions are present in a matrix of lower oxides. With the exception of brief comment by Margrave (*5*), suggesting that Ca(O$_2$)$_2$ is expected to be unstable, nothing has been published concerning the thermodynamic properties of Ca(O$_2$)$_2$. The present work was undertaken to predict the standard heat, entropy, and free energy of formation of Ca(O$_2$)$_2$ in order to establish its thermodynamic stability relative to the lower oxides of calcium.

Theoretical Approach and Discussion of Results

Since Ca(O$_2$)$_2$ is assumed to be an ionic compound, by analogy with known superoxides, the standard heat of formation, $\Delta H^\circ_{f,298}$, can be determined by use of a

* Present address: Phillips Petroleum Co., R & D Division, Bartlesville, Okla. 74004.

Born–Haber cycle in the following manner,

$$\Delta H^\circ_{f,298} = \Delta H_{sub} + IP + 2 \times EA$$

$$+ U + \int_0^{298} \Delta C_p \, dT, \qquad (1)$$

$$\Delta C_p = C_{p_{Ca(O_2)_{2(s)}}} - C_{p_{Ca(g)}} - 2C_{p_{O_2(g)}},$$

where ΔH_{sub} is the heat of sublimation of calcium at 298°K, C_p is the molar heat capacity, IP is the ionization potential of calcium, EA is the electron affinity of O$_2$, and U is the lattice energy of Ca(O$_2$)$_2$. With the exception of the lattice energy and the heat capacity of Ca(O$_2$)$_2$ all of the quantities in Eq. (1) are well known.

The lattice energy, U, can be determined using the classical Born–Meyer method for an ionic solid (*6*). According to this method the lattice energy is represented as

$$U = N \cdot \phi(r), \qquad (2)$$

where N is the Avogadro's number. The potential function $\phi(r)$ gives the energy per molecule as a function of the interionic

distance r and is expressed as

$$\phi(r) = -\frac{Me^2}{r} - \frac{C}{r^6} + B(r) + \phi_0, \qquad (3)$$

where M is the Madelung constant, e is the electronic charge, C is a constant characteristic of $Ca(O_2)_2$, $B(r)$ is a potential function, and ϕ_0 is the zero-point energy of $Ca(O_2)_2$. The expression given by Ladd and Lee (7) can be used to represent the repulsive potential $B(r)$

$$B(r) = b \exp(-r/\rho), \qquad (4)$$

where b is the intensity parameter and ρ is the range parameter. Substitution of Eq. (4) into Eq. (3) gives

$$\phi(r) = -\frac{Me^2}{r} - \frac{C}{r^6} + b \exp(-r/\rho) + \phi_0. \qquad (5)$$

The parameter b in Eq. (5) can be eliminated by recognizing that at the equilibrium interionic distance r_0,

$$\left.\frac{d\phi}{dr}\right|_{r=r_0} = 0. \qquad (6)$$

Differentiation of eq. (5) and evaluation of the result at r_0, lead to the expression

$$b \exp(-r_0/\rho) = \left[\frac{Me^2}{r_0^2} + \frac{6C}{r_0^7}\right]\rho. \qquad (7)$$

Thus, at the equilibrium interionic distance, r_0, Eq. (5) can be written as

$$\phi(r_0) = -\frac{Me^2}{r_0} - \frac{C}{r_0^6} + \left[\frac{Me^2}{r_0^2} + \frac{6C}{r_0^7}\right]\rho + \phi_0$$

$$= -\frac{Me^2}{r_0}\left[1 - \frac{\rho}{r_0}\right] - \frac{C}{r_0^6}\left[1 - 6\frac{\rho}{r_0}\right] + \phi_0. \qquad (8)$$

For simple ionic solids the van der Waals term, C/r_0^6, usually corresponds to 1–3% of the lattice energy (8) although calculations by D'Orazio and Wood (9) indicate that this interaction can be about 5% of the lattice energy for the alkali metal superoxides.

However, as we shall see later, the ratio ρ/r_0 for $Ca(O_2)_2$ is about 0.13. Thus the term in the second set of braces in Eq. (8) is 0.22, and the second term in Eq. (8) constitutes not more than about 1% of the lattice energy. Furthermore, the zero-point energy, ϕ_0, is about 1% or less of the lattice energy and this term is opposite in sign to that of the second term. The combined contribution of the last two terms in Eq. (8) is negligibly small compared to the first term, with the result that Eq. (8) can be approximated by

$$\phi(r_0) = -\frac{Me^2}{r_0}\left[1 - \frac{\rho}{r_0}\right]. \qquad (9)$$

To determine the Madelung constant for $Ca(O_2)_2$ it is first necessary to establish the crystal structure of the solid. A useful guide for this purpose is the ratio of anion to cation radii, r_a/r_c. A value of 0.97 Å is taken for the radius of Ca^{2+} (8). The radius of O_2^- is evaluated as 1.64 Å, using the measured heat of formation and crystal structure of NaO_2 (10). These figures yield a value of 1.69 for r_a/r_c, which suggests that $Ca(O_2)_2$ is likely to have a rutile-type crystal lattice. On the basis of this conclusion, the Madelung constant for $Ca(O_2)_2$ is chosen to be the same as that for rutile. In doing so we have taken advantage of the fact that Madelung constants for two ionic solids of the same crystal structure will be the same. For the present work a value of $M = 4.79$ was used (11).

For simple crystals the range parameter ρ does not vary by more than 2–3% (12). As a result the value of ρ for $Ca(O_2)_2$ is taken to be 0.32 Å by analogy with values for alkali halides (12). The equilibrium distance r_0 is simply the sum of r_a and r_c and is equal to 2.63 Å. Introduction of the values of M, r_0, and ρ leads to a value of $U = -532.2$ kcal/mole.

The next step in evaluating $\Delta H°_{f,298}$ is to determine the magnitude of ΔC_p. An approximate guide for estimating specific heats for unknown solids involving gaseous

reactants has been given by Kubaschewski *et al.* (*13*). For a reaction such as

$$A \text{ (s)} + xB_2 \text{ (g)} = AB_{2x} \text{ (s)},$$

$$\Delta C_p = C_{PAB_{2x} \text{ (s)}} - C_{PA \text{ (s)}} - x \cdot C_{PB_2 \text{ (g)}}$$

$$= 3x \text{ cal/(°C)(mole)}. \quad (10)$$

In the case of NaO₂ (s), Eq. (10) yields a value of ΔC_p which is within 20% of the value calculated from experimentally determined specific heats for NaO₂ (s), Na (s), and O₂ (g) at 25°C. For KO₂ the calculated value of ΔC_p differs by 50% from that determined using the experimental specific heats. The effect of a 50% error in ΔC_p is to introduce an error of 8% in the C_p for KO₂ (s) if it is calculated from ΔC_p and the C_p of K (s) and O₂ (g). It is anticipated that a similar level of error should hold for Ca(O₂)₂ (s).

As a further assumption ΔC_p for Ca(O₂)₂ is considered to be constant between 160 and 500°K. This assumption is based on the following observations. Over the specified temperature range, the specific heat of oxygen varies by only 6% while that for calcium varies by less than 3%. Thus the variation in the specific heat of Ca(O₂)₂ should be no more than a few percent. Such a conclusion is found to be valid for NaO₂ and KO₂ (*14*). Furthermore, evaluation of the term containing ΔC_p indicates that it contributes no more than 2 to 3% to the magnitude of $\Delta H°_{f,298}$.

The heat of formation of Ca(O₂)₂ at 298°K can now be evaluated from Eq. (1). The magnitude of each term in the Born–Haber cycle together with its source is given in Table I. A final value of $\Delta H°_{f,298} = -94.4$ kcal/mole is obtained.

The standard entropy of formation at 298°K, $\Delta S°_{f,298}$, can be determined using Latimer's ion contribution technique (*15*). This procedure is based on the assumption that for ionic solids the entropy at 298°K can be evaluated by a summation of the contributions from the cation and anion. Since the

TABLE I

VALUES OF THE TERMS APPEARING IN Eq. (1)

Term	Value (kcal/mole)	Source
ΔH_{sub} for Ca at 298°K	40.3	(*16*)
IP for Ca as Ca^{2+}	414.5	(*18*)
EA for O₂ as O_2^-	−10.1	(*18*)
U for Ca(O₂)₂	−532.2	Eq. (2)
$\int\limits_{298}^{0} \Delta C_p \, dt$	3.2	Eq. (10)

entropies of NaO₂ and KO₂ at 298°K are known, the contribution due to O_2^- can be calculated by subtracting the contribution due to Na^+ and K^+, respectively. The contributions due to O_2^- calculated for these two superoxides differ by 7.5%. An arithmetic mean of the two values was taken for the present calculations. No further correction was made to this figure to account for the higher valence of Ca^{2+} relative to Na^+ or K^+. The entropy contribution of Ca^{2+} was taken from Latimer's calculation (*15*) and the entropies of Ca (s) and O₂ (g) from standard references (*16, 17*). The final value of $\Delta S°_{f,298}$ obtained by this procedure is −58.37 e.u.

Using the information developed above, the standard free energy of formation, $\Delta G°_{f,T}$ can be evaluated at different temperatures from the equation

$$\Delta G°_{f,T} = \Delta H°_{f,298} + \int\limits_{298}^{T} \Delta C_p \, dT$$

$$- T \left[\Delta S°_{f,298} + \int\limits_{298}^{T} \frac{\Delta C_p \, dT}{T} \right]. \quad (11)$$

A plot of $\Delta G°_{f,T}$ versus T is shown in Fig. 1. Free energies of formation are also shown for CaO and CaO₂ in the same figure. Data for these two oxides were taken from the literature (*16, 18*). For CaO₂ the standard free
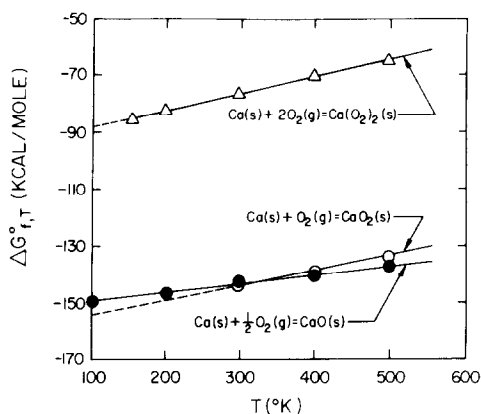
FIG. 1. Standard free energies of formation of $Ca(O_2)$, CaO, and CaO_2 as functions of temperature.

energy of formation was not available for temperatures below 298°K. Below this temperature, standard free energy was linearly extrapolated (dotted line).

It is observed that $\Delta G^\circ_{f,T}$ for $Ca(O_2)_2$ is highly negative for the entire temperature range considered. However, the values of $\Delta G^\circ_{f,T}$ for CaO or CaO_2 are even more negative than that for $Ca(O_2)_2$ over the same temperature range. For example, at room temperature $\Delta G^\circ_{f,T}$ for $Ca(O_2)_2$ is about 65 kcal less negative than the values for CaO or CaO_2. Corresponding differences at other temperatures are of similar magnitude. This means that the thermodynamic driving force for conversion of $Ca(O)_2)_2$ to CaO and CaO_2 is extremely large. Thus, even if $Ca(O_2)_2$ were formed it would be expected to decompose to CaO or CaO_2 unless the kinetics of the decomposition were very slow. The repeated failure to synthesize pure $Ca(O_2)_2$ under a variety of conditions suggests that the reaction products always achieve the most thermodynamically stable form.

References

1. I. I. VOL'NOV, "Peroxides, Superoxides and Ozonides of Alkali and Alkaline Earth Metals" (A. W. Petrocelli Ed.), Plenum, New York (1966).
2. A. W. PETROCELLI AND R. CHIARENZELLI, Report No. 4-413-62-219 General Dynamics, Electric Boat Division (December 31, 1962).
3. C. BROSSET AND N. G. VANNERBERG, Nature (London) 117, 4 (1965).
4. T. WYDEVEN, NASA Ames Research Center, Biosystems Division, Moffett Field, Calif., personal communication.
5. J. L. MARGRAVE, Chem. Eng. News 31, 39, 4012 (1953).
6. H. BORN AND J. E. MEYER, Z. Phys. 75, 1 (1932).
7. M. F. C. LADD AND W. H. LEE, J. Inorg. Nucl. Chem. 11, 264 (1959).
8. F. A. COTTON AND G. WILKINSON, "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York (1972).
9. L. A. D'ORAZIO AND R. H. WOOD, J. Phys. Chem. 69, 8 (1965).
10. P. SADHUKHAN, Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley (1975).
11. Q. C. JOHNSON AND D. H. TEMPLETON, J. Chem. Phys. 34, 6 (1961).
12. C. KITTEL, "Introduction to Solid State Physics," 4th ed., Wiley, New York, 1973.
13. O. KUBASCHEWSKI, E. EVANS, AND C. B. ALCOCK, "Metallurgical Thermochemistry," 4th ed., Pergamon, Elmsford, N.Y. (1967).
14. S. S. TODD, J. Amer. Chem. Soc. 75, 1229 (1953).
15. W. M. LATIMER, J. Amer. Chem. Soc. 73, 1480 (1951).
16. "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U.S. Department of Commerce, Washington, D.C. (1952).
17. "JANAF Thermochemical Data," Dow Chemical Co., Midland, Mich. (1961).
18. "Handbook of Chemistry and Physics," 50th ed., Chem. Rubber Pub. Co., Cleveland, Ohio (1970).