Experimental Techniques for Thermodynamic Measurements of Ceramics

Nathan S. Jacobson
Glenn Research Center, Cleveland, Ohio

Robert L. Putnam and Alexandra Navrotsky
University of California at Davis, Davis, California

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EXPERIMENTAL TECHNIQUES FOR THERMODYNAMIC MEASUREMENTS OF CERAMICS

Nathan S. Jacobson
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio 44135

Robert L. Putnam and Alexandra Navrotsky
University of California at Davis
Thermochemistry Facility
Department of Chemical Engineering and Materials Science
Davis, California 95616

INTRODUCTION

Ceramic materials include oxides, nitrides, carbides, and borides. Many applications for these materials involve high temperatures where their chemical stability is critical. Thermodynamics provides a useful tool for predicting chemical stability, particularly at high temperatures. Thus there is a continuing need for accurate thermodynamic data for existing and future ceramic materials. Methods of obtaining thermodynamic data for ceramic materials are generally similar to those employed for metallic materials. However there are a number of critical issues for ceramic materials which are emphasized here. In general ceramic materials are used at higher temperatures and therefore high temperature thermodynamic data are needed. Obtaining thermodynamic data at high temperature sometimes requires the use of extreme conditions that are incompatible with typical thermodynamic methods and instruments. One particular challenge is need for an inert reaction container at high temperatures. Ceramic materials also present a wide range of thermodynamic stabilities—certain refractory oxides are exceptionally stable (e.g. ThO_2) whereas certain carbides, nitrides, and borides are barely more stable than the constituent elements (e.g. Mo_2C) (ref. 1)

To characterize a system thermodynamically, the following data are needed at a minimum (ref. 2):

(1) The molar heat of formation from the elements in their standard states, e.g.,

$$\Delta_f H_m^o(298) \quad \text{for} \quad M(s) + 1/2\,O_2(g) = MO(s)$$
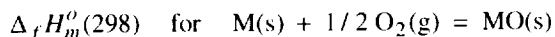
(2) Standard entropy, usually at 298.15 K, S^o (298).

(3) Heat capacity to high temperatures, $C_p^o(T)$.

(4) Heats of phase transformation, $\Delta_{tr}H(T)$.

These data are usually obtained with calorimetry. The formation enthalpies are typically measured using some form of combustion or solution calorimetry. Heat capacities are commonly measured using adiabatic, drop, or differential scanning calorimetry. From the heat capacity and the formation enthalpy, high temperature values for H, G, and S can easily be obtained using equations (1) to (3) (ref. 2).

$$\Delta_f H^o(T) = \Delta_f H^o(298) + \int_{298}^{T} C_p^o(T)\,dT \tag{1}$$

$$S^o(T) = S^o(298) + \int_{298}^{T} \frac{C_p^o(T)}{T}\,dT \tag{2}$$

$$\Delta_f G^o(T) = \Delta_f H^o(T) - T\Delta S^o(T) \tag{3}$$

In some materials with disorder a configurational entropy term must be included in equation (2) (ref. 3).

Many ceramic materials form solid solutions with wide ranges of nonstoichiometry. Examples include $ZrO_{2-\delta}$ and $MoC_{1-\delta}$. For these compounds, it is important to know the partial thermodynamic quantities, such as the thermodynamic activities. The most common experimental methods are gas equilibration, vapor pressure, and electromotive force (emf) measurements. The measured activities are related to the partial molar free energy by (ref. 4):

$$\Delta \overline{G_i} = RT \ln a_i \tag{4}$$

which allows the derivation of the partial molar enthalpy and entropy by:

$$\Delta \overline{S_i} = -\left(\frac{\partial \Delta \overline{G_i}}{\partial T}\right)_p \tag{5}$$

$$\Delta \overline{H_i} = \Delta \overline{G_i} + T \Delta \overline{S_i} = \Delta \overline{G_i} - T\left(\frac{\partial \Delta \overline{G_i}}{\partial T}\right)_p \tag{6}$$

As noted by Kubachewski, et al. (ref. 2) , caution should be taken in ascribing too much significance to data derived from slopes and intercepts. Generally entropies determined from calorimetric measurements or estimates are preferred. Estimates may be made from spectroscopic data or comparison to similar compounds.

If the activities are determined for each component, then the free energy of formation can be calculated. Consider the oxide formation example:

$$M(s) + 1/2\,O_2(g) = MO(s) \qquad \Delta_f G^o = RT \ln a_M a_{O_2}^{1/2} \tag{7}$$
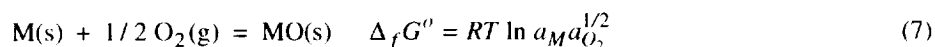
Ideally this can be compared to the value determined calorimetrically.

In this section we begin with a discussion of calorimetry as applied to ceramic materials. We then cover gas equilibration, vapor pressure, and emf techniques. This will cover the major approaches in use today for obtaining thermodynamic quantities of ceramic materials. The references will provide the reader with more details on these and other techniques.

TECHNIQUES YIELDING FORMATION ENTHALPIES

Highly pure, single phase materials are the most desirable for enthalpy measurements. If the highest purity material is unavailable then impurities should be identified and compensated for in the thermodynamic calculations yielding the standard molar enthalpy of formation from the elements, $\Delta_f H_m^o(298.15K)$. This requires that any impurity phases be known and have known thermodynamic functions.

Combustion Calorimetry

Combustion calorimetry is a powerful calorimetric tool used in determining the enthalpy of formation of many materials. The most common forms of combustion calorimetry on ceramic materials involve the reaction of a precursor with fluorine or oxygen gas to measure the energetics of reactions of the type:

$$M1M2(s) + n/2\,X_2(g) = M1X_n(s\ or\ g) + M2X_n(s\ or\ g) \tag{8}$$
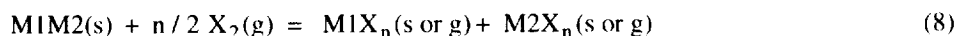
where X = O or F. Several requirements must be met for combustion calorimetry to be useful on ceramic materials. A candidate for combustion calorimetry must react completely with the oxidant to be used (e.g., $Si_3N_4 + O_2$) (ref. 5). The reaction products must be known, reproducible in composition and crystal structure, and have known or measurable enthalpies of formation.

Recently O'Hare (refs. 6 and 7) and Tomaszkiewics et al. (refs. 8 and 9) have determined the enthalpies of formation of several MSi_{2+x} alloys where M = W or Mo. Their studies used F_2 bomb calorimetry since each component in their system (Si, W, and Mo) reacts completely with F_2 to form exactly one known product

{$SiF_4(g)$, $WF_6(g)$ and $MoF_6(g)$}. Calculation of an enthalpy of formation is straightforward once the enthalpy of combustion is known. Using $WSi_{2.060}$ as an example (ref. 6) the molar enthalpy of combustion, $\Delta_c H_m^o$, after corrections unique to each calorimeter, represents the reaction:

$$WSi_{2.060}(cr) + 7.12\,F_2(g) = WF_6(g) + 2.06\,SiF_4(g) \qquad \Delta_c H_m^o \qquad (9)$$
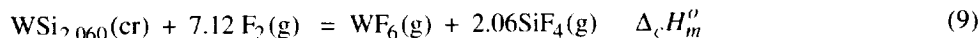
With the standard enthalpies of formation for the products $\Delta_f H_m^o(WF_6, g, 298.15K)$ (ref. 10) and

$\Delta_f H_m^o(SiF_4, g, 298.15K)$ (ref. 11) the enthalpy of formation for $WSi_{2.060}$ can thus be calculated by

$$\Delta_f H_m^o(WSi_{2.06}, cr, 298.15K) = 2.06\,\Delta_f H_m^o(SiF_4, g, 298.15K) + \Delta_f H_m^o(WF_6, g, 298.15K) - \Delta_c H_m^o \qquad (10)$$

O'Hare has recently reviewed (ref. 12) F_2 bomb calorimetry. An oxygen bomb calorimeter is simpler in design to that described by O'Hare but the basic technique remains the same. Generally, combustion bomb calorimetry is limited to non-oxide ceramics or alloys including carbides, nitrides, and some borides. A difficulty in forming oxides by combustion is their tendency to form poorly crystalline or finely grained (nanophase) materials.

Solution Calorimetry

Solution calorimetry is a common method for measuring formation enthalpies of ceramic materials. The material is dissolved in a solvent and the energetics of the reaction are measured in a calorimeter. Two general types of solution calorimetry are used on ceramic materials. Aqueous solution calorimetry (refs. 13 to 17) uses aqueous acidic solutions at 298 to 335 K as a solvent and is thus used for less refractory, easily soluble materials. These materials tend to be the higher valent oxides and water containing materials while many of the newer, more technologically interesting materials tend to be more refractory and less susceptible to aqueous solution calorimetry. High-temperature oxide-melt solution calorimetry (refs. 18 to 29) uses a molten oxide-melt at elevated temperatures to dissolve more refractory materials that often cannot be dissolved using aqueous techniques. We emphasize the oxide-melt technique in this discussion and refer the reader to the more detailed references on aqueous solution calorimetry for examples of its use. The basic thermodynamics of the two techniques are the same.

There is one principal requirement for solution calorimetry. Samples must dissolve completely and rapidly in the solvent and must form reproducibly solvated species. It is convenient for oxide-melt solution calorimetry if solutions are dilute enough to be in the Henry's law regime, so that the enthalpy of solution depends neither on the amount of solute added nor on the presence of comparable amounts of other solutes. In aqueous acid solution calorimetry this is not possible because of the presence of the acid, care must therefore be taken that the final concentration of dissolved species in the reference experiment is equivalent to the final concentration dissolved species from the unknown sample. This is because in aqueous solution calorimetry the measured enthalpy is concentration dependent.

There are several techniques for sample introduction into the solvent. Table I lists some sample introduction techniques and a brief description of each. In most cases a blank or control experiment is necessary to correct for heat affects caused by sample introduction. For example, the heat effect of ampoule breakage or dissolution must be compensated for if an ampoule is used to introduce the sample.

The typical instrument used for oxide-melt solution calorimetry is a twin cell calorimeter described in detail by Navrotsky (refs. 18 to 19) and designed to operate isothermally at a given temperature, T_2 in the example below, for an extended period of time, and with a number of different solvents. Table II lists examples of ceramic materials that have been examined recently and the calorimeter temperatures and solvents used for calorimeters of this design (refs. 18 to 19).

The dissolution of a sample in a solution calorimeter results in a reaction of the form

$$ABO_x(cr, T_1) = AO_y(sol, T_2) + BO_{x-y}(sol, T_2) \qquad \Delta_r H_m^o(ABO_x, cr, T_1) \qquad (11)$$
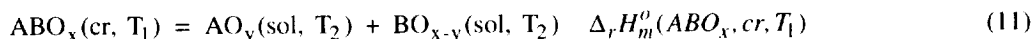
where T_1 is the sample temperature before introduction and T_2 is the calorimeter and solvent temperature. T_1 and T_2 are not necessarily the same temperature and $\Delta_r H_m^o(ABO_x, cr, T_1)$ is the measured heat effect of the reaction. In fact, in most cases of high-temperature solution calorimetry T_1 and T_2 are of necessity different to accommodate a molten oxide-melt as a solvent. An exception being, experiments where an inert platform,

table I, is used for sample introduction. We use the notation AO_{x-y} (sol, T_2) to indicate that little is known or needs to be known about the actual speculation of the solute to derive an enthalpy of formation. We need only know that the material dissolves in the solvent.

An enthalpy of formation for ABO_x(cr) at $T = T_1$ can then be obtained using equation (12) if the values of $\Delta_f H_m^0$ for AO_y(cr, T_1) and BO_{x-y}(cr, T_1) are known or have been similarly measured. Equivalent equations or thermodynamic cycles can be written for nonoxide materials. Typically, experiments are designed to have $T_1 = 298.15$ K, yielding $\Delta_f H_m^0 (298.15K)$ directly.

$$\Delta_f H_m^0 (ABO_x, cr, T_1) = \Delta_f H_m^0 (AO_y, cr, T_1) + \Delta_f H_m^0 (BO_{x-y}, cr, T_1) - \Delta_f H_m^0 (ABO_x, cr, T_1) \qquad (12)$$

Techniques Yielding Heat Capacities and Entropies

In addition to the enthalpy of formation, as shown by equation (3), the entropy is needed to calculate the Gibbs energy of formation for a ceramic material. Several techniques are used in determining $C_p = f(T)$ for the determination of $S^0(T)$ (eq. (2)).

Adiabatic calorimetry yields most of the low temperature (T < 100 K), a good portion of the intermediate temperature (100 < T < 500 K), and even some of the high temperature (500 < T < 1500 K) C_p data accurate to 0.1 percent. Differential scanning calorimetry (DSC) is used primarily for obtaining high temperature (T > 500 K) data but also has been used for some low temperature work (T > 100 K). It is limited in its accuracy to about 3 to 5 percent, under normal conditions, and with extreme care, can be improved to roughly 1 to 2 percent. A third technique, drop calorimetry, is limited to only the high temperature region, although in theory it could be applied at low temperature given a specialized calorimeter. The accuracy of drop calorimetry is comparable to DSC derived data. We start our discussion of entropy measurements by examining each of these techniques for obtaining C_p. Calorimeters capable of drop calorimetry and DSC instruments are available commercially while adiabatic calorimeters are custom built instruments and their use is limited to a few specialized laboratories (refs. 30 to 35).

Drop Calorimetry

A common technique for obtaining high-temperature C_p on ceramic materials is drop calorimetry. Two forms of drop calorimetry are used. Transposed-temperature (cold to hot) drop calorimetry (TTDC) is similar to the high-temperature oxide-melt solution calorimetry described above but does not use a solvent. A sample, at some temperature T_1, is dropped into a calorimeter maintained at some higher temperature T_2. The calorimetric effect, $\Delta_{T1}^{T2} H$, is the enthalpy increment of the sample from T_1 to T_2 and is related to C_p by

$$C_p^* = \frac{(\Delta_{T1}^{T2} H)}{\Delta T} \qquad (13)$$

where C_p^* is defined as the average heat capacity from T_1 to T_2 and is normally attributed to the midpoint temperature, T^*, between T_1 and T_2. Regular drop (hot to cold) calorimetry (DC) maintains the sample in a temperature controlled and heated dropping mechanism at T_2 and the sample is dropped from the higher temperature (T_2) into a calorimeter maintained at a lower temperature (T_1). The heat effect measured is still $\Delta_{T1}^{T2} H$ and equation (13) is still applied. The accuracy of C_p determinations using drop calorimetry is limited only by the sensitivity of the calorimeter to the measurement of $\Delta_{T1}^{T2} H$ and to the magnitude and accuracy of ΔT. Successive measurements of $\Delta_{T1}^{T2} H$ while varying the value of T_2 can allow for the determination of $C_p = f(T)$ needed for equation (2) as shown by the following example:

Example. $\Delta_{T1}^{T2} H$ is measured n times for ABO_3 with T_2 being increased from 600 K to T_n in 25 K increments. Measured are: $\Delta H_1 = \Delta_{T1}^{600K} H$, $\Delta H_2 = \Delta_{T1}^{625K} H$ ... $\Delta H_n = \Delta_{T1}^{T_n} H$. $C_p = f(T)$ is obtained by fitting the curve determined by the $n-1$ points defined by:

$$\left(C_p^*(i),\ T^*(i)\right) = \left(\left\{\frac{\Delta H_{i+1} - \Delta H_i}{25}\right\},\ \{612.5 + 25(i-1)\}\right)._{i=1\,to\,n}$$

With care, determinations of $C_p = f(T)$ including phase transitions (ref. 36) can be obtained to within a few percent. However, this method is usually reserved for situations where the accuracy of a more difficult technique, adiabatic calorimetry, is not required. It is also used for obtaining C_p at temperatures significantly above room temperature.

Differential Thermal Methods

Differential scanning calorimetry, DSC, can be used in two ways to obtain heat capacities. These are the scanning method and the enthalpic method. We will briefly describe each here and refer the reader to Boerio-Goates and Callanan (ref. 37) and their accompanying references for greater detail.

The scanning method for obtaining heat capacities from DSC requires that scans of an empty pan, a reference material, and the unknown sample be taken over a large range in temperature, usually at least 150 K. The heat capacity of the sample is derived by difference using the DSC traces of the reference material and the unknown material after the contribution of the empty sample pan has been subtracted from each. Errors associated with instrumental drift with time and resulting from the need for three different DSC runs (sample, reference, and empty pan) per experiment limit the accuracy of determining C_p by this technique. Some of this error can be compensated for by bracketing the sample run by runs using the reference material necessitating a fourth DSC run. In this way some of the errors associated with instrument drift can be compensated for by assuming that any difference in the two reference runs is a result of instrumental drift.

In the enthalpic (step scan) method a series of short heat pulses are introduced into the sample. Each pulse is followed by a short equilibration time. The DSC signal which resembles a series of high peaks, caused by the heat pulses, followed by valleys of a low, nearly linear, signal during the thermal equilibration periods can then be used to determine C_p. The heat capacity is calculated using equation (13) where the area under an individual peak is related to $\Delta_{T1}^{T2}H$ and T* is the midpoint temperature between T_1 and T_2. Calibration of $\Delta_{T1}^{T2}H$ requires that control experiments be run on an empty pan and a reference sample. Because of the use of small heat pulses and the need for short (~a few minutes) equilibration times, this technique is less sensitive to instrumental drift; however errors are associated with the multiple DSC runs per experiment.

It is possible to modify these DSC techniques to allow both the sample and the reference material to be run simultaneously reducing the number of DSC runs per experiment (ref. 37). In this case, a compensated measurement, yielding ΔC_p between the sample and the reference material is obtained. Using ΔC_p and C_p of the reference material, the heat capacity of the sample may be derived.

Adiabatic Calorimetry

Adiabatic calorimetery is a more accurate technique than DSC or drop calorimetry. Accuracies to within 0.1 per cent at T = 298.15 K are typically attained. The range in temperature over which C_p measurements can be made begins near T = 0 K and reaches as high as T = 1500 K. This temperature region is not accessible by a single calorimeter due to the complex and exacting design requirements (ref. 38) for adiabatic calorimeters that require significant modifications for operations at temperatures above about 350 K. Typically cryogenic calorimeters are used for work from near T = 0 K to about T = 400 K (refs. 30 to 35). High temperature designs are used for work from room temperature to near T = 1500 K (refs. 32 and 34).

The principle behind the use of an adiabatic calorimeter is the stepwise addition of heat into a known sample mass followed by a measurement, after thermal equilibration has been attained, of the change in temperature caused by that addition of heat. Throughout the experiment heat exchange between the sample and the surroundings must be eliminated to attain true adiabatic conditions. Through the use of resistive heating over a given amount of time a known energy input, ΔE, causes a change in temperature, ΔT, from T_1 to T_2 and allows the calculation of C_p using a modification of equation (13):

$$C_p^* = \frac{\Delta E}{\Delta T} \tag{14}$$

As in drop calorimetry, the temperature, T^*, at which this heat capacity point is determined is the midpoint of T_1 and T_2. Through careful control of the magnitude of ΔT in an adiabatic sample environment, $C_p = f(T)$ is obtained through a series of equivalent experiments over a range of temperatures.

Ideally, adiabatic conditions for the sample would mean that no heat is exchanged with the surroundings through radiation, conduction, or convection. True adiabaticity is not attainable however, and therefore minimization of heat exchange is sought. The necessary shielding and control electronics that minimize these heat exchanges lead to the complexity of adiabatic calorimeters (refs. 33 to 35 and 38).

Many materials have been studied with a combination of solution calorimetry and high-temperature heat capacity data to yield thermodynamic quantities from 0 to 1500 K. Examples of such studies are given in the references 21, 22, 30 and 34.

TECHNIQUES YIELDING PARTIAL MOLAR QUANTITIES

We now turn to techniques for obtaining partial molar quantities in ceramics such as thermodynamic activities. The most common techniques are gas equilibration, Knudsen cell vapor pressure techniques, and emf techniques.

Gas Equilibration Techniques

One of the oldest and most useful techniques for determining partial molar quantities is gas equilibration. Consider the equilibration of a metal carbide, MC, with a CH_4/H_2 mixture

$$CH_4(g) = \underline{C}\,(in\,MC) + H_2(g) \quad K = \frac{a(C\,in\,MC)\,P(H_2)}{P(CH_4)} \tag{15}$$
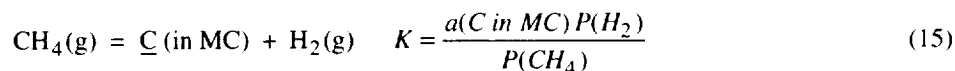
Here K is the known equilibrium constant for the above reaction, $a(C\,in\,MC)$ is the activity of carbon in the metal carbide, $P(H_2)$ is the partial pressure of hydrogen, and $P(CH_4)$ is the partial pressure of methane. Thus measurements of the partial pressures of hydrogen and methane are used to calculate a carbon activity in the metal carbide. An independent chemical analysis of the carbon content of the carbide is done after the experiment. Table III (ref. 39), lists some commonly used gas mixtures (refs. 40 to 45). Gases are flowed continuously or recirculated over the sample. The mixtures are analyzed with a variety of techniques including gas chromatography, mass spectrometry, and various spectroscopic techniques.

There are a number of critical experimental issues in these experiments. The gases must be at the same temperature as the sample, the gases analyzed must be the same composition as those which equilibrate with the sample, and thermal diffusion effects must be minimized. The latter leads to migration of lighter gases to the hot furnace regions and heavier gases to the cold furnace regions. Thermal diffusion is minimized by preheating the inlet gases, using a gas mixture containing an inert gas, and increasing flow rates (refs. 41). In general, experiments should be done at several flow rates.

The CH_4/H_2 mixture is particularly susceptible to moisture effects and gases must be thoroughly dried. To avoid any errors due to moisture, Wada et. al. (ref. 42) have used solid iron along with their unknowns. Since the activity of carbon in iron as a function of composition is well-known, this gives the activity for a given methane to hydrogen ratio, eliminating any errors from the gas analysis. Another factor with the hydrogen-containing gas-mixtures is reactions with silica-containing refractories to form SiO(g), which may lead to silicide formation in the samples. Therefore it is best to use highly pure alumina or zirconia refractories in the hot zone. The use of ammonia to set a nitrogen potential is useful only to about 600 °C, since ammonia decomposes above this temperature (ref. 4). Thus at higher temperatures, nitrogen gas is used directly to set nitrogen activities.

Table III also lists a metal/metal oxide mixture to set an oxygen potential (ref. 44) or metal/metal sulfide mixture to set a sulfur potential (ref. 45) over another condensed phase material. This is referred to as a "Rhines Pack" and is generally done in a sealed ampoule with the metal/metal oxide mixture on one end and the metal to be treated on the other. Again care must be taken to avoid SiO(g) which forms if low oxygen potentials are present in a silica ampoule. In addition, the effects of a static gas in the ampoule as opposed to a flowing gas in the gas mixtures must be considered. However deleterious effects of secondary gas mixture components are avoided (ref. 45).

Knudsen cell-based methods have been extensively reviewed by a number of authors (refs. 46 to 49) and are summarized here as they apply to ceramic materials. The Knudsen cell technique enables direct measurement of the component thermodynamic activities in a solid from the component vapor pressures over that solid, which will be the focus of this section. First, general considerations in the Knudsen cell technique are discussed and then specific methods of vapor analysis are discussed.

A Knudsen cell is a small enclosure (typically ~1 cm in diameter and ~1 cm high) which allows a condensed phase to equilibrate with its vapor. A small orifice of well-defined dimensions allows the vapor to be sampled. Dimensions of the orifice are such that molecule/wall collisions dominate over molecule/molecule collisions. A good deal of information is available on the proper geometrical design of a Knudsen cell (refs. 46 to 49 and associated references).

The cell material must be inert to both the condensed phase and the vapor above it. Table IV lists some selected studies on ceramics and the choice of cell material. In general, refractory metals (Pt, Ir, Re, Mo, W, Ta) (ref. 48) are the most inert with ceramic materials. Caution must be taken however, if tantalum is to be used, due to its high affinity for oxygen. With Mo and W cells the volatile metal oxide equilibria can be used to determine a partial pressure of oxygen in the cell (ref. 48). Consider the $MoO_2(g)$ and $MoO_3(g)$ equilibria:

$$MoO_2(g) + 1/2\, O_2(g) = MoO_3(g) \qquad K = \frac{P(MoO_3)}{P(MoO_2)[P(O_2)]^{1/2}} \qquad (16)$$
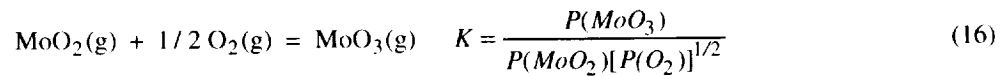
Since the partial pressures of MoO_2 and MoO_3 can be measured and the equilibrium constant is well-known, a value for the partial pressure of oxygen can be calculated. This is clearly an important parameter in a thermodynamic study of oxides. Rhenium is an inert container for many oxide materials, but expensive and difficult to machine. The silicon component in SiC and Si_3N_4 is very reactive and there is no material which is completely inert to silicon (refs. 50 to 53).

The Knudsen cell may be heated by resistance heating, electron bombardment, or induction heating. Precise temperature measurement is done by attaching a thermocouple to the cell or through the use of optical pyrometry.

Ceramic materials often exhibit kinetic barriers to vaporization and the measured vapor pressure from a Knudsen cell may be different than the equilibrium value. The Whitman-Motzfeld (refs. 62 to 64) equation has been used to correct for some of this effect:

$$P_m = P_{eq} - \left(\frac{1}{\alpha} + \frac{1}{W_A} - 2\right)\frac{P_m W_B B}{A} \qquad (17)$$

Here P_m is the measured vapor pressure, P_{eq} is the equilibrium vapor pressure, W_A is the Clausing factor of the cell, W_B is the Clausing factor of the orifice, A is the cross-sectional area of the cell, B is the cross-sectional area of the orifice, and α is the vaporization coefficient. The Clausing factor is simply the fraction of molecules which escape under molecular flow conditions (ref. 46). Measurements are taken with several orifice sizes and a plot of P_m versus $\frac{P_m W_B B}{A}$ thus yields P_{eq} as the intercept and $\left(\frac{1}{\alpha} + \frac{1}{W_A} - 2\right)$ as the slope. Thus the vaporization coefficient may be extracted from the slope. The vaporization coefficient may be defined as the ratio of the number of molecules which should leave the surface to generate an equilibrium vapor pressure to the number of molecules which actually do leave the surface. There are numerous discussions of the vaporization coefficient (ref. 64) and modifications of equation (17) (ref. 48). However the important point is that vaporization coefficients for ceramic materials are often less than unity and this type of Whitman-Motzfeld extrapolation is necessary to obtain equilibrium vapor pressures.

The vapor effusing from the cell may be analyzed via a variety of methods. These include: weight loss, torsion effusion, target collection, and mass spectrometry. Weight loss or thermogravimetric methods are extremely useful. Weight changes may be measured in situ with an automatic recording balance or by weighing the sample before and after heating. The weight loss per unit time area of the orifice is a flux, which can be related to vapor pressure according to the Hertz-Knudsen-Langmuir equation:

$$J = P\sqrt{\frac{M}{2\pi RT}} \qquad (18)$$

Here P is the pressure (in units of force/area), M is the molecular weight of the vapor species, R is the gas constant, and T is the absolute temperature. Note that the molecular weight of the effusing species must be known.

As pointed out by Cater (ref. 46), effusate collection and weighing has advantages over weight of the cell. Any weight changes incurred by the cell are now not considered. However the vapor must be readily condensable and a very accurate weighing or assay is necessary. Tuenge et. al., (ref. 66) have used an electron microprobe. For a radioactive element, accurate assaying is possible.

Vapor pressure can be directly measured via a torsion effusion apparatus (ref. 67). In this case two Knudsen cells are mounted in a small rectangular box which is suspended from a wire in the center. The cell orifices are located equidistant from the center and facing opposite directions. Thus the vapor effusing from the cells creates a torque on the wire. The total vapor pressure is given by

$$P_T = \frac{2\tau\theta}{A_1 d_1 f_1 + A_2 d_2 f_2} \approx \frac{\tau\theta}{Ad} \qquad (19)$$

Here P_T is the total vapor pressure, τ is the torsion constant of the wire, A_1 and A_2 are the areas of the two torsion orifices, d_1 and d_2 are the distances between the suspension axis and the two effusion orifices, and f_1 and f_2 are the Searcy-Freeman correction factors (ref. 68). This elegant technique is a first-principles measurement of vapor pressure and has been used to study a variety of ceramic systems. Kulkarni and Worrell (ref. 69) have examined chromium carbides by measuring $CO(g)$ vapor pressures. In theory, torsion effusion can be applied to all ceramic systems. The variation of torsion constant of a wire suspended from a cold zone to a hot zone may limit the technique to lower temperature systems. Selenides (ref. 70), sulfides (ref. 71), and sulfates (ref. 72) have been successfully studied with torsion effusion techniques.

The torsion effusion and weight loss techniques have been combined into one apparatus. Edwards (ref. 73) has developed such a system with fully automated data collection. Simultaneous measurement of flux and pressure leads to an average molecular weight, by substitution of equation (19) above into equation (18). This technique has been used very successfully to describe the complex decomposition behavior of sulfates (ref. 72) and chromates (ref. 74).

A versatile method of vapor analysis is mass spectrometry. Magnetic sector, quadrupole, and time-of-flight instruments have been used to analyze the molecular beam emerging from the Knudsen cell. Magnetic sector instruments are generally preferred due to the lack of mass discrimination and high sensitivity. The instruments are differentially pumped, with high speed pumps on the Knudsen cell chamber and clean, oil-free pumps on the ionization and detection chambers. There are numerous excellent reviews on the technique (refs. 47 to 49, and 75).

Knudsen cell mass spectrometric studies of ceramic materials involve the same consideration discussed previously—selection of an inert cell material, vaporization coefficients much less than one, and the need for high temperatures. A fourth consideration is that ceramic materials vaporize to complex species. For example, SiC vaporizes to $Si_n(g)$ (n = 1 – 7), $SiC_2(g)$, $Si_2C(g)$, $SiC(g)$, $Si_2C_2(g)$, $Si_3C(g)$, $Si_4C(g)$, $Si_3C_2(g)$ and determination of the thermodynamic activity of silicon in SiC requires selection of the appropriate solid/vapor species equilibria (refs. 50 and 51).

The ultimate issue in mass spectrometry is to precisely relate a measured ion intensity to a vapor pressure of a parent molecule. The assignment of observed ions to neutral parents has been discussed extensively (ref. 75). Once the parent molecule has been unambiguously identified the measured current of that particular ion must be converted to the vapor pressure of the parent molecule. In mass spectrometry, the ion current I is related to vapor pressure P by the following expression:

$$P = \frac{kIT}{\sigma} \qquad (20)$$

Here k is the machine constant and σ is the ionization cross section.

First consider the machine constant. This is determined by a calibration material of known vapor pressure, such as gold and silver; although CsCl, ThO_2, and La_2O_3 have also been used (ref. 48). A problem with this calibration technique is the variation of k from run to run. Near perfect alignment of the cell and ion source and constancy of the ionization process are required to achieve a constant k. Some mass spectrometers have been designed for this; while most have not.

In order to circumvent the problem of a varying calibration constant, there are two major approaches. One involves the use of ion-current ratios and a Gibbs-Duhem integration (ref. 76). This approach has been applied to numerous metallic alloy systems and some ceramic systems as well (ref. 48). Consider a compound AB. The

ion current ratios $\dfrac{I(B^+)}{I(A^+)}$ are measured across the composition range and the activity of A, a_A is given by a graphical integration.

$$\ln a_A = - \int_{x_B=0}^{x_B=x_B} x_B \, d\ln \frac{I(B^+)}{I(A^+)} \tag{21}$$

Here x_B is the mole fraction of B. This technique has been extensively used and is discussed in more detail for ceramics in reference (ref. 48).

The second approach involves the use of multiple cells (ref. 77). Assume a solution AB in one cell and a standard A in an adjacent cell at the same temperature. The cells are translated in and out of the sampling region in the mass spectrometer. Thus the activity of component A is simply:

$$a_A = \frac{P_A(in\ AB)}{P_A^o(in\ pure\ A)} \tag{22}$$

The complication with this technique is mixing between the effusing vapor of A from the solution and the standard. To avoid this, Chatillon uses an ionization chamber entrance aperture smaller than the Knudsen cell orifice so that the ionizer effectively 'sees' only inside the cell (ref. 77). Alternatively another standard may be used, with appropriate corrections for difference in vapor pressures and ionization cross sections (ref. 78).

Precise determination of ionization cross sections, σ, remains a major issue in mass spectrometry. For atoms, several recent measurements (ref. 79) and compilations present reliable data (ref. 80). However for molecules such as are often encountered in vaporization of ceramics, this remains a problem. Generally the additivity rule is used (ref. 81), but this gives an estimate which is too large. Experimental studies with dimers suggest a factor of 0.75 should be applied to the sum of the ionization cross sections (ref. 48). This has been extended to larger molecules, but it is only an approximation.

Electrochemical Techniques

Electrochemical measurements of free energies were first demonstrated by Kiukkola and Wagner (ref. 82). Since then the technique has evolved into one of the most versatile and widely used methods in recent years. This has been possible due to the development of solid electrolytes with nearly total ionic conductivity. Several excellent reviews are available on this technique (refs. 2, 83 and 84).

Consider a general cell for determining the free energy of formation of the oxide MO:

$$Pt|M',M'\,O|ZrO_2(+Y_2O_3)|M,MO|Pt \tag{23}$$
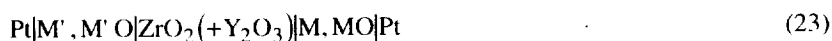
According to standard notation, the vertical lines represent phase boundaries. The reference is the oxygen potential set by a known mixture, designated as M', M'O. The electrolyte is ZrO_2 doped with Y_2O_3, which is an oxygen anion conductor. The two half reactions, which occur at the right and left hand side of the electrolyte are

$$2e^- + AO = A + O^{2-} \tag{24a}$$

$$\underline{B + O^{2-} = BO + 2e^-} \tag{24b}$$

$$B + AO = BO + A \tag{24c}$$

The net reaction is known as a 'virtual reaction' since such a cell is design for "open circuit" operation with no net flow of current. The measured emf, E, from the above cell is related to the activity gradient through the electrolyte as:

$$E = \frac{RT}{zF} \int_{a_{o_2}^{'}}^{a_{o_2}^{''}} t_{o_2}\, d\ln a_{O_2} \tag{25}$$

Here R is the gas constant, T is the temperature, z is the number of electrons transferred, F is the Faraday constant, t_{o_2} is the transference number, and a_{o_2} is the activity of oxygen with the prime and double prime indicating each electrode. In the case of the above displacement reaction (eq. (24c)) and a pure ionic conductor, equation (25) reduces to:
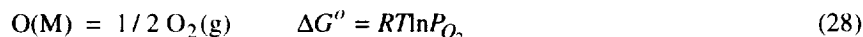
$$\Delta G^o = -2FE \tag{26}$$

Here ΔG^o is the free energy change associated with reaction (eq. (24c)). The entropy and enthalpy of the above reaction can be determined from the temperature dependence of the measured emf (eqs. (5) and (6)). There are numerous experimental considerations in developing such a cell. Foremost is the electrolyte selection. It must be a purely ionic conductor and impervious to gas. Dense pellets of the electrode and electrolyte are made and put into a furnace with high purity argon. In instances where the electrodes have high vapor pressure, it may be necessary to isolate the atmosphere of each electrode. Table V lists the three most common electrolytes and some illustrative applications (refs. 82, 85 and 88).

The necessary stabilizing compounds (typically 10 to 15 mole percent CaO, MgO, or Y_2O_3) for ZrO_2 introduce oxygen anion lattice vacancies and lead to ionic conduction. Additions are also made to ThO_2 to increase ionic conductivity. The use of ThO_2 extends the lower oxygen potential limit. CaF_2 exhibits ionic conductivity over the widest range of temperatures and activities. However particular care must be taken in the handling of CaF_2 to avoid oxidation and hydration.

There are numerous variations on the basic cell described above. Although the cell above is measuring the free energy change in a simple displacement reaction, it can also be regarded as a concentration cell. Consider the following cell:

$$\text{Pt, } O_2 \big| ZrO_2\big(+Y_2O_3\big) \big| M, O - \text{dissolved} \tag{27}$$
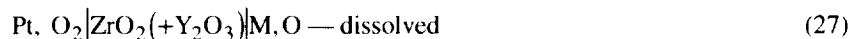
So the virtual reaction is:

$$O(M) = 1/2\, O_2(g) \qquad \Delta G^o = RT\ln P_{O_2} \tag{28}$$

Note that the reference in this cell is air or oxygen. As Pratt (ref. 84) points out, this has the advantage of maintaining ionic conductivity in the reference side of the cell and thus allowing measurements to lower oxygen potentials. However particular care must be taken to avoid permeation of the electrolyte by oxygen gas.

Rickert (ref. 84) describes two types of cells. For cells of the first type, the activity of a species which is the same as the mobile species in the electrolyte is measured. Examples of these are the oxygen activity cells which have been discussed. For cells of the second type, the activity of a species which is different than the mobile species in the electrolyte is measured. This second type of cell allows application of this technique to a wide range of ceramic materials. Under the second type of cells are two subcategories.

In the first subcategory are cells where oxygen potential with an oxide anion conductor is measured and related to another species chemical potential. This is illustrated by a recent elegant study of α-SiC and β-SiC by Klekamp (ref. 87). He uses the cell

$$Pt\big|Re\big|\beta - SiC, C, SiO_2\big|Th(Y)O_2\big|SiO_2, C, \alpha - SiC\big|Re\big|Pt \tag{29}$$
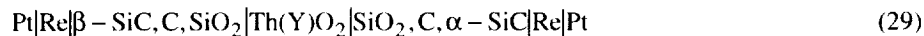
The Re phases are barriers to prevent reactions between the Pt and Si. The two half reactions are

$$\beta - SiC + 2\,O^{2-} = SiO_2 + C + 4e^- \tag{30a}$$

$$SiO_2 + C + 4e^- = \alpha - SiC + 2\,O^{2-} \tag{30b}$$

Thus the oxygen activity measured is due to the small difference between β-SiC/SiO$_2$ and α-SiC/SiO$_2$ and the measured EMF indicates the small free energy difference between the two phases of SiC. Prior to this study, this quantity had not been measured.

The second subcategory involves primarily the CaF$_2$ electrolyte. Although the mobile ion in CaF$_2$ is F, it can be applied to measure oxygen activities as well (refs. 89 and 90). Ramanarayanan et al. (ref. 89) have shown that conduction is due to the flourine ion. The oxygen at the surface of the CaF$_2$ electrolyte reacts to generate this mobile F species. The wide range of ionic conductivity of CaF$_2$ makes it a particularly attractive electrolyte.

CONCLUSIONS

The major techniques for thermodynamic studies of ceramic materials have been discussed. Total molar quantities are determined from calorimetry--heats of reaction, heat capacities, and heats of transformation. Partial molar quantities are determined from gas equilibration techniques, Knudsen cell based vapor pressure measurements, and emf techniques. In each case, the problems unique to ceramics have been emphasized.

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TABLE I.—SAMPLE INTRODUCTION TECHNIQUES FOR SOLUTION CALORIMETRY

Sample Introduction technique	Description
Inert sealed ampoule—aqueous experiments Inert capsule—oxide-melt experiments	Sealed: A small ampoule, usually glass, is broken and its contents mixed into the solvent allowing dissolution of the sample. Capsule: An uncovered and inert, usually Pt, pan or capsule is dropped into the solvent where the contents are dissolved.
Soluble ampoule—oxide-melt experiments	A small ampoule, usually made of hardened solvent material, is dropped into the solvent where it, along with the sample, dissolves.
Inert platform—both aqueous and oxide-melt experiments.	A platform on the end of a manipulation rod is equilibrated above the solvent and then lowered into the solvent and then agitated to allow for sample dissolution. Correction for mechanical stirring.
Pellet—oxide-melt experiments.	A pressed pellet of the sample material is dropped into the solvent where it dissolves. No correction is required.

TABLE II.—EXAMPLES OF MATERIALS STUDIED USING HIGH-TEMPERATURE OXIDE-MELT SOLUTION CALORIMETRY

Material studied/reference	Points of interest in study	Solvent and Temperature used
$CaZrTi_2O_7$ (ref. 21) $CaHfTi_2O_7$ (ref. 22)	Nuclear waste materials Highly refractory oxides	$2PbO - B_2O_3$ 973, 1043, and 1073 K
$Ca_3Al_2[(OH)_4]_3$ (ref. 23)	Hydrous phases	$2PbO - B_2O_3$ 969 K
$MgAl_2O_4$ [24]	Nanophase materials	$2PbO - B_2O_3$ 975 K
Li_3BN_2, Li_3AlN_2, $Ca_3B_2N_4$ (ref. 25) α-Si_3N_4, β-Si_3N_4 (ref. 26)	Nitrides	$3Na_2O - 4MoO_3$ 979 K 52 wt% $LiBO_2$ – 48 wt% $NaBO_2$ $K_2O - 3V_2O_5$
SiO_2, Al_2O_3 (ref. 27)	Element partitioning in silicate melts	$K_2O - SiO_2$ 1760 K $K_2O - 3SiO_2$
Zeolites (ref. 28)	Zeolites, meso- and microporous materials	$2PbO - B_2O_3$ 977 K
$YBa_2Cu_4O_8$, Y_2BaCuO_5, $Y_2Cu_2O_5$, and $BaCuO_{2.01}$ (ref. 29)	Superconductor materials and mixed valencies	$2PbO - B_2O_3$ 977 K

TABLE III.— GAS MIXTURES FOR SETTING CHEMICAL POTENTIALS

Reactant mixture/reference	Potential set
CO-CO_2 (ref. 40)	O_2, C
H_2-H_2O (ref. 41)	O_2
CH_4-H_2 (ref. 42)	C
NH_3-H_2 (ref. 43)	N_2
MO, M (ref. 44)	O_2
MS, M (ref. 45)	S_2

TABLE IV.—SOME REPRESENTATIVE KNUDSEN CELL STUDIES OF CERAMICS AND CHOICE OF CELL MATERIALS

Ceramic/reference	Knudsen Cell Material
SiC (refs. 50 and 51)	Graphite
Si_3N_4 (refs. 52 and 53)	Si_3N_4
Al_2O_3 (ref. 54)	Mo, W
ZrO_2-Y_2O_3 (ref. 55)	W
SiO_2 (ref. 56)	Ta with ZrO_2 liners
Y_2O_3 (ref. 57)	W
Y_2O_3 (ref. 58)	Ir, thoria
U-UO_2 (ref. 59)	Urania
TiC, ZrC, HfC, ThC (ref. 60)	W, Ta with graphite liners
AlN (ref. 61)	Graphite

TABLE V.—SAMPLE SOLID ELECTROLYTE STUDIES

Solid electrolyte	Example of study/reference
Stabilized ZrO_2	$\Delta_f G$ for FeO (ref. 82)
	a(NiO) in NiO-MgO (ref. 85)
ThO_2	$\Delta_f G$ TiO (ref. 86)
	$\Delta_f G$ for α-SiC, β-SiC (ref. 87)
CaF_2	$\Delta_f G$ for Mn Carbides (ref. 88)

REPORT DOCUMENTATION PAGE

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1999	3. REPORT TYPE AND DATES COVERED Technical Memorandum

4. TITLE AND SUBTITLE

Experimental Techniques for Thermodynamic Measurements of Ceramics

5. FUNDING NUMBERS

WU–523–21–13–00

6. AUTHOR(S)

Nathan S. Jacobson, Robert L. Putnam and Alexandra Navrotsky

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
John H. Glenn Research Center at Lewis Field
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–11812

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—1999-209385

11. SUPPLEMENTARY NOTES

Proposed Book Chapter for Experimental Thermodynamics, Volume 7, (ed. by R.D. Weir and T. deLoos) International Union of Pure and Applied Chemistry. Nathan S. Jacobson, NASA Glenn Research Center, Robert L. Putnam and Alexandra Navrotsky, University of California at Davis, Thermochemistry Facility, Department of Chemical Engineering and Materials Science, Davis, California 95616. Responsible person, Nathan S. Jacobson, organization code 5160, (216) 433–5498.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Categories: 05 and 13   Distribution: Nonstandard

This publication is available from the NASA Center for AeroSpace Information, (301) 621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Experimental techniques for thermodynamic measurements on ceramic materials are reviewed. For total molar quantities, calorimetry is used. Total enthalpies are determined with combustion calorimetry or solution calorimetry. Heat capacities and entropies are determined with drop calorimetry, differential thermal methods, and adiabatic calorimetry. Three major techniques for determining partial molar quantities are discussed. These are gas equilibration techniques, Knudsen cell methods, and electrochemical techniques. Throughout this report, issues unique to ceramics are emphasized. Ceramic materials encompass a wide range of stabilities and this must be considered. In general data at high temperatures is required and the need for inert container materials presents a particular challenge.

14. SUBJECT TERMS

Thermodynamics; Ceramics; Calorimetry; Knudsen cell; Electrochemical measurements

15. NUMBER OF PAGES
20

16. PRICE CODE
A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

NSN 7540-01-280-5500