THERMODYNAMICS OF MINERALS AND MINERAL REACTIONS

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Keywords: barometer, continuous reaction, discontinuous reaction, entropy, equilibrium, Gibbs energy, isograd, mineral reaction, mole fraction, oxygen fugacity, pseudosections, self-consistent thermodynamics, solvus, solid solution, thermodynamic calculation, thermodynamic database, thermometer, thermobarometer

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Summary

Thermodynamic properties of minerals are useful in the calculation of chemical equilibria at high pressures and temperatures. Combination of reversed experiments on equilibrium relations at high pressures and temperatures with available entropy and volume data permits generation of self-consistent sets of Gibbs energy and enthalpy for many geological compounds. Thermodynamic properties of solids have been made self-

consistent by simultaneous inverse calculation of many input data. Self-consistent data sets are available in recent tabulations that accompany computer programs and may be used to calculate many new phase equilibria. The phase diagrams can be applied to metamorphic or igneous assemblages that are judged from textures to have equilibrated. Analysis of the solid solutions with correction for dilutions using activity-composition data is usually necessary. An assemblage that is judged to be in equilibrium at a given pressure and temperature is usually obtained from thermobarometry of other assemblages in the same or nearby rocks. Minerals that are equilibrated may be analyzed for their solid solutions, and the locus of various univariant equilibria where the Gibbs energy of reaction is zero may be calculated from initial pressure and temperature using only volume and entropy data. If entropy data are lacking for a phase, they may be estimated by various algorithms. This allows calculation of the Gibbs energy of a phase if all other phases in the reaction have known properties. Addition of the thermodynamic properties of a new phase to the standard compilations greatly expands their utility. Application of thermodynamic calculations to metamorphic assemblages judged to be in equilibrium allows estimates of pressure and/or temperature of assemblages. In addition, estimates of the magnitude of certain chemical parameters, such as oxygen fugacity or the mole fractions of species in a fluid, may be made in igneous and metamorphic rocks.

1. Introduction

Thermodynamic theory was developed in a series of papers by J. Willard Gibbs (1839–1903) of Yale University late in the nineteenth century. Thermodynamic calculations were first applied to inferred reactions between minerals in metamorphic rocks by Victor Goldschmidt (1888–1947) and Pentti Eskola (1883–1964) early in the twentieth century. A much deeper understanding of metamorphic systems has evolved in the last few decades from application of the capabilities offered with the modern electron microprobe, which can provide quantitative *in situ* analysis of major and minor elements in a given mineral down to a spot size of a few μm^3 in volume on a polished thin section. Monitoring the intensity of back-scattered electrons (BSE images) emitted from a polished thin section of a rock when scanned with an electron beam in an electron microprobe or scanning electron microscope, provides spectacular images of chemical zoning—if any—and mineral textures, each of which offers tests of an approach to equilibrium in a given sample.

Given the chemical complexity and the widely variable chemical composition of many minerals, the number of possible reactions among various end-members greatly exceeds 10^{100}. This remarkable complexity means that a full insight of metamorphic reactions is still in progress. Research continues to intensify on experiments constraining mineral equilibria that may be applied to metamorphic and igneous rock systems. Moreover, interest in experimental phase equilibria on likely phases from deep in the mantle has been rekindled. New phases, discovered in the laboratory, that are found to be stable at high pressure and/or temperature have subsequently been found to have natural analogues and vice versa. With the use of calculated phase equilibria, the study of crystalline rocks continues to provide suggestions for new experimental tasks. These in turn lead to constraints on new thermodynamic properties for those phases and may be used to consider new equilibria that may be useful to the geologist. This bootstrapping

process has led to a marked expansion in thermodynamic properties and phase equilibria of minerals and mineral systems. It is anticipated that thermodynamic studies will continue to provide new insights to many geological problems for the foreseeable future.

2. Measurement of Thermodynamic Data

Thermodynamic properties of minerals and synthetic analogues have attracted a great deal of attention because of their usefulness in the calculation of chemical equilibria. The sources of many of the data are hidden in cited or even uncited references and it is far too easy to accept the results of a thermodynamic computation provided by a thermodynamic computer program without critical insight. The basis of the data sources is therefore reviewed below.
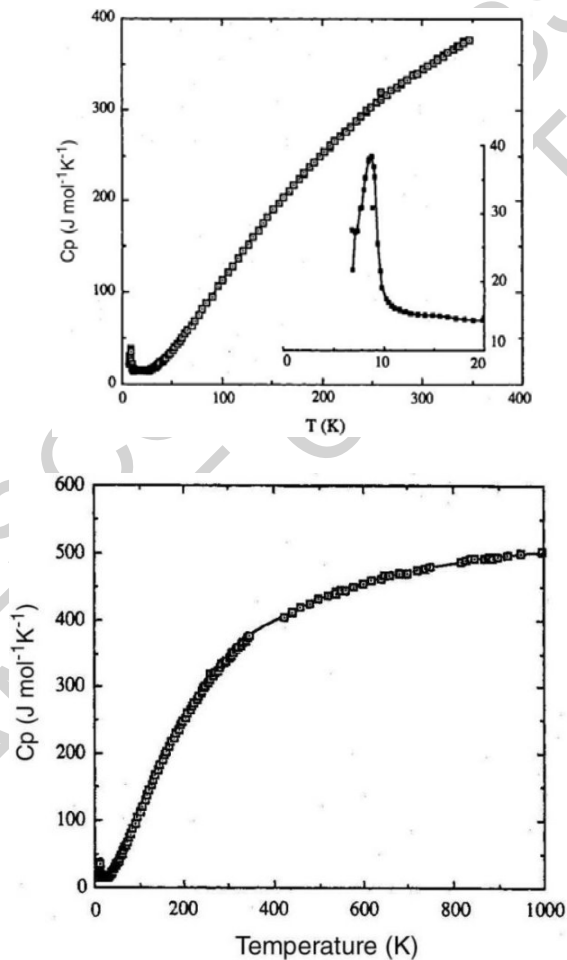
2.1. Measurement of Entropy

Figure 1. The heat capacity of almandine ($Fe_3Al_2Si_3O_{12}$) measured between 4 K and 1000 K. The top figure represents measurements with an adiabatic calorimeter between 4 K and 350 K, and the bottom figure shows the adiabatic measurements as well as DSC measurements between 420 K and 1000 K. The low-temperature peak is due to an antiferromagneitc ordering transition that must be considered in integrating the heat capacity to obtain the entropy of almandine.

The measurement of entropy at room temperature requires heat capacity measurements between 0 K and 298 K. This involves measurement using adiabatic calorimetry, which is currently possible in only a few laboratories around the world. Adiabatic calorimetry involves placing compounds in an adiabatic calorimeter, cooling them down to low temperature—typically to liquid helium temperatures of 4.2 K—then slowly warming them in a calorimeter that is a closed thermal system. Measurement of the energy required to be input allows calculation of the heat capacity of the compound after subtraction of the heat capacity of the container and thermometer (Figure 1 shows the measured heat capacity of almandine, $Fe_3Al_2Si_3O_{12}$). The zero-point entropy, which is contributed from any residual disorder, is added to the integral of heat capacity in order to calculate the entropy at any temperature.

2.2. Measurement of Enthalpy and Calculation of Gibbs Energy

The measurement of enthalpy is usually obtained by measurement of the heat produced by dissolution of the compound into a solvent at or near room temperature, or into a molten salt at high temperature, usually near 1000 K. The heats of solution of individual oxides or elements obtained in the same solvent at the same temperature are subtracted from the heat of solution of the compound in order to obtain its enthalpy change from its constituent oxides or elements. Measurement of enthalpy for refractory compounds yields significant errors (often tens of kJ mol^{-1}), requiring a large number of measurements to be averaged to reduce the errors. Such imprecision limits the usefulness of enthalpy measurements for many refractory compounds.

Once the enthalpy and entropy of a compound have been measured, the Gibbs energy of a phase may be calculated from the relation:

$$\Delta G^{\circ}_T = \Delta H^{\circ}_T - T\Delta S^{\circ}_T \tag{1}$$

where the superscript indicates measurement at standard pressure (1 bar or 10^5 Pa) for a given temperature. The Gibbs energy of compounds is tabulated conventionally at 1 bar and T from the most stable elements at those conditions. The ΔS is computed for:

$$\Delta S^{\circ}_T = S^{\circ}_T(compound) - \Sigma n_i(S^{\circ}_T)_i \text{ for the equivalent stable elements} \tag{2}$$

where n_i is the number of moles of each element in the compound. Both the ΔG°_T and ΔH°_T are for the reaction forming the compound from the stable elements. The largest error in the calculation of ΔG from Eq. (1) is from error in the enthalpy.

2.2. Direct Measurement of Gibbs Energy

The Gibbs energy of transition metal compounds may also be obtained directly from electromotive force (emf) measurements of the energy required to reduce them to metals. Measurement of emf yields very accurate Gibbs energy, to be preferred over calculation of Gibbs energy from enthalpy and entropy. A drawback to emf measurements is that most emf cells only operate in a limited range of oxygen fugacity (fO_2), preventing measurement of Gibbs energy for compounds stable only at very reducing conditions.
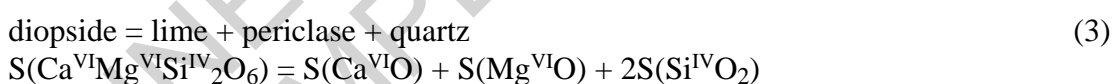
The measurement of emf on complex compounds such as silicates is complicated by the difficulty of determining which of several oxidation/reduction reactions may have occurred. At present, accurate measurement of emf is restricted to simple compounds such as oxides. The Gibbs energy of a phase can also be extracted from experimental data obtained at high pressures and temperatures (compare Section 4). Knowledge of the entropy and volume of all the phases involved in a reaction allows calculation of Gibbs energy at other pressures (P) and temperatures (T). Combined with a data base for Gibbs energy of oxides and more common silicates, such data permit generation of a data base for additional phases based on the experimental reversals.

3. Estimated Thermodynamic Data

In cases where some but not all thermodynamic parameters have been measured for a phase, estimates of the missing parameters can be made with adequate accuracy in some cases. Because of the lack of currently functional adiabatic calorimetry laboratories, entropy data for less common crystalline phases may not be available, and it would be useful to obtain estimates of the entropy in such cases. In general, the errors in entropy estimates are small enough that they are acceptable in deriving Gibbs energy from enthalpy. On the other hand, using entropy estimates to extrapolate Gibbs energy over a large change in temperature may lead to amplified errors for those values, often of the order of tens of kJ/mol over a 1000 °C change in temperature.

3.1. Entropy Estimates Using Oxide Summation

The entropy of compounds has been estimated using the sum of the constituent oxides. This is a variant of Kopp's Law, which states that the heat capacity of a compound is additive from the heat capacity of its elements. These approaches work well when the structure and coordination number of additive phases are similar to those in the compound. For instance, the entropy of diopside ($CaMgSi_2O_6$) is approximated as follows:

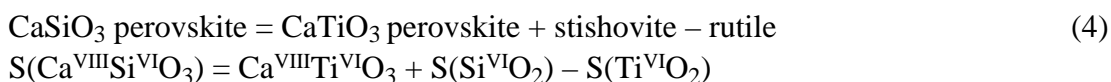diopside = lime + periclase + quartz $\qquad\qquad\qquad\qquad\qquad\qquad$ (3)
$S(Ca^{VI}Mg^{VI}Si^{IV}_2O_6) = S(Ca^{VI}O) + S(Mg^{VI}O) + 2S(Si^{IV}O_2)$

The S^o_{298}(diopside) estimated with this approach is 148.0 J/mol·K, within 4% of the measured value, 142.7 J/mol·K. A correction is sometimes provided for the ΔV of the estimation, although any estimate involving a large ΔV is probably suspect.

The variation in coordination number of cations between oxides and silicates may also affect the estimated entropy. For instance, the strong variation in the entropy of the Al_2SiO_5 polymorphs—at standard P and T (STP): 82.8 J/mol. K for kyanite, 91.4 J/mol. K for andalusite, and 95.4 J/mol. K for sillimanite—is in part related to the change in Al coordination from IV to V to VI in those structures. Algorithms have been developed for entropy estimates of silicates wherein each chemical element is assigned an entropy for a coordination number. This technique is more powerful and more flexible than the other summation methods, and it should be employed more often. A different algorithm should be developed for sulfides and intermetallic compounds than that intended for

ionic compounds such as silicates, oxides, carbonates, and most other minerals with oxygen in the structure.

3.2. Entropy Estimates Using Isostructural Compounds

Entropy may be estimated using isostructural phases for which entropy data are available. For instance, the entropy of Ca-Si perovskite ($CaSiO_3$) cannot easily be measured as it cannot be quenched from its stability field above 10–14 GPa. Its entropy may be estimated with an isostructural approximation:

$$CaSiO_3 \text{ perovskite} = CaTiO_3 \text{ perovskite} + \text{stishovite} - \text{rutile} \qquad (4)$$
$$S(Ca^{VIII}Si^{VI}O_3) = Ca^{VIII}Ti^{VI}O_3 + S(Si^{VI}O_2) - S(Ti^{VI}O_2)$$

where the isostructural compounds stishovite and rutile are used to obtain an entropy estimate for $CaSiO_3$ perovskite from that for $CaTiO_3$ perovskite. The result, 70.8 J/mol·K at STP, is somewhat higher than value (65.9 J/mol·K) obtained from the sum of stishovite and lime, and a published value (67.3 J/mol·K) derived from an evaluation of experimental phase equilibria at high pressure and temperature.

3.3. Third Law Calculations of Entropy

Entropy has also been estimated by the so-called "third-law technique," in which enthalpy and Gibbs energy measurements obtained at different temperatures are used to back out the entropy of a compound. These calculations often have very large errors, and entropy estimates are usually more reliable. Experimental determinations of the slope of a univariant reaction can also be used to obtain the ΔS_r with the use of the Clausius–Clapeyron equation for the slope of a univariant reaction:

$$dP/dT = \Delta S_r / \Delta V_r \qquad (5)$$

If the entropy of all phases but one is known the latter can be calculated with this relation. Successful application of this approach requires tightly reversed reactions, which are seldom available.

3.4. Estimates of Volume

The molar volumes of nearly all compounds are available at STP unless that phase is spontaneously unstable (β-quartz [SiO_2], ε-iron [Fe], $CaSiO_3$ perovskite). Measurement of the change in the volume of the unstable phase over a substantial pressure and/or temperature range may permit extrapolation to STP for a fictive volume that can then be used in calculations. The volume, compressibility and thermal expansion of compounds may also be estimated by isostructural methods similar to those summarized above (compare Sections 3.1–3.4). The volumes of compounds are influenced by their structure as well as chemical compositions, so an isostructural approximation is preferable to an oxide sum.

3.5. Problems in Estimations of Gibbs Energy and Enthalpy

There have been many attempts to estimate the enthalpy and Gibbs energy of compounds by summation techniques, especially in the case of complexly interlayered phases such as clay minerals. These approximations are far less reliable than entropy or volume estimates because of W.S. Fyfe's "plague of small Gs." This aphorism refers to the small ΔG generally encountered for solid–solid equilibria, yet that small difference in ΔG between reactants and products provides the driving force for reaction and controls equilibrium. The large errors in summation techniques, often on the order of tens of kJ mol^{-1} when tested against measurement, indicate that they should not be used for calculation of ordinary phase equilibria. The estimates of enthalpy and free energy should generally be avoided, and certainly they should be viewed as very approximate at best if they are employed.

4. Compilation of Thermodynamic Data

The available compilations of thermodynamic data have widely variable quality. They range from sets of data provided without attribution to referenced data, to elaborate discussions of the reasons for selection of certain data over others. Compilations that are designed to be consistent with the basic JANAF data set (see Chase *et al.*, 1985) are to be preferred over those that do not impose that constraint. In general, self-consistent data sets are more reliable because outlier data tend to be discarded at least in the case of over-determined systems.

However, self-consistent data sets also include data that were derived by long extrapolation and assuming often untested mixing models; which clearly have less reliability. Unless the compilation indicates consistency with another data set, data from different sources should not be mixed with impunity. A good test of a given data set is to compare the calculated locus of a univariant curve with experimental reversals obtained at high pressures and temperatures for some set of experiments that were not included to generate the thermodynamic data.

Experiments that were published after the compilation was made provide an independent data set that can be used to provide a test of the quality of the data. Although there can be no question that the quality of thermodynamic data has improved greatly over the last 40 years, some poor data remain that are mixed with high-quality results, and in many cases it is not easy to discern which are which. Any data obtained by long extrapolation, such as using a partition coefficient, K_D, and the free energy of three of the end-members to calculate that of a fourth, are suspect.

5. Self-Consistent Thermodynamic Data Sets

An alternative approach to the measurement of enthalpy and entropy has been to combine experiments on equilibrium relations at high P-T with available entropy and volume data to generate self-consistent sets of Gibbs energies and enthalpies for many geological compounds usually represented in two to five component systems. This is an inverse calculation to those described above, and one that finds a best fit to all the

available data. It usually yields more accurate estimates of the thermodynamic properties, especially of refractory silicates.

Moreover, the thermodynamic properties of the solids are made self-consistent with a large number of input data, including as many experimental reversals of equilibria as possible. Such self-consistent data sets are represented in recent tabulations accompanied with useful computer programs. These programs may be used to calculate a large number of new phase equilibria from the data sets for specified phases in an assemblage, usually involving corrections for observed solid solutions. There are some problems with using self-consistent data sets that are not widely recognized. One concern is with the quality of some of the data (compare Section 4).

5.1. Experimental Constraints on Equilibrium

Experimental studies of phase equilibria are critical to the quality of self-consistent data sets. However, some experiments are of limited use because they represent unreversed reactions, and those results are often accepted uncritically by others. The only experimental constraint on the locus of an univariant equilibrium is through the use of reversed experiments, in which the reactant assemblage is shown to form the product assemblage and vice versa, with a small displacement in pressure and/or temperature. Use of metastable starting phases such as glasses, oxide mixtures, gels, and ultra fine-grained starting materials has little value and should be avoided altogether. To avoid problems of nucleation, both reactants and products should be mixed together in the starting materials. The interpretation of having reached equilibrium when experiments at successively longer increments of time yield the same results is also misleading unless results approaching the same end point from the product side are also shown.

Experiments involving phases with solid solutions are best investigated using compositional reversals at constant pressure and temperature. These require direct chemical analysis of run products to show that the different initial sets of compositions converge on a single value. Equilibrium experiments on solvus gaps also require compositional reversals where the two-phase boundary is bracketed from compositions both outside and within the miscibility gap. The use of powder X-ray diffraction to identify the reaction direction and infer the composition of the run products is unacceptable when evaluating solvi and solid solutions because mixtures of unreacted reactant and neoformed product phases may be confused with an erroneous averaged composition and abundance. Run products should be examined with BSE images and the neoformed areas analyzed with the electron microprobe or perhaps in some cases with an analytical transmission electron microscope (TEM). If compositional reversal brackets are overstepped both runs must be discarded. In such cases another solid solution was not addressed, one or both the experiments was not at the correct P-T, or at least one phase changed its structural state or composition in some undetermined way during the run. Unaddressed problems of order–disorder, variable oxidation state, or variable occupancy of the hydroxyl (OH) site in the case of hyroxyl silicates may be involved. Calibration of such widely used barometers as those for phengite reactions, Al-in-hornblende, orthopyroxene-garnet, and Si^{VI}-in-garnet, and thermometers such as hornblende-plagioclase, garnet-biotite, and garnet-clinopyroxene is based on flawed experiments and yet continue to be applied to many geological problems incautiously.

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Biographical Sketch

Eric J. Essene was born in Berkeley, CA, USA, in 1939, the son of Professor Frank J. Essene and Rieva (Molly) Blazek Essene. He graduated from Lafayette High School in Lexington, KY, USA, where his father was Professor of Anthropology and his mother ran a well-known day-care center. He attended MIT, MA, USA, graduating with a BSc in Geology in 1961. He completed a Ph.D. in Geology from the University of California, Berkeley, in 1967. His dissertation was focused on high-pressure rocks and minerals from the Franciscan Formation of California, which was supervised by Professors Bill Fyfe and Frank Turner. He was an NSF Postdoctoral Fellow at Cambridge University, UK, with Dr Stuart Agrell and Professor Cecil Tilley, followed by three years at ANU, Australia, as a Research Fellow with Professors Dave Green and Ted Ringwood. He joined the faculty at University of Michigan, MI, USA, in 1970 and has remained there until the present. He received the first Sokol Award at the University of Michigan for excellence in graduate education. He is most proud of the 30 Ph.D. students with whom he has worked over the last 30 years at Michigan. He developed expertise with electron microprobe analysis at Berkeley in training with Professor Bernard Evans. He raised funds for electron microprobes first at ANU with Nick Ware, then at Michigan with Professor Wilbur Bigelow, and more recently with Carl Henderson. He and his students have undertaken research on thermodynamic and chemical properties of minerals, stable isotope studies of various metamorphic rocks, experimental studies of petrologic phase equilibria at high pressures and temperatures, argon isotope and U-Pb isotope studies of metamorphic minerals, and petrologic and chronological studies of granulites and eclogites, as well as mineralogical studies of various rock-forming minerals and thermodynamic considerations of clay minerals with his colleague Professor Donald Peacor.