Thermodynamics

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Basic Definition of Thermodynamics

The Oxford English Dictionary says: "Thermodynamics: the theory of the relations between heat and mechanical energy, and of the conversion of either into the other." In simpler terms, we can think of thermodynamics as the science that tells us which minerals or mineral assemblages will be stable under different conditions.

In practical terms, thermodynamics not only allows us to predict what minerals will form at different conditions (*forward modeling*), but also allows us to use mineral assemblages and mineral compositions to determine the conditions at which a rock formed (*thermobarometry*). The calculations are often complex and are best carried out using thermodynamic modeling programs or programs specifically designed for thermobarometry.

The Basis for Thermodynamic Calculations

All phases, whether mineralogical or not, have an associated Gibbs Free Energy of Formation value abbreviated ΔG_f. The ΔG_f value describes the amount of energy that is released or consumed when a phase is created from other phases.

We can calculate the Gibbs Free energy of any reaction (ΔG_{rxn}) by summing the energies of the right-hand side of the reaction and subtracting the energies of the left hand side. If the calculation reveals that $\Delta G_{rxn} < 0$, the reaction proceeds to the right. If the $\Delta G_{rxn} > 0$, the reaction proceeds to the left.

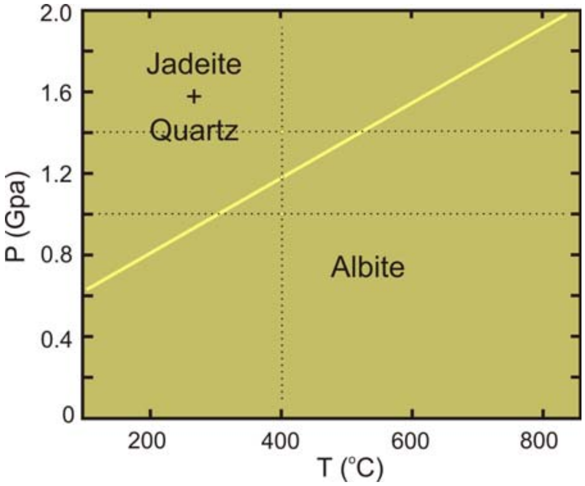

Figure 1. Phase diagram showing the reaction albite = jadeite + quartz. Along the reaction line, the *Gibbs Energy of Reaction*, $\Delta G_{rxn} = 0$. Above the line $\Delta G_{rxn} < 0$; below the line $\Delta G_{rxn} > 0$.

Consider the reaction albite = jadeite + quartz (Figure 1). Under normal earth surface conditions, the Gibbs Energy of this reaction is greater than zero. Consequently albite is stable and the assemblage jadeite + quartz is unstable.

The ΔG_f of a mineral varies with changes in pressure (P), temperature (T) and mineral composition (X). Consequently, the ΔG_{rxn} for any reaction will vary with P, T and X, being positive in some portions of P-T-X space and negative in others. The result is that we can plot reactions on phase diagrams, such as the one in Figure 1. Along any reaction line, such as the one separating the albite and jadeite + quartz fields shown in Figure 1 $\Delta G_{rxn} = 0$.

Doing thermodynamic calculations requires reliable thermodynamic data. Additionally, although the calculations can be done by hand or with a calculator, they are complicated and time consuming.

Gibbs Free Energies of a Mineral

Gibbs Free Energy values have been tabulated for many phases. Gibbs Energy values are, most often today, given in units of joules/mole or (less commonly) calories/mole.

Consider, for example, enstatite ($MgSiO_3$). The Gibbs Free Energy of Formation for enstatite from pure elements (Mg, Si and O) = ΔG_f (enstatite, elements) is about -1,460.9 KJ/mole at room temperature and pressure. The Gibbs Free Energy of Formation for enstatite from oxides (MgO and SiO_2) = ΔG_f(enstatite, oxides) is about -35.4 KJ/mole at room temperature and pressure.

The ΔG_f values given above for enstatite are both negative. This means that enstatite is more stable than, and will form from, the separate elements or separate oxides at room temperature and pressure (although reaction rate is extremely slow). Some of the energy produced will be given off as heat; some will contribute to entropy.

Gibbs Free Energies are Relative Values

Gibbs free energies are relative values, not absolute values. They allow us to compare energies of different phases but individual values by themselves have no significance. Because Gibbs Energy values are relative, we can arbitrarily assume some values in order to calculate others. So, by convention the ΔG_f for any pure element is assumed to be as zero.

The Gibbs Free Energy of Reaction

We can calculate the Gibbs Free energy of any reaction by summing the energies of the right-hand side of the reaction and subtracting the energies of the left hand side. For example, we can write a reaction describing the formation of enstatite from separate elements:

$Mg + Si + 3O = MgSiO_3$ (rxn 1)

The ΔG for reaction (1) is the Gibbs Free Energy of formation of enstatite from the elements (-1,460.9 J/mole at room temperature and pressure):

$\Delta G_1 = \Delta G_f(\text{enstatite, elements}) = \Delta G_f(\text{enstatite}) - \Delta G_f(\text{Mg}) - \Delta G_f(\text{Si}) - 3\,\Delta G_f(\text{O})$ (Eqn 1)

All minerals (and reactions) have an associated ΔG_f (and ΔG_{rxn}) value, but the values vary with pressure and temperature (T). If we wish to make thermodynamic calculations involving ΔG_f for some particular phases, we must either look the values up in a book for the P-T conditions of interest, or calculate the values using standard equations.

Determining the Location of Metamorphic Reactions

Consider the reaction shown on a PT diagram in Figure 2:

albite = jadeite + quartz (rxn 2)

For this reaction:

$\Delta G_{rxn} = \Delta G_2$
$= \Delta G_f$ (jadeite, elements) + ΔG_f (quartz, elements) - ΔG_f (albite, elements) (Eqn 2)

or

$\Delta G_2 = \Delta G_f$ (jadeite, oxides) + ΔG_f (quartz, oxides) - ΔG_f (albite, oxides) (Eqn 3)

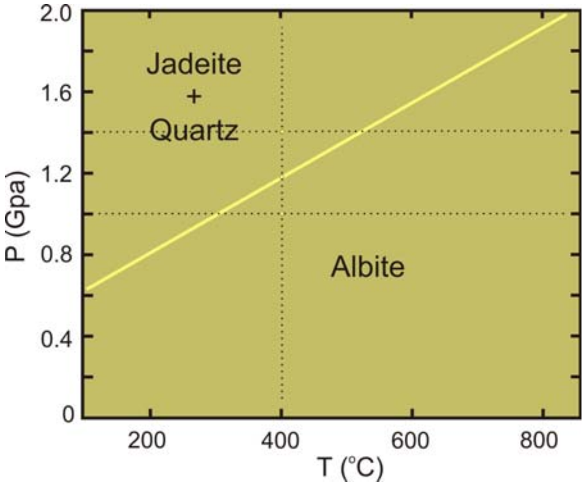

Figure 2. Phase diagram showing the reaction albite = jadeite + quartz. Along the reaction line, the *Gibbs Energy of Reaction*, $\Delta G_{rxn} = 0$. Above the line $\Delta G_{rxn} < 0$; below the line $\Delta G_{rxn} > 0$.

These two values will always come out to be the same, but most reference books list values relative to the elements. If we look up ΔG_f values in a reference book, we will find that:

At 400° and 1.0 GPa: $\Delta G_2 > 0$
At 400° and 1.4 GPa: $\Delta G_2 < 0$

So, at 400° and 1.0 GPa, albite is stable form, but at 1.4GPa albite will react to form jadeite + quartz. At about 400° and 1.18 GPa, on the reaction line, $\Delta G_2 = 0$.

For any reaction under a given set of P-T conditions: If the $\Delta G_{rxn} < 0$, the reaction proceeds to the right. If the $\Delta G_{rxn} > 0$, the reaction proceeds to the left.

Internal Energy (E), Enthalpy (H), Entropy (S), Volume (V) of

Phases and Reactions

The Gibbs Free Energy of any phase varies with pressure and temperature. The fundamental relationship is:

$G = E + PV - TS$ (Eqn 2)

or

$G = H - TS$ (Eqn 3)

In the above expressions, P and T refer to pressure and temperature. E, V, H and S refer to the internal energy, volume, enthalpy and entropy of the phase. It follows that:

$H = E + PV$ (eqn 4)

Similarly, for any reaction, the Gibbs Free Energy of reaction varies with pressure and temperature:

$\Delta G_{rxn} = \Delta E_{rxn} + P\Delta V_{rxn} - T\Delta S_{rxn}$ (Eqn 5)

or

$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn}$ (Eqn 6)

As above, P and T refer to pressure and temperature ΔG_{rxn} is the Gibbs energy of reaction, ΔE_{rxn} is the internal energy of reaction, ΔV_{rxn} is the volume of reaction, ΔH_{rxn} is the enthalpy of reaction and ΔS_{rxn} is the entropy or reaction.

Look closely at Equation (5). The right hand side contains three terms. The first is the change in internal energy -- a constant depending on the phases involved. The second is a PV term -- it equates Gibbs Energy with volume and pressure. More voluminous phases have greater Gibbs Free Energy. (Recall that the energy of an ideal gas = PV = nRT.) The third term involves entropy (S). Entropy is a measure of disorder. Some phases can absorb energy simply by becoming disordered. Temperature may not increase, volume may remain the same, but energy disappears.

Chemical systems seek to minimize energy and, consequently, phases of greater Gibbs Free Energy are unstable with regard to phases with lower Gibbs Free Energy. So, at high temperature, phases with high entropy are very stable. This is because the TS term in Equation (5) has a negative sign. Similarly, at high pressure, phases with high volume are unstable. The PV term has a positive sign. (Although your intuition may not work well when considering entropy, it should seem reasonable that low volume, very dense, phases are more stable at high pressure than phases of less density.)

Intensive and Extensive Variables, and Units

P and T are termed intensive variables. G, E, H, V and S are extensive variables. The difference is that intensive variables (P and T) do NOT depend on the size of the system or the amount of material present. G, E, H, V and S do depend on system size (e.g., the larger the system, the larger the volume).

Pressure is typically given in units of pascals (Pa), Gigapascals (GPa), bars (bar) or Kilobars (Kbar). G, E, and H are typically given in units of J/mole. V is in cm^3/mole, and entropy in J/deg-mole. (Calories may be substituted for Joules, 1 cal = 4.186 J). Note: The PV term in the above expressions is not in the same units as the other terms. A necessary conversion factor is 1 J = 10 cc-bar.

What is the significance of the different thermodynamic variables?

* The Gibbs Free Energy (ΔG_{rxn}) tells us whether a reaction will take place. ΔG_{rxn} is the Gibbs Free Energy of the right hand side of a reaction, minus the Gibbs Free Energy of the left hand side. If $\Delta G_{rxn} < 0$, the reaction will proceed to the right; if it is > 0, the reaction will proceed to the left.

* The Enthalpy of Reaction (ΔH_{rxn}) tells us how much heat will flow in or out of the system. If $\Delta H_{rxn} < 0$, the reaction is exothermic -- it releases heat. For example, combustion of carbon based compounds ($C + O_2 = CO_2$) gives off a lot of heat. If $\Delta H_{rxn} > 0$, the reaction is endothermic -- it consumes heat. Melting ice [H_2O(ice) = H_2O (water)] is endothermic and, consequently, cools our gin and tonics in the summer.

* The entropy of a reaction (ΔS_{rxn}) tells us whether the products or reactants are more disordered. For example the reaction of liquid water to steam (boiling) has a large associated entropy. The steam molecules are more dispersed, are less well bonded together, and have greater kinetic energy.

* The volume of a reactions (ΔV_{rxn}) tells us whether the products or the reactants have greater volume. The reaction of graphite to diamond, both made entirely of carbon, proceeds at high pressure because diamond is more dense (has smaller volume) than graphite.

Internally Consistent Thermodynamic Data Bases

Thermodynamic data are obtained by calorimetry (enthalpy and entropy values), X-ray diffraction (volumes) or derived on the basis of experimental studies, each with associated uncertainties. Combining thermodynamic values from different sources (especially Gibbs Free energy values) can lead to erroneous or misleading results because :

- some calorimetry or experiments may be unreliable
- systematic errors may skew some results one way and others a different way
- different studies have different amounts of uncertainty

There is need then, data sets that do not include erroneous data, that reconcile calorimetric and phase equilibrium data, and that are internally consistent. Different workers have approached this problem in different ways, leading to the well-known datasets of Holland and Powell or of Berman (see many references, below).

Computer Programs for Thermodynamic Calculations and Modeling

The important thermodynamic variables (G, E, H, V and S) vary with pressure (P), temperature (T) and composition (X). The relationships are not simple, and evaluating the various functions requires integral calculus. Although, in principle, it is possible to do thermodynamic calculations by hand, today most practitioners rely on computer programs.

Fortunately, a number of different authors have created programs designed for calculating thermodynamic equilibria and making phase diagrams. Some of the most popular and complete programs are:

TWQ is an easy to use Windows based program, created by Rob Berman, that allows you to calculate the position of phase equilibria in P-T, T-XCO_2, and P-XCO_2 space. You can also use it to calculate various activity diagrams. Find out more about TWQ, and how to get a copy, at:

http://serc.carleton.edu/dev/research_education/equilibria/TWQ.html .

Thermocalc performs the same calculations as TWQ for a much larger number of phases and includes more complicated types of calculations. The program was created by Roger Powell and Tim Holland. Find out more about Thermocalc, and how to get a copy, at:

http://serc.carleton.edu/dev/research_education/equilibria/THERMOCALC.html .

Melts is the only widely available program that allows thermodynamic calculations to be made for equilibria involving magmas. The program was first created by Mark Ghiorso and Richard Sack and subsequently modified by others. Find out more about Melts and how to download a copy, at:

http://serc.carleton.edu/dev/research_education/equilibria/MELTS.html .

Perplex is a thermodynamic calculation package suitable for rapidly creating phase diagrams of all types, creating pseudosections (phase diagrams that include only those reactions experienced by a particular bulk composition). Find out more about Perplex, and how to get a copy, at:

http://serc.carleton.edu/dev/research_education/equilibria/Perplex.html

Phase Diagrams: The Results of Thermodynamic Calculations

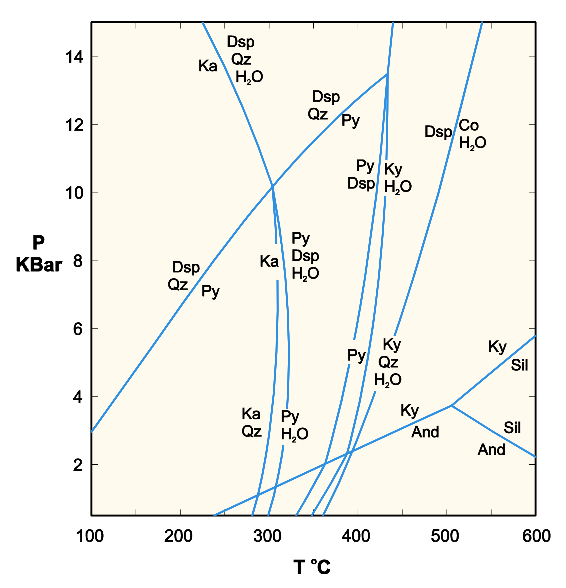

Figure 3. Phase diagram showing reactions in the system Al_2O_3-SiO_2-H_2O

Phase diagrams are graphical representations of the equilibrium relationships between minerals (or others phases). These relationships are governed by the laws of thermodynamics. Standard phase diagrams show how phases or phase assemblages change as a function of temperature, pressure, phase composition, or combinations of these variables.

Some phase diagrams (those for 1-component diagrams) depict relationships involving multiple phases having the same composition (for example, the relationships between the vapor, liquid and solid forms of H_2O). Other diagrams (such as the one shown on the right), depict the relationships between a number of compounds having different compositions. Still others show how compositions of phases change under different conditions.

Thermobarometry

Thermobarometry refers to the quantitative determination of the temperature and pressure at which a metamorphic or igneous rock reached chemical equilibrium. Many programs exist to facilitate such calculations, but most are only applicable to specific kinds of rocks and mineral assemblages.

The Math behind the Calculations

The basis for calculating a reaction curve (a curve/line on a phase diagram) is the understanding that the Gibbs Free Energy of a reaction (?Grxn) can be calculated for any P-T-X conditions, provided a starting point and the requisite thermodynamic data are available. The fundamental relationship is:

$$0 = \Delta G^{o}_{P2,T2} = \Delta G^{o}_{P1,T1} + \int_{P1}^{P2} \Delta V^{o}_{P,T}\, dP - \int_{T1}^{T2} \Delta S^{o}_{P,T}\, dT$$

ΔG, ΔV, and ΔS refer to the Gibbs Energy, volume and entropy of reaction. The degree superscript reminds us that these values are for pure phases. The P and T subscripts remind us that the values change with pressure and temperature.

The starting Gibbs Free Energy value, $\Delta G_{P1,T1}$, may be directly obtained from calorimetric studies. Alternatively, and more commonly, experimental studies may provide a reference point at which a particular reaction is in equilibrium ($\Delta G_{P,T} = 0$). In either case, the equation above is solved to find the location of the reaction curve, points at which ΔG= 0. The result is a curve (often nearly a straight line) in P-T-X space that separates fields of stability for different minerals or mineral assemblages.

For reactions involving pure, end member minerals, the above equation suffices. However, many minerals are solid solutions, so the effective activity (reactivity) of mineral components is diluted. The basic thermodynamic equation is modified to take this into account by adding a term involving the equilibrium constant (K):

$$0 = \Delta G^{o}_{P2,T2} + RT\ln K$$

The equilibrium constant for a reaction (K) is the product of the activities of the reaction products, divided by the product of the activities of the reactants:

$$K = \frac{a_{p1}\, a_{p2}\, a_{p3} \ldots}{a_{r1}\, a_{r2}\, a_{r3} \ldots}$$

Putting It All Together: An Example

For an example, let's combine the above equations, and consider the reaction:

3 anorthite = grossular + 2 kyanite + quartz

For this reaction, the conditions for thermodynamic equilibrium are:

$$0 = \Delta G^{o}_{P2,T2} = \Delta G^{o}_{P1,T1} + \int_{P_1}^{P_2} \Delta V^{o}_{P,T}\,dP - \int_{T_1}^{T_2} \Delta S^{o}_{P,T}\,dT + R\,T \ln \frac{a_{Gr}\, a^{2}_{Ky}\, a_{Q}}{a^{3}_{An}}$$

The exponents on the activity terms for kyanite and anorthite are because the reaction involves 3 moles of anorthite and 2 moles of kyanite.

If a mineral assemblage contains kyanite and quartz, they are generally nearly pure, so their activities = 1. The above equation then becomes:

$$0 = \Delta G^{o}_{P2,T2} = \Delta G^{o}_{P1,T1} + \int_{P_1}^{P_2} \Delta V^{o}_{P,T}\,dP - \int_{T_1}^{T_2} \Delta S^{o}_{P,T}\,dT + R\,T \ln \frac{a_{Gr}}{a^{3}_{An}}$$

This equation is the basis for the GASP geobarometer used by some petrologists to calculate metamorphic pressures (Figure 4).

Calculating Activities

Some minerals, like quartz, are so pure that, when present, their activities are 1. Other minerals are more variable in composition. Consequently, the activity of a given component may vary, depending on composition. So, we use activity models to calculate the activities of the components we care about, so that we may put the values into the equations above. Activity models vary from being quite simple to very complex and may require computer programs to be useful.

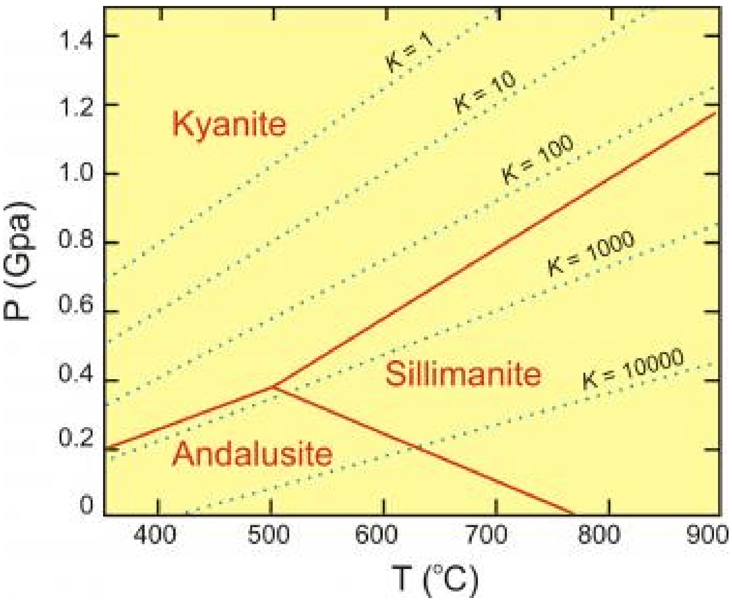

Figure 4. Phase diagram showing values of the equilibrium constant, K for the GASP reaction 3An = Gr + Ky + 2Q. Given the compositions of coexisting minerals, K, can be calculated and, if metamorphic temperature is know, the metamorphic pressure may be read from this diagram. Also shown are the stability fields for andalusite, kyanite, and sillimanite. Depending on pressure and temperature, the GASP barometer may involve andalusite or sillimanite instead of kyanite.

The Slope of a Reaction Curve

Sometimes, petrologists have a starting point, perhaps from experimental studies, and only need to know the slope of a reaction in order to plot it on a phase diagram. Differentiation of the equations above reveals that the slope may be calculated:

$dP/dT = \Delta S_{P,T}/\Delta V_{P,T}$

This relationship is called the Clausius-Clapeyron equation.

Books on Fundamental Thermodynamics

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