An Introduction to Thermodynamics

Questions to be Considered in this Chapter:

1. How can we determine the stability range of a mineral or of the mineral assemblages that constitute rocks so that we can judge whether a given rock (or some chemically equivalent alternative) is stable under a particular set of physical conditions?

2. How can we evaluate or predict the effects on a stable geologic system of changing some parameter, such as pressure or temperature, or of adding some chemical constituent?

3. How can we qualitatively evaluate phase diagrams and use them to understand the nature of the systems involved?

Petrologists use a knowledge of thermodynamics in two principal ways. First, thermodynamic principles can be applied *qualitatively*, to assess a geologic system or predict the effects that a change in pressure (P), temperature (T), or composition (X) may have on a stable rock/fluid/melt assemblage. Qualitatively, we might answer important questions such as, "What would be the general effect of increased pressure on half-molten rock?" or "What would happen if H_2O were added to a rock near its melting temperature?" Second, if some fundamental basic data can be experimentally determined, we can calculate *quantitatively* whether a certain assemblage of minerals (i.e., a rock), with or without a fluid phase or melt, is stable at some particular combination of P, T, and X. Both of these approaches are based on an understanding of equilibrium and energy.

Through years of experiments, we have compiled sufficient data for minerals and gases that we can quantitatively calculate the stability ranges of many mineral and mineral–fluid assemblages. Because the compositions of melts are so complex and variable compared to those of minerals and gases, we are only in the early stages of being able to quantitatively treat igneous systems. I will thus postpone developing the quantitative approach until we deal with metamorphism and have occasion to apply the results. For the present, I will develop the general thermodynamic basics and then concentrate on the qualitative approach, which will help us assess a variety of igneous phenomena.

1 ENERGY

A **system** is some portion of the universe that one might isolate (either physically or mentally) in order to study it. The **surroundings** are the adjacent portions of the universe outside the system in question. All natural systems are governed by energy. Any macroscopic change in a system is accompanied by the conversion of energy from one form to another. For instance, the dropping of an object, such as a rock, involves the conversion of **potential energy** (associated with its height) to **kinetic energy** (motion). Lifting the rock involves the transfer of **chemical energy** (stored in your body) to kinetic energy (the motion of your muscles, and eventually the rock). Likewise, the mixing of a strong acid and base is the conversion of stored chemical energy to **thermal energy** as they react to and neutralize each other, heating up the beaker

in the process. The compression of air in a bicycle pump as you inflate a tire involves the conversion of **mechanical energy** to thermal energy.

If we consider the system plus the immediate surroundings, energy is conserved in all processes. If, on the other hand, we consider only the system, such as a rock, energy can be lost to, or gained from, the surroundings. Lifting the rock, for example, adds energy from the surroundings, thereby increasing the potential energy of the rock system. Of course, if we remove support from the rock, it will fall to Earth, spontaneously losing potential energy as it is converted to kinetic energy, which in turn is converted to heat (friction) and mechanical energy as it hits the Earth and deforms it a bit. The original potential energy is a useful commodity. It is capable of doing work, if we attach it to a pulley and let a string turn a generator. One could describe a mass such as a rock at a high elevation as having a higher energy content than a similar mass at a lower elevation. It should be obvious that an unsupported mass will spontaneously fall to the lowest point that it can. An unsupported rock falls until it hits the Earth, not stopping halfway down. This leads us to an important and fundamental property of natural systems: *Systems naturally tend toward configurations of minimum energy*. Such minimum energy configurations, such as the rock on the ground, are referred to as **stable**. A rock hurled aloft is in an **unstable** configuration (or *state*) because it will quickly fall to Earth under the influence of gravity.

Fortunately, not all natural systems change spontaneously to the minimum energy state. Some systems may exist in a state that is low in energy but not the lowest possible. There may be some energy barrier that must be overcome before the true minimum energy state can be attained. Returning to our falling rock analogy, suppose that the rock hits a sloping area of the ground and stops in a depression (Figure 1). Clearly, this is not the most stable configuration possible, as there are lower elevations nearby to which it would roll if it could. However, this elevation is lower than all immediately adjacent possibilities. It would have to roll upward briefly, thereby *increasing* its potential energy momentarily, before it could roll to the lowest elevation available. There thus exists an energy barrier that prevents the rock from easily reaching the lowest energy state. Such states, neither stable (lowest energy possible) nor unstable (capable of spontaneous change), are called **metastable** (Figure 1). We can also think of systems as being either at **equilibrium** or in a state of **disequilibrium**. Any system that is not undergoing some form of transition is said to be at equilibrium. It can be either stable equilibrium (such as the rock at the bottom of the slope) or metastable equilibrium (such as the perched rock).

The energy barriers that maintain metastable states may be potential energy, as in the rock in Figure 1, or kinetic in nature. Kinetic barriers keep many familiar materials from reverting to the most stable state. When your car is scratched, the iron doesn't immediately become oxidized to rust. Diamonds do not invert to graphite, and rocks at the Earth's surface do not instantly weather to clays. This is because the energy barriers involved in breaking bonds for the
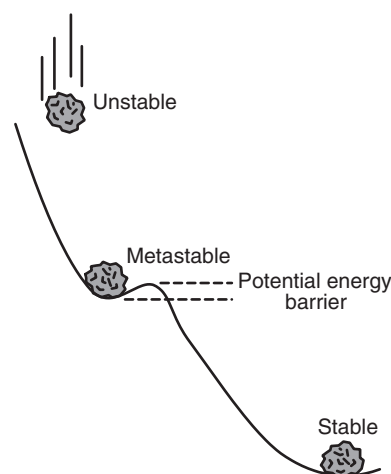

FIGURE 1   Stability states.

reactions to take place are too high for the low kinetic (vibrational) energies of the bonds at the low temperatures near the Earth's surface. It is indeed fortunate that metastable states exist, or most of the materials and energy sources that we use today would not be available.

2 GIBBS FREE ENERGY

Addressing systems in terms of energy is a useful approach. The crucial point is to find the proper energy expressions and the variables that control them (**variables of state**). **Mechanics** is the study of motion, such as projectiles or our falling rock. By dealing with potential, kinetic, and gravitational energy, as well as with mass, velocity, and momentum, mechanics has permitted us to understand the motion of projectiles and planets sufficiently well to place a person on the moon and predict the collision of a comet with Jupiter. The field of **thermodynamics**, as the name implies, deals with the energy of heat and work. Thermodynamics can help us understand a number of things, from steam engines to refrigeration. The work of J. Willard Gibbs elegantly related thermodynamic concepts to the understanding of chemical systems. Gibbs formulated an energy parameter, **Gibbs free energy**, that acts as a measure of the energy content of chemical systems. The Gibbs free energy at a specified pressure and temperature can be defined mathematically as:

$$G = H - TS \qquad (1)$$

where: G = Gibbs free energy

H = **enthalpy** (or heat content)

T = temperature in kelvins

S = **entropy** (most easily perceived as randomness)

As a simple example of enthalpy, consider heating water on a stove. The enthalpy of the water increases as it is warmed because you are adding heat to it. When it boils, the steam has a higher enthalpy than the water, even when both are at

the same temperature (the boiling point), because you had to add heat to the water to convert it to steam. As for entropy, imagine the ordered structure of a crystal lattice. This is low entropy. Liquids have much less ordered arrangement of atoms and, hence, greater entropy. Gases have even more entropy than liquids because the atoms or molecules are much more widely distributed.

Using the Gibbs free energy parameter, we can assess the stability of chemical systems, just as we used potential energy for the rock in Figure 1. In a manner analogous to the rock situation, under a particular set of conditions, a chemical system should proceed to a state that minimizes the appropriate energy parameter. In other words:

> *Stable forms of a chemical system are those with the minimum possible Gibbs free energy for the given conditions.*

The Gibbs energy parameter is ideal for petrologists and geochemists because it varies as a function of pressure, temperature, and composition, the most important determining variables (variables of state) in nature. We will use Gibbs free energy to analyze the behavior of a variety of igneous and metamorphic systems. We begin with some relatively basic concepts, applying them to very simple chemical systems. We can then add new thermodynamic principles and techniques later as we require them to treat more complex systems.
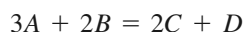
A variety of petrologic processes, from polymorphic transformations, to metamorphism, to crystallization and melting, can be expressed as chemical *reactions* of the type $A + B + \ldots = Q + R + \ldots$, where each letter represents a chemical species, such as a mineral, liquid, gas, or ionic species in solution. The species on the left side of the reaction are called the **reactants**, and those on the right are called the **products**. Of course, the reaction must balance stoichiometrically, in that the number of atoms of each element must be the same on both sides of the reaction. Because the stable form of a system at any value of pressure (P), temperature (T), and composition (X) is the form with the lowest Gibbs free energy, our object is to determine the Gibbs free energy for the alternative forms (reactants vs. products) of the system at the P, T, and X of interest. For a reaction, this comparison can be accomplished for *any* variable (in this case G) by defining:

$$\Delta G = \Sigma(n_{products}G_{products} - n_{reactants}G_{reactants}) \qquad (2)$$

where: Σ = sum

n = stoichiometric coefficient for each phase in the reaction

For example, consider the hypothetical reaction:

$$3A + 2B = 2C + D$$

ΔG can be expressed as:

$$\Delta G = G_D + 2G_C - 3G_A - 2G_B$$

If ΔG is negative, then the products have a lower total free energy than the reactants (meaning that they are more stable), and the reaction should run from left to right, as written. Thus, if we knew G for each **phase** (mineral, gas, liquid) and ionic species (if included) in a reaction at some pressure and temperature, we could compare the values, summed for the reactants and for the products, to evaluate which side of the reaction is stable at the conditions of interest. Similarly, we could use the Gibbs free energies of the constituents to determine the *P-T-X* conditions under which the reactants and products are equally stable: the **equilibrium** condition for the reaction. In order to do all of this, we must first be able to determine a value for the Gibbs free energy of any phase (or ionic species) at any temperature, pressure, and composition of interest. It is then simply a matter of combining them using Equation (2) to do the rest.

3 THE GIBBS FREE ENERGY FOR A PHASE

Let's deal for now with a simple system composed of a substance of *fixed composition* (putting off the rather complex relationships between free energy and composition until later). For a *single phase*, such as a mineral or a liquid, we would like to be able to determine the Gibbs free energy at any specific pressure and temperature. Although we can measure volume, temperature, pressure, and various other properties for a phase, it is impossible to measure an absolute value of chemical free energy of any phase, compound, ion, etc. We can, however, determine *changes* in the free energy of phases as the variables of state change. If we can measure the changes, we need only choose some arbitrary state (a "reference state") of a phase and assign any value of G that we choose. We can then use the changes in G as conditions vary to assign values of G for any other state.

The most common reference state is to consider pure elements in their natural (stable) form at 25°C (298.15 K) and atmospheric pressure (0.1 MPa), the conditions in a typically overheated laboratory, and assign a Gibbs free energy of zero joules (0 J) to that state. The reference Gibbs free energy for oxygen, for example, is 0 J for pure O_2 gas, and for silicon it is 0 J for pure Si metal, both at 298.15 K and 0.1 MPa. Note that G is an **extensive variable of state**, in that it is dependent upon the quantity of material in the system (the *extent* of the system). We can avoid this problem by expressing G in terms of **molar** free energy, or the number of joules per mole of the substance. The molar Gibbs free energy of Si, then, is an intrinsic constant property of the element. For a compound such as quartz, we can measure the heat (enthalpy) *change* (ΔH) associated with the reaction of 1 mole Si + 1 mole O_2 to 1 mole SiO_2 (by a technique called **calorimetry**). We can also calculate the entropy of quartz based on the assumption that the entropy of any substance is zero at 0 K (based on the third law of thermodynamics), and calculate the change in entropy between 0 K and 298.15 K (as discussed in the following section). From these values of H and S, we can compute the Gibbs free energy for low quartz using Equation (1). The result is known as the **molar Gibbs free energy of formation** (from the elements)

and given the symbol $\Delta\overline{G}_f^{\circ}$, where the subscript stands for *formation* (from the elements), the superscript refers to the **reference state** of 298.15 K and 0.1 MPa, and the bar above the G indicates that it is a molar quantity.

For quartz, $\Delta\overline{G}_f^{\circ}$ is −856.3 kJ/mol (Robie and Hemingway, 1995). This represents ΔG for the reaction Si (metal) + O_2 (gas) = SiO_2 (quartz). Note that the large negative free energy value tells us that the product (quartz) is much more stable than the reactants (Si and O_2), which is why we find quartz, and not silicon metal, in our oxygen-rich environment. The free energies for other compounds, including minerals, gases, ions, etc., are determined in a similar fashion. $\Delta\overline{G}_f^{\circ}$ is the value used for the Gibbs free energy (G) of various phases at 298.15 K and 0.1 MPa, and it is the basis for most thermodynamic calculations. Thermodynamic data are tabulated and available from a number of sources, including published compilations, such as Robie and Hemingway (1995), or computer databases (commonly as part of a program that performs the calculations as well). Minor variations in the values reported reflect experimental inaccuracies in the calorimetry or even the technique used. Lately we have devised ways to extract thermodynamic data from high-temperature and high-pressure experiments at equilibrium.

3.1 Variations in the Gibbs Free Energy for a Phase with Pressure and Temperature

Once we have the reference state data for geological phases of interest, we can determine the value of the Gibbs free energy (G) of a phase at elevated temperatures and pressures. We can do this by using the following differential equation:

$$dG = VdP - SdT \qquad (3)$$

where: G = Gibbs free energy of the phase
V = volume
S = entropy

The equation also holds true for molar properties ($\overline{G}$, $\overline{V}$, and $\overline{S}$). I will henceforth treat all these parameters as molar and dispense with the bar symbols. Equation (3) thus formalizes the variation in G with P and T. G also changes with composition, and parameters for this variation can be added to Equation (3), but I have decided to hold composition constant for the time being to ease our initiation process. As changes in temperature (dT) and/or pressure (dP) occur, G will also change (dG) in a determinable way. Thus G for a phase, such as forsterite, will be different at different temperatures and pressures. We solve for G at different pressures and temperatures by integrating Equation (4):

$$G_{P_2,T_2} - G_{P_1,T_1} = \int_{P_1}^{P_2} VdP - \int_{T_1}^{T_2} SdT \qquad (4)$$

where: P_2 = pressure of interest

T_2 = temperature of interest

P_1 = initial pressure (e.g., 0.1 MPa)

T_1 = initial temperature (e.g., 298 K)

To perform the integration accurately, we need to know how V varies with P and how S varies with T. The variation in V with respect to P (called the **isothermal compressibility**) is sufficiently small for solids that V can be treated as a constant for a fairly large range of pressures, but the volume of liquids and particularly gases will certainly change with pressure, so, for them, calculations that assume a constant V will be in error. S varies appreciably with T for most phases, whether solid, liquid, or gas. The relationship can be expressed as $dS = (C_p/T)dT$, where C_p is the **heat capacity** (the amount of heat required to raise 1 mole of the substance 1°C). Substances with a high heat capacity can absorb considerable heat with only a small temperature change. Consider the amount of heat you must add to a pot of water (high heat capacity) to raise the temperature 50° versus the much smaller quantity of heat required to do so for the same volume of air (low heat capacity). The process is complicated in that the heat capacity is itself a function of T and varies in a nonlinear fashion. Polynomial equations, usually of the form $C_p = a + bT - c/T^2$, are empirically determined for each phase and are reported in most sources (including Robie and Hemingway, 1995), allowing us to calculate S accurately at any temperature.

If the variation in pressure and temperature (dP and dT) are small, we can assume that V and S are constant as a first approximation, and Equation (4) reduces to a simple algebraic form. We will make this assumption (for solids at least) in the problems and exercises in this text and avoid calculating the integrals that include compressibility and polynomial heat capacity functions. Fortunately, some computer programs do the integration for us, so we can still derive more accurate results if we need to. Some programs have V, S, H, and C_p data for many common minerals, liquids, and gases so that the calculations, including corrections for compressibilities and changes in S and H with T are performed instantly. We can understand enough of the theory and application by using the algebraic form and let the computer perform the more complex mathematics. In the following sample problem, we will get some experience with handling the algebraic form of Equation (3) and compare our results for quartz to the integrated form in order to get some idea of the magnitude of the errors that our simplification introduces.

SAMPLE PROBLEM: Calculating the Gibbs Free Energy of Quartz at Elevated *P* and *T*

As an example, we shall use Equation (3) to calculate G for quartz at 500°C and 500 MPa. Because Equation (3) deals with *changes* in G with P and T, we must first know the value of G_{quartz} at some initial temperature and pressure. We will use the common reference state of 298.15 K and 1 atmosphere pressure, at which G_{quartz} is −856.3 kJ (± ~1 kJ: the analytical error) per mol (from Robie and Hemingway, 1995). T in Celsius (C) equals T in kelvins (K) minus 273.15, but we commonly round to the nearest degree, which is precise enough for geological work. Thus 298 K is

25°C, or "room temperature." To calculate G_{quartz} at higher pressures, say 0.5 GPa, we also need to know the molar volume of quartz, which is 22.69 cm^3/mol. Because G is expressed in joules (m^{2}kg/sec^{2}mol) and P in pascals (kg/sec^{2}m), V must be expressed in m^3/mol if the units are to remain consistent. However, cm$^3 = 10^{-6}$ m^3 and MPa $= 10^6$ Pa, so we can avoid the very small and very large numbers by using joules for G, cm^3/mol for V, and MPa for P, and the exponents will cancel when we multiply $V \cdot P$. The choice is up to you, but always remember to be careful with the units in your calculations.

We begin with the pressure correction, calculating G_{quartz} at 0.5 GPa and 298.15 K. Because T is constant, $dT = 0$, and Equation (3) reduces to $dG = VdP$. We can integrate this to get:

$$G_{P_2} - G_{P_1} = \int_{P_1}^{P_2} V dp \qquad \text{(constant } T \text{)} \qquad (5)$$

If V is constant as pressure changes, V can be removed from the integral, and Equation (5) becomes algebraic:

$$G_{P_2} - G_{P_1} = V \int_{P_1}^{P_2} dP = V(P_2 - P_1) \qquad (6)$$

where $P_2 = 500$ MPa and $P_1 = 0.1$ MPa at constant T:

$G_{0.1}$ is $-856,300$ J, so $G_{500,298} = G_{0.1,298} + V(500 - 0.1)$
$= -856,300 + 22.69(499.9) = -844,957$ J
$(\text{or} -845.0 \text{ kJ})$.

If we wanted to correct for temperature first, we could use a similar process to calculate G at 500°C (773 K) and 0.1 MPa. Because P is constant, Equation (3) becomes:

$$G_{T_2} - G_{T_1} = \int_{T_1}^{T_2} - S dT \qquad \text{(constant } P \text{)} \qquad (7)$$

and, if we assume that S is also constant over this temperature range, this reduces to:

$$G_{T_2} - G_{T_1} = -S(T_2 - T_1) \qquad (8)$$

$S_{0.1,298} = 41.46$ J/K mol (Robie and Hemingway, 1995), yielding $G_{0.1,773} = G_{0.1,298} -41.46(773 - 298) = -876.0$ kJ.

Finally we can perform both operations in sequence (either one first) to get G at any temperature and pressure. If we use Equation (6) to get $G_{500,298}$ and then use Equation (8) at a constant pressure of 500 MPa, we get $G_{500,773} = -844,957 - 41.46(773 - 298) = -864.6$ kJ.

Now we can compare our results with the computer method that integrates the equations to see how our assumptions of constant V and S worked. Table 1 lists the results for low quartz generated by the computer program SUPCRT (Helgeson et al., 1978).

The first thing to notice is that SUPCRT uses its own database, so even the reference state value of G_{quartz} differs

TABLE 1 Thermodynamic Data for Low-Quartz. Calculated Using Equation (1) and SUPCRT

Low Quartz		Eq (6) (8)	SUPCRT		
P(MPa)	T(C)	G(J)	G(J)	V(cm³)	S(J/K)
0.1	25	−856,288	−856,648	22.69	41.36
500	25	−844,946	−845,362	22.44	40.73
0.1	500	−875,982	−890,601	23.26	96.99
500	500	−864,640	−879,014	23.07	96.36

from the Robie and Hemingway (1995) value (although by less than 400 J, which is less than 0.04% of G, or half the reported analytical error). Next, we can see that our constant V assumption is not perfect (column 5), but apparently it is good enough because our calculated G at 500 MPa and 25°C agrees with the integrated SUPCRT value (again within about 400 J). In fact, if we had used the same standard-state value for G in Equation (3) that SUPCRT used, the agreement would have been excellent, differing by about 50 J. So, for solid phases at least, the assumption that volume remains constant is fine for pressure changes less than 1 GPa (the thickness of the crust). This will be true for most solids, as long as no pressure-induced phase transitions take place. Low quartz inverts to coesite at about 2 GPa, with a significant volume change.

Our assumption that S remains constant as temperature changes is not as good. The difference between the free energy extrapolated linearly (our hand calculation at constant S) and as a curve (integrated by SUPCRT) over 475°C temperature change is 14,619 J. In column 6 of Table 1, we see that the entropy has more than doubled over this range. Nonetheless, the relative error in G is only about 2%. If we calculate G at 800°C, the difference increases to 35,247 J, or 4%.

In summary, we can use Equation (3) to calculate the change in Gibbs free energy for a mineral, liquid, or gas phase with changes in temperature and pressure. If we can determine G for a phase at some initial P–T state (tabulated in several sources), we can then determine G at other pressures and/or temperatures. Pressure calculations are relatively easy for solid phases because we can assume that V is a constant and use a simple algebraic form [Equation (6)] without sacrificing much accuracy. Temperature corrections using the algebraic form [Equation (8)] are less precise, and the integration may be necessary if dT is large.

The result of these calculations is just a number. What does the number mean? Remember, G is a measure of the stability of a phase or a system. If there are two (or more) alternative forms that a system may have (e.g., SiO$_2$ may occur as low quartz, high quartz, tridymite, cristobalite, a melt, etc.), the form with the lowest G, at a given pressure and temperature, will be the stable form. We could determine this by calculating G for each form at any P and T in question and then compare them. Alternatively, we might treat the

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difference between the free energies of two competing forms directly, obviating the need to check every conceivable alternative form. The transition from one form to another is a *reaction*, so we would then be dealing with the changes in *G* involved during such a reaction.

4 GIBBS FREE ENERGY FOR A REACTION

Now that we can calculate the Gibbs free energy of a phase at any temperature and pressure, we proceed to considering a reaction. Because we are embarking on igneous petrology, I have chosen a simple melting reaction. As an example, the schematic **phase diagram** in Figure 2 shows the limits of stability of a solid mineral phase (*S*) and its corresponding liquid melt (*L*) in terms of the variables *P* and *T*. The reaction in question can be written *S* = *L*. I use the equality sign instead of *S*   *L* to imply that the two sides of the equation are chemically equivalent, and the reaction could run either way, depending on the conditions. Only when the direction in which a reaction progresses is important will I use an arrow.

We must now compare and consider the free energies of both phases involved in the reaction. If we follow the logic of the boxed statement above (that all natural systems tend toward the lowest energy state), it should be clear that the solid must be more stable than the liquid of equivalent composition anywhere in the field labeled "Solid" in Figure 2, whereas the liquid is the more stable phase anywhere in the field labeled "Liquid." In other words, the value of *G* for the solid must be lower than that of the liquid at any point (such as point A) in the solid field. Likewise, the free energy of the liquid must be lower than that of the solid at any point (such as B) in the liquid field. We can summarize the stability concept for a reaction with the statement:

> *The side of a reaction equation with lowest G under a given set of conditions is the most stable.*

4.1 Variation in the Gibbs Free Energy for a Reaction with Pressure and Temperature

In the case for the reaction *S* = *L*, we have two phases, each with the same composition, and each of which has a Gibbs fre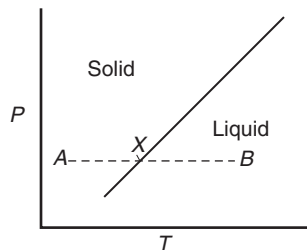e energy as defined by Equations (1) to (4). Will our system be in the liquid or the solid state, and how will the answer vary with temperature and pressure? This may be best illustrated if we isolate a single variable in Equation (3), so let's address only temperature. For any phase at a constant pressure, we can take the partial differential of Equation (3) with respect to temperature for a phase and get:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{9}$$

where the subscript *P* denotes constant pressure. Equation (9) expresses the manner in which *G* for a given phase varies with changes in *T* (at constant *P*). In other words, $-S$ is the *slope* of a line representing the value of *G* on a graph of *G* versus *T*. Entropy can be considered a measure of randomness, and there is no such thing as negative randomness. According to the third law of thermodynamics, entropy drops to zero at 0 K (complete order, not even vibration), and it cannot go lower. Because *S* must be positive so far above 0 K, the slope of *G* versus *T* for any phase must be negative according to Equation (9), as shown in Figure 3. The slope is steeper for the liquid than for the solid because $S_L > S_S$ (because liquids have a more random atomic structure than crystalline solids). Points A and B in Figure 3 represent the endpoints of the **isobaric** (constant pressure) temperature increase shown in Figure 2. At point A, the solid phase has a lower *G* than the liquid and is thus more stable. As *T* is increased, *G* of both phases decreases (as in Table 1), but *G* of the liquid decreases more rapidly than *G* of the solid. By the time we reach point B, the liquid has a lower *G* and is thus stable. Because *S* varies (increasing with *T*), the slopes of the curves in Figure 3 are not linear: they increase somewhat with increasing *T*.

An identical approach can be taken with an **isothermal** (constant temperature) traverse from low *P* to high *P*. If we take the partial differential of Equation (3) for a phase with respect to pressure at constant temperature, we get:

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{10}$$

Because *V* is positive, so is the *G* versus *P* slope, and V_{liquid} is greater than V_{solid}, and the slope of *G* versus *P* for

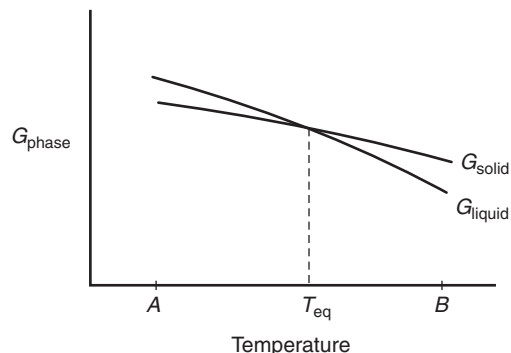**FIGURE 2** Schematic *P-T* phase diagram of a melting reaction.

FIGURE 3 Relationship between Gibbs free energy and temperature for the solid and liquid forms of a substance at constant pressure. T_{eq} is the equilibrium temperature.
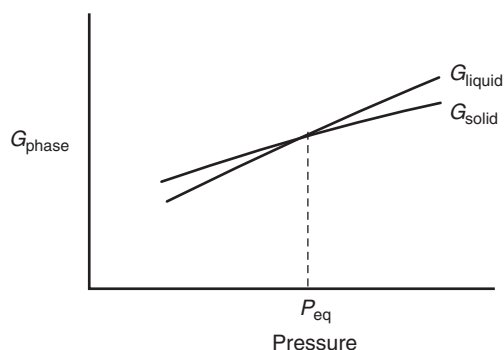
FIGURE 4 Relationship between Gibbs free energy and pressure for the solid and liquid forms of a substance at constant temperature. P_{eq} is the equilibrium pressure.

the liquid is greater than that for the solid (Figure 4). The liquid is more stable than the solid at low pressure, but it is less stable at high pressure, in agreement with Figure 2.

Next we apply Equation (3) directly to our reaction *S = L. It is important to clearly write the reaction before we can deal with it quantitatively*. It is customary to place the high entropy side of a reaction on the right. Applied to a reaction, Equation (3) becomes:

$$d\Delta G = \Delta V dP - \Delta S dT \qquad (11)$$

Δ and *d* both denote changes, but they denote different types of changes. *d* represents a finite change in the variables of state, such as pressure and temperature, whereas Δ represents the change in some variable as a result of the reaction [as defined by Equation (2)]. For our simple reaction, *S = L*, therefore, $\Delta V = V_L - V_S$. In other words, ΔV is the change in volume that occurs when the reaction progresses—in this case, when the solid melts. The solid form of most materials is more dense than the corresponding liquid at the same temperature because the ordered crystal lattice is more compact than the disordered liquid. Imagine the difference between a neatly stacked array of bricks and a random pile of the same bricks. The random pile, including the air spaces between the bricks, would occupy a larger total volume than the stacked pile. A notable exception to this general rule is the case for water and ice. The polar nature of the H_2O molecule permits closer packing of the molecules in the liquid than in the hexagonal ice lattice. Assuming that we are not melting water in our reaction, but are melting some mineral, ΔV must be positive for the reaction *S = L* as written. In a similar fashion, we can deduce that because $S_S < S_L$, ΔS is also positive.

ΔG, the difference in *G* between the reactants and the products, is not as easy to predict as are ΔV and ΔS. That is why we have Equation (2), so that we can calculate the change in *G* from the more easily understood variables. Remember that *dG* represents the change in *G* for a phase as *T* and/or *P* change (*dT* and/or *dP*). $d\Delta G$ is therefore the change in ΔG for the reaction as *T* and/or *P* change. Be-

cause *G* for each phase varies differently with *T* and *P*, the value of ΔG for a reaction must vary with *T* and *P* as well. Compare Figures 2 and 3, and you can determine that ΔG, as defined for the reaction ($G_{liquid}-G_{solid}$), must be positive at point A in the solid field and negative at point B in the liquid field. ΔG, in this case, thus has to decrease with increasing *T*.

4.2 The Equilibrium State

At point x in Figure 2, or at any point on the curve that separates the solid and liquid fields, both phases are equally stable, so that they *coexist at equilibrium*. The curve is thus called the (stable) **equilibrium curve**. Because both phases are equally stable at equilibrium, they must have the same value of *G*. Hence $\Delta G = 0$, *which must be true anywhere along the equilibrium curve*. This is another fundamental axiom:

ΔG for a reaction at equilibrium = 0

The concept of equilibrium, as it applies to our system of equally stable reactants and products, is extremely important. Such systems might appear to be static, but they certainly are not. Equilibrium represents a *dynamic* state of flux, but the fluxes in this case cancel one another. For our coexisting liquid and solid, the reactions $S \rightarrow L$ and $L \rightarrow S$ both happen continuously, but the rates at which they proceed are equal. The amount of each phase will thus remain the same over time if the conditions are unchanged. The dynamic nature of this equilibrium state can be observed macroscopically because the shapes of the crystals will slowly change as they exchange atoms with the liquid.

Le Châtelier's Principle tells us how such a state of dynamic equilibrium will react to changes imposed upon it. *A system will react in a fashion that acts so as to mitigate the changes*. For instance, if we heat the system, the $S \rightarrow L$ process will take place at a faster rate than the $L \rightarrow S$ one, so that there will gradually be more liquid and less solid (some of the crystals appear to melt). This process absorbs the added heat and maintains the system at the same temperature, thereby mitigating the change imposed by adding heat. If our system is in a compressible container, and we press on a piston to increase the pressure, the $L \rightarrow S$ process will outpace the $S \rightarrow L$ one, thereby reducing the volume in an attempt to offset the change. Le Châtelier's Principle can be stated as follows:

Le Châtelier's Principle

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

This is an eclectic principle and has applications beyond simple chemical systems (e.g., marriages, freeway traffic, even first dates).

4.3 Thermodynamic Evaluation of Phase Diagrams

Although thermodynamic data are sparse for melts, we can still use Equation (3) to *qualitatively* evaluate practically any phase diagram such as Figure 2. Doing so will help us understand the results of any calculations that we may perform, and greatly improve our ability to interpret phase diagrams we may create and those we encounter in the rest of the text.

There are five interrelated variables in Equation (3): *G*, *S*, *V*, *P*, and *T*. We can use these variables to understand various aspects of phase diagrams, such as the slope of an equilibrium curve or why the solid is on the high pressure–low temperature side. The approach is simple and qualitative but provides us with a powerful tool to assess reactions and equilibria.

For example, as pressure increases, volume naturally decreases, as you could imagine with a piston-and-cylinder apparatus, such as Figure 5. Applying pressure on the piston will force it downward, and the pressure in the cylinder below the piston will increase. Similarly, if there are two (or more) possible configurations or states for a given chemical system, the one with the lowest volume will be favored at higher pressure because the lower volume is a preferred response to the pressure increase. This is an application of Le Châtelier's Principle. Consider the transition of quartz to the polymorph coesite and then to stishovite as pressure increases. These transitions are crystallographic changes by which SiO_2 responds to increased pressure. The structure of a polymorph will compress only so far before inverting to different polymorphs with successively more compact structures. Lower-volume phases are thus favored at higher *P*. Following a vertical line in Figure 2, representing increasing *P* at constant *T* (isothermal), the system passes from a liquid to a solid, confirming that $V_S < V_L$ (as we previously established).

In a similar fashion, increasing *T* at a constant *P* (isobaric heating) should create more kinetic and vibrational motion in atoms and thus greater entropy. Note that a horizontal line in Figure 2, representing such an isobaric *T* increase, moves us from the solid to the liquid field above,
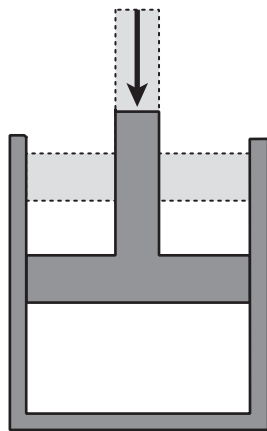
confirming our previous assertion that $S_S < S_L$. Because both decreasing pressure and increasing temperature can cause a solid to melt, the curve separating the solid and liquid fields must have a *positive* slope. This is true for any material of geological interest (except H_2O).

Equation (11) can be applied to Figure 2 in the same way. In a manner similar to the *G* versus *T* treatment for Equation 3, we can take the partial differential of ΔG with respect to *T* in Equation (11) and get:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad (12)$$

which is negative for the reaction *S* = *L* because we have already determined that ΔS $(S_L - S_S)$ is positive $(S_S < S_L)$. ΔG therefore decreases with increased *T*, so increasing *T* from equilibrium (where $\Delta G = 0$) results in negative ΔG, meaning that the reaction product (liquid) has a lower *G* than the reactant (solid), and the reaction (*S* = *L*) runs toward the right (liquid). This is true, as you can see from Figure 2. A path of increasing *T* moves from the solid into the liquid field. Likewise:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \qquad (13)$$

which is positive (liquid has a higher *V* than solid), and increasing *P* from equilibrium makes ΔG positive (the reactant has a lower *G*) and drives the reaction toward the reactant (solid).

Finally, let's choose any two points on the equilibrium curve in Figure 2. ΔG at both points must be zero. Thus:

$$d\Delta G = 0 = \Delta V dP - \Delta S dT \qquad (14)$$

and thus $\Delta V dP = \Delta S dT$, so:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \qquad (15)$$

Equation (15) is called the **Clapeyron equation**, which gives the slope of the equilibrium curve that separates the *L* and *S* fields in a pressure versus temperature phase diagram, such as Figure 2. Although in our example we do not know the exact values of ΔV and ΔS, we do know their signs. In this case, because both ΔS and ΔV have the same sign, the slope is positive, agreeing with our previous conclusion.

Thermodynamic data for melts are only beginning to become available (see the references at the end of this chapter) and are less reliable than for minerals. We will thus settle for a qualitative to semi-quantitative approach to igneous thermodynamics, use this technique to estimate the slopes of melting reactions in phase diagrams, and assess the relative stabilities of reactants and products. It is possible to proceed from this point to develop quantitative methods to

FIGURE 5   Piston-and-cylinder apparatus to compress a gas.

calculate the *P-T* and *P-T-X* conditions for metamorphic re-actions based upon thermodynamic data for the mineral and gas phases involved in common metamorphic reactions.

This approach is routinely performed on metamorphic min-erals and fluids because relatively accurate data are avail-able for these phases.

Summary

Thermodynamics deals with the stability of various chemical and mechanical systems and how they respond to their sur-roundings. All systems tend toward states with minimum en-ergy. Gibbs free energy (G) is a measure of energy content of chemical systems and, hence, a measure of the relative stabil-ity of minerals, fluids, melts, etc. $G = H - TS$, where H = en-thalpy (heat content), T = temperature (in K) and S = entropy (most easily thought of as randomness). Because we can only measure *changes* in thermodynamic properties such as G, el-ements at some reference (standard) state (typically 298 K and 0.1 MPa) are arbitrarily assigned zero values of G. We can then determine the molar Gibbs free energy of formation ($\Delta \overline{G}_f^\circ$) for any phase (i.e., mineral, fluid, melt) from this ref-erence by addressing the reaction by which the phase is cre-ated from the stable elemental constituents. Quartz, for example, may be created by the reaction Si (metal) + O_2 (gas) = SiO_2 (quartz). The change in any variable resulting from a reaction (in this case, the change in G) is $\Delta G = \Sigma(n_{products}G_{products} - n_{reactants}G_{reactants})$ so that $\Delta \overline{G}_f^\circ = G_{Quartz} - G_{O_2(gas)} - G_{Si_{(metal)}}$ (the latter two values = 0), which in this case = –856.3 kJ/mol, determined from mea-sured enthalpies as the reaction proceeds in the lab and from theoretical (third law of thermodynamics) entropies. The negative value of ΔG indicates that the product of the reaction (quartz) is more stable (lower G) than the reac-tants, which is why quartz is so common and metallic sili-con does not occur in nature where O_2 is present. The value of G for any phase (actually $\Delta \overline{G}_f^\circ$, but we shall accept the shorthand), once determined, can be extended to any pres-sure and temperature by using Equation (4):

$$G_{P_2,T_2} - G_{P_1,T_1} = \int_{P_1}^{P_2} V dP - \int_{T_1}^{T_2} S dT$$

Determining the change in Gibbs free energy of *reac-tions* between phase assemblages is a very powerful exten-sion of the free energy concept, allowing us to determine the relative stability of a reactant phase or phase assemblage and the compositionally equivalent products under a particular set of physical conditions. This permits us to know the pres-sure–temperature stability range of a particular mineral as-semblage and the *P-T* conditions of the equilibrium state under which the reactant and product assemblages coexist (the *equilibrium curve* separating the stability field of the re-actants from that of the products).

Le Châtelier's Principle is a powerful concept that al-lows us to qualitatively assess the effect of changing some variable of state on a system at equilibrium. Because equi-librium is a dynamic, rather than static, state, the rates of the forward and reverse reaction will vary in such a way as to offset or absorb any change imposed. Simple thermody-namic considerations can also be used to qualitatively assess phase diagrams, allowing us to deduce some information about the phases involved with a particular equilibrium curve or even to detect errors in diagrams. For example, the phase assemblage (reactants or products) on the high-pressure side of an equilibrium curve must occupy less volume than the assemblage on the low-pressure side, and the phase as-semblage on the high-temperature side of an equilibrium curve must have higher entropy and enthalpy than the assem-blage on the low-temperature side. The slope of the equilib-rium curve can also be determined using the Clapeyron equation [Equation (15)].

Key Terms

System	Enthalpy	Phase diagram
Surroundings	Entropy	Equilibrium curve for a reaction
Phase	Reactants/products	Le Châtelier's Principle
Stable/unstable/metastable	Reference state	Clapeyron equation
Equilibrium	Extensive variable of state	
Thermodynamics	Heat capacity	
Gibbs free energy	Gibbs free energy of reaction	

Review Questions and Problems

Review Questions and Problems are located on the author's web page at the following address: **http://www.prenhall.com/winter**

Important "First Principle" Concepts

- All natural systems tend toward states of minimum energy. Stable systems, then, are at equilibrium at the lowest possible energy state under a particular set of physical conditions.
- Practically everything in this chapter addresses systems at equilibrium. Unstable and metastable systems cannot easily be dealt with using the concepts of thermodynamic equilibrium.
- For chemical systems, the governing energy parameter to be minimized is the Gibbs free energy (G).
- G can be determined for virtually any mineral or fluid phase at 298 K and 0.1 MPa from compiled standard-state thermodynamic data and can then be extended to any pressure and temperature, using appropriate compressibility and heat capacity values.
- Reactions are conventionally written with the *reactants* (low enthalpy) on the left and the *products* (high enthalpy) on the right.
- For the change in any parameter (for example, G) due to a reaction, $\Delta G = \Sigma(n_{\text{products}}G_{\text{products}} - n_{\text{reactants}}G_{\text{reactants}})$, where n represents the stoichiometric coefficients of the phases in the reaction.
- The side of a reaction that is most stable under a particular set of conditions is the side with the lower G.
- It follows from above that if $\Delta G < 0$ the products are more stable than the reactants, if $\Delta G > 0$ the reactants are more stable than the products, and if $\Delta G = 0$ the reactants and products are equally stable, so the system is at equilibrium with all of them coexisting.

- Equilibrium is generally a dynamic thing, with the forward reaction occurring at the same rate as the reverse reaction so that neither the reactants nor the products are totally consumed.
- Le Châtelier's Principle is an elegant concept that addresses the effect of an imposed change on the dynamic equilibrium state. It states that *a system will react in a fashion that acts so as to mitigate the changes*.
- We can extract useful information from phase diagrams. They typically indicate the stability limits of the reactants, the products, and the equilibrium curve (conditions under which the reactants and products coexist) for one or more reactions. When we address an equilibrium curve, the phase or assemblage on the high-pressure side has the lower volume, and the phase or assemblage on the high-temperature side has higher entropy and enthalpy. As a general rule, solids have lower molar volumes, entropies, and enthalpies than liquids, and both have lower molar volumes, entropies, and enthalpies than gases.
- The slope of the equilibrium curve at any pressure and temperature is given by the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

Suggested Further Readings

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