Chapter 2: Energy, Entropy and Fundamental Thermodynamic Concepts

2.1 The Thermodynamic Perspective

We defined geochemistry as the application of chemical knowledge and techniques to solve geological problems. It is appropriate, then, to begin our study of geochemistry with a review of physical chemistry. Our initial focus will be on *thermodynamics*. Strictly defined, thermodynamics is the study of energy and its transformations. Chemical reactions and changes of states of matter inevitably involve energy changes. By using thermodynamics to follow the energy, we will find that we can predict the outcome of chemical reactions, and hence the state of matter in the Earth. In principle at least, we can use thermodynamics to predict at what temperature a rock will melt and the composition of that melt, and we can predict the sequence of minerals that will crystallize to form an igneous rock from the melt. We can predict the new minerals that will form when that igneous rock undergoes metamorphism, and we can predict the minerals and the composition of the solution that forms when that metamorphic rocks weathers. Thus thermodynamics allows us to understand (in the sense that we defined understanding in Chapter 1) a great variety of geologic processes.

Thermodynamics embodies a *macroscopic* viewpoint, i.e., it concerns itself with the properties of a system, such as temperature, volume, heat capacity, and it does not concern itself with how these properties are reflected in the internal arrangement of atoms. The *microscopic* viewpoint, which is concerned with transformations on the atomic and subatomic levels, is the realm of *statistical mechanics* and *quantum mechanics*. In our treatment, we will focus mainly on the macroscopic (thermodynamic) viewpoint, but we will occasionally consider the microscopic (statistical mechanical) viewpoint when our understanding can be enhanced by doing so.

In principle, *thermodynamics is only usefully applied to systems at equilibrium*. If an equilibrium system is perturbed, thermodynamics can predict the new equilibrium state, but cannot predict how, how fast, or indeed whether, the equilibrium state will be achieved. (The field of *irreversible thermodynamics*, which we will not treat in this book, attempts to apply thermodynamics to non-equilibrium states. However, we will see in Chapter 5 that thermodynamics, through the *principle of detailed balancing* and *transition state theory*, can help us predict reaction rates.)

Kinetics is the study of rates and mechanisms of reaction. Whereas thermodynamics is concerned with the ultimate equilibrium state and not concerned with the pathway to equilibrium, kinetics concerns itself with the pathway to equilibrium. Very often, equilibrium in the Earth is not achieved, or achieved only very slowly, which naturally limits the usefulness of thermodynamics. Kinetics helps us to understand how equilibrium is achieved and why it is occasionally not achieved. Thus these two fields are closely related, and together form the basis of much of geochemistry. We will treat kinetics in Chapter 5.

2.2 Thermodynamic Systems and Equilibrium

We now need to define a few terms. We begin with the term *system*, which we have already used. A thermodynamic system is simply that part of the universe we are considering. Everything else is referred to as the *surrounding*. A thermodynamic *system* is defined at the convenience of the observer in a manner so that thermodynamics may be applied. While we are free to choose the boundaries of a system, our choice must nevertheless be a careful one as the success or failure of thermodynamics in describing the system will depend on how we have defined its boundaries. Thermodynamics often allows us this sort of freedom of definition. This can certainly be frustrating, particularly for someone exposed to thermodynamics for the first time (and often even the second or third time). But this freedom allows us to apply thermodynamics successfully to a much broader range of problems than otherwise.

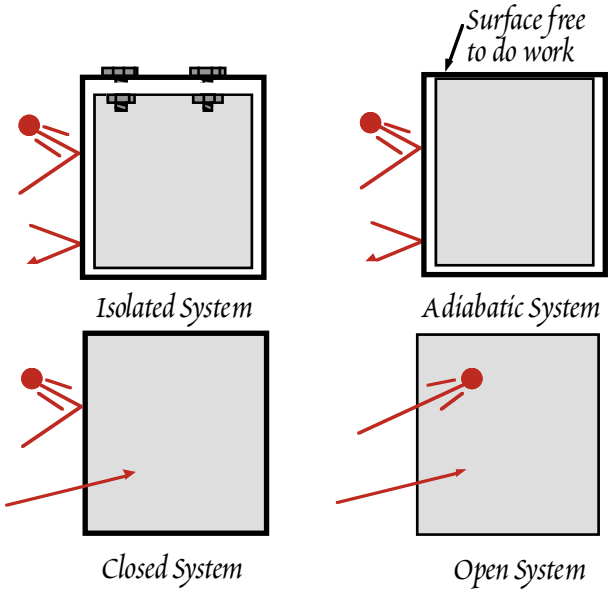


Figure 2.1. Systems in relationship to their surroundings. The ball represents mass exchange, the arrow represents energy exchange.

A system may be related to its environment in a number of ways. An *isolated* system can exchange neither energy (heat or work) nor matter with its surroundings. A truly isolated system does not exist in nature, so this is strictly a theoretical concept. An *adiabatic* system can exchange energy in the form of work, but not heat or matter, with its surroundings, that is to say it has thermally insulating boundaries. Though a truly adiabatic system is probably also a fiction, many geologic systems are sufficiently well insulated that they may be considered adiabatic. *Closed* systems may exchange energy, in the form of both heat and work with their surrounding but cannot exchange matter. An *open* system may exchange both matter and energy across it boundaries. The various possible relationships of a system to its environment are illustrated in Figure 2.1.

Depending on how they behave over time, systems are said to be either in *transient* or *time-invariant* states. Transient states are those that change with time. Time-independent states may be either *static* or *dynamic*. A dynamic time-independent state, or *steady-state*, is one whose thermodynamic and chemical characteristics do not change with time despite internal changes or exchanges of mass and energy with its surroundings. As we will see, the ocean is a good example of a steady-state system. Despite a constant influx of water and salts from rivers and loss of salts and water to sediments and the atmosphere, it composition does not change with time (at least on geologically short time scales). Thus a steady-state system may also be an open system. We could define a static system is one in which nothing is happening. For example, an igneous rock or a flask of seawater (or some other solution) is static in the macroscopic perspective. From the statistical mechanical viewpoint, however, there is a constant reshuffling of atoms and electrons, but with no net changes. Thus static states are generally also dynamic states when viewed on a sufficiently fine scale.

Let's now consider one of the most important concepts in physical chemistry, that of *equilibrium*. One of the characteristics of the *equilibrium state* is that it is static from a macroscopic perspective, that is, it does not change measurably with time. Thus the equilibrium state is always time-invariant. While a reaction A→B may appear to have reached static equilibrium on a macroscopic scale this reaction may still proceed on a microscopic scale but with the rate of reaction A→B being the same as that of B→A. Indeed, a kinetic definition of equilibrium is that the forward and reverse rates of reaction are equal.

The equilibrium state is entirely independent of the manner or pathway in which equilibrium is achieved. Indeed, once equilibrium is achieved, no information about previous states of the system can be recovered from its thermodynamic properties. Thus a flask of CO_2 produced by combustion of graphite cannot be distinguished from CO_2 produced by combustion of diamond. In achieving a new equilibrium state, all records of past states are destroyed.

Time-invariance is a necessary but not sufficient condition for equilibrium. Many systems exist in metastable states. Diamond at the surface of the Earth is not in an equilibrium state, despite its time-invariance on geologic time scales. Carbon exists in this metastable state because of kinetic barriers that inhibit transformation to graphite, the equilibrium state of pure carbon at the Earth's surface. Overcoming these kinetic barriers generally requires energy. If diamond is heated sufficiently, it will transform to graphite, or in the presence of sufficient oxygen, to CO_2.

The concept of equilibrium versus metastable or unstable (transient) states is illustrated in Figure 2.2 by a ball on a hill. The equilibrium state is when the ball is in the valley at the bottom of the hill, because its gravitational potential energy is minimized in this position. When the ball is on a slope, it is in an unstable, or transient, state and will tend to roll down the hill. However, it may also become trapped in small depressions on the side of the hill, which represent metastable states. The small hill bordering the depression represents a kinetic barrier. This kinetic barrier can only be overcome when the ball acquires enough energy to roll up and over it. Lacking that energy, it will exist in the metastable state indefinitely.

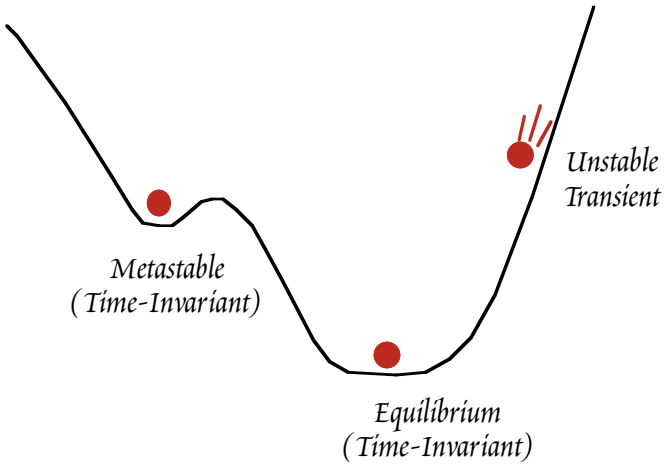


Figure 2.2. States of a system.

In Figure 2.2, the ball is at equilibrium when its (gravitational) potential energy lowest (i.e., at the bottom of the hill). This is a good definition of equilibrium in this system, but as we will soon see, is not adequate in all cases. A more general statement would be to say that *the equilibrium state is the one toward which a system will change in the absence of constraints*. So in this case, if we plane down the bump (remove a constraint), the ball rolls to the bottom of the hill. At the end of this Chapter, we will be able to produce a thermodynamic definition of equilibrium based on the Gibbs Free Energy. We will find that, for a given pressure and temperature, the chemical equilibrium state occurs when the Gibbs Free Energy of the system is lowest.

Natural processes proceeding at a finite rate are *irreversible*: under a given set of conditions; i.e., they will only proceed in one direction. Here we encounter a problem in the application of thermodynamics: if a reaction is proceeding, then the system is out of equilibrium and thermodynamic analysis cannot be applied. This is one of the first of many paradoxes in thermodynamics. This limitation might at first seem fatal, but we get around it by imagining a comparable reversible reaction. *Reversibility and local equilibrium* are concepts that allow us to 'cheat' and apply thermodynamics to non-equilibrium situations. *A "reversible" process is an idealized one where the reaction proceeds in sufficiently small steps that it is in equilibrium at any given time (thus allowing the application of thermodynamics).*

Local equilibrium embodies the concept that in a closed or open system, which may not be at equilibrium on the whole, small volumes of the system may nonetheless be at equilibrium. There are many such examples. In the example of mineral crystallizing from magma, only the rim of the crystal may be in equilibrium with the melt. Information about the system may nevertheless be derived from the relationship of this rim to the surrounding magma. Local equilibrium is in a sense the spatial equivalent to the temporal concept of reversibility and allows the application of thermodynamics to real systems, which are invariably non-equilibrium at large scales. Both local equilibrium and reversibility are examples of simplifying assumptions that allow us to treat complex situations. In making such assumptions, some accuracy in the answer may be lost. Knowing when and how to simplify a problem is an important scientific skill.

2.2.1 Fundamental Thermodynamic Variables

In the next two chapters we will be using a number of variables, or properties, to describe thermodynamic systems. Some of these will be quite familiar to you, others less so. Volume, pressure, energy, heat, work, entropy, and temperature are most fundamental variables in thermodynamics. As all other thermodynamic variables are derived from them, it is worth our while to consider a few of these properties.

CHAPTER 2: FUNDAMENTAL CONCEPTS OF THERMODYNAMICS

Energy is the capacity to produce change. It is a fundamental property of any system, and it should be familiar from physics. By choosing a suitable reference frame, we can define an absolute energy scale. However, it is changes in energy that are generally of interest to us rather than absolute amounts. Work and heat are two of many forms of energy. Heat, or thermal energy, results from random motions of molecules or atoms in a substance and is closely related to kinetic energy. Work is done by moving a mass, M, through some distance, x = X, *against* a force *F*:

$$w = -\int_0^X F\,dx \qquad 2.1$$

where *w* is work and force is defined mass times acceleration:

$$F = -M\frac{dv}{dt} \qquad 2.2$$

(the minus signs are there because of the convention that *work done on a system is positive*, *work done by a system is negative*). This is, of course, Newton's first law. In chemical thermodynamics, pressure–volume work is usually of more interest. Pressure is defined as force per unit area:

$$P = \frac{F}{A} \qquad 2.3$$

Since volume is area times distance, we can substitute equation 2.3 and $dV = Adx$ into 2.1 and obtain:

$$w = -\int_{x_0}^{x_1} \frac{F}{A} A dx = -\int_{V_0}^{V_1} P dV \qquad 2.4$$

Thus work is also done as a result of a volume change in the presence of pressure.

Potential energy is energy possessed by a body by virtue of its position in a force field, such as the gravitational field of the Earth, or an electric field. Chemical energy will be of most interest to us in this book. Chemical energy is a form a potential energy stored in chemical bonds of a substance. Chemical energy arises from the electromagnetic forces acting on atoms and electrons. Internal energy, which we denote with the symbol U, is the sum of the potential energy arising from these forces as well as the kinetic energy of the atoms and molecules (i.e., thermal energy) in a substance. It is internal energy that will be of most interest to us.

We will discuss all these fundamental variables in more detail in the next few sections.

2.2.1.1 Properties of State

Properties or variables of a system that depend only on the present state of the system, and not on the manner in which that state was achieved are called *variables of state* or *state functions*. *Extensive* properties depend on total size of the system. Mass, volume, and energy are all extensive properties. Extensive properties are additive, the value for the whole being the sum of values for the parts. *Intensive* properties are independent of the size of a system, for example temperature, pressure, and viscosity. They are not additive, e.g., the temperature of a system is not the sum of the temperature of its parts. In general, an extensive property can be converted to an intensive one by dividing it by some other extensive property. For example, density is the mass per volume and is an intensive property. It is generally more convenient to work with intensive rather than extensive properties. For a single component system not undergoing reaction, specification of 3 variables (2 intensive, 1 extensive) is generally sufficient to determine the rest, and specification of any 2 intensive variables is generally sufficient to determine the remaining intensive variables.

A final definition is that of a *pure substance*. A pure substance is one that cannot be separated into fractions of different properties by the same processes as those considered. For example, in most processes, the compound H_2O can be considered a pure substance. However, if electrolysis were involved, this would not be the case.

2.3 EQUATIONS OF STATE

Equations of state describe the relationship that exists among the state variables of a system. We will begin by considering the ideal gas law and then very briefly consider two more complex equations of state for gases.

2.3.1 IDEAL GAS LAW

The simplest and most fundamental of the equations of state is the *ideal gas law*†. It states that pressure, volume, temperature, and the number of moles of a gas are related as:

$$\boxed{PV = NRT} \qquad 2.5$$

where P is pressure, V is volume, N is the number of moles, T is thermodynamic, or absolute temperature (which we will explain shortly), and R is the ideal gas constant* (an empirically determined constant equal to 8.314 J/mol-K, 1.987 cal/mol-K or 82.06 cc-atm/deg-mol). This equation describes the relation between two extensive (mass dependent) parameters, volume and the number of moles, and two intensive (mass independent) parameters, temperature and pressure. We earlier stated that if we defined two intensive and one extensive system parameter, we could determine the remaining parameters. We can see from equation 2.5 that this is indeed the case for an ideal gas. For example, if we know N, P, and T, we can use equation 2.5 to determine V.

The ideal gas law, and any equation of state, can be rewritten with intensive properties only. Dividing V by N we obtain the *molar volume*, $\bar{V}$. Substituting $\bar{V}$ for V and rearranging, the ideal gas equation becomes:

$$\bar{V} = \frac{RT}{P} \qquad 2.6$$

The ideal gas equation tells us how the volume of a given amount of gas will vary with pressure and temperature. To see how molar volume will vary with temperature alone, we can differentiate equation 2.6 with respect to temperature holding pressure constant and obtain:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial\left(NRT/P\right)}{\partial T} \qquad 2.7$$

which reduces to:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{P} \qquad 2.8$$

It would be more useful to know to *fractional* volume change rather than the absolute volume change with temperature, because the result in that case does not depend on the size of the system. To convert to the fractional volume change, we simply divide the equation by V:

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{NR}{PV} \qquad 2.9$$

Comparing equation 2.9 with 2.5, we see that the right hand side of the equation is simply 1/T, thus

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T} \qquad 2.10$$

The left hand side of this equation, the fractional change in volume with change in temperature, is known as the *coefficient of thermal expansion*, α:

---

† Frenchman Joseph Gay-Lussac (1778-1850) established this law based on earlier work of Englishman Robert Boyle and Frenchman Edme Mariotte.

* We will often refer to it merely as the gas constant.

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad 2.11$$

For an ideal gas, the coefficient of thermal expansion is simply the inverse of temperature.

The *compressibility* of a substance is defined in a similar manner as the fractional change in volume produced by a change in pressure at constant temperature:

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad 2.12$$

TABLE 2.1. VAN DER WAALS CONSTANTS FOR SELECTED GASES

Gas	a liter^2-atm/mole^2	b liter/mole
Helium	0.034	0.0237
Argon	1.345	0.0171
Hydrogen	0.244	0.0266
Oxygen	1.360	0.0318
Nitrogen	1.390	0.0391
Carbon Dioxide	3.592	0.0399
Water	5.464	0.0305
Benzene	18.00	0.1154

Geologists sometimes use the *isothermal bulk modulus*, K_T, in place of compressibility. The isothermal bulk modulus is simply the inverse of compressibility: $K_T = 1/\beta$. Through a similar derivation to the one we have just done for the coefficient of thermal expansion, it can be shown that the compressibility of an ideal gas is $\beta = 1/P$.

The ideal gas law can be derived from statistical physics (first principles), *assuming the molecules occupy no volume and have no electrostatic interaction.* Doing so, we find, $R = N_0k$, where k is *Boltzmann's constant* (1.381×10^{-16} erg/K) and N_0 is Avagadro's Number (the number of atoms in one mole of a substance). k is a fundamentally constant that relates the average molecular energy, *e*, of an ideal gas to its temperature (K) as **e = 3kT/2**.

Since the assumptions just stated are ultimately invalid, it is not surprising that the ideal gas law is only an approximation for real gases, it applies best in the limit of high temperature and low pressure. Deviations are largest near the condensation point of the gas.

The *compressibility factor* is a measure of deviation from ideality and is defined as

$$Z = PV/NRT \qquad 2.13$$

By definition, Z= 1 for an ideal gas.

2.3.2 EQUATIONS OF STATE FOR REAL GASES

2.3.2.1 VAN DER WAALS EQUATION:

Factors we need to consider in constructing an equation of state for a real gas are the finite volume of molecules and the attractive and repulsive forces between molecules arising from electric charges. The Van der Waals equation is probably the simplest equation of state that takes account of these factors. The Van der Waals equation is:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2} \qquad 2.14$$

Here again we have converted volume from an extensive to an intensive property by dividing by N.

Let's examine the way in which the Van der Waals equation attempts to take account of finite molecular volume and forces between molecules. Considering first the forces between molecules, imagine two volume elements v_1 and v_2. The attractive forces will be proportional to the number of molecules or the concentrations, c_1 and c_2, in each. Therefore, attractive forces are proportional to $c_1 \times c_2 = c^2$. Since c is the number of molecules per unit volume, c=n/V, we see that attractive forces are proportional to $1/\overline{V}^2$. Thus it is the second term on the right that takes account of forces between molecules. The *a* term is a constant that depends on the nature and strength of the forces between molecules, and will therefore be different for each type of gas.

In the first term on the right, $\overline{V}$ has been replaced by $\overline{V} - b$. *b* is the volume actually occupied by molecules, and the term $\overline{V} - b$ is the volume available for movement of the molecules. Since different

gases have molecules of differing size, we can expect that the value of *b* will also depend on the nature of the gas. Table 2.1 lists the values of *a* and *b* for a few common gases.

2.3.2.2 Other Equations of State for Gases

The *Redlich-Kwong Equation (1949)* expresses the attractive forces as a more complex function:

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{T^{1/2}\overline{V}\ (\overline{V} + b)} \qquad 2.15$$

The *Virial Equation* is much easier to handle algebraically than the van der Waals equation and has some theoretical basis in statistical mechanics:

$$P\overline{V} = A + BP + CP^2 + DP^3 + \ldots \qquad 2.16$$

A, B, C, ... are empirically determined (temperature dependent) constants.

2.3.3 Equation of State for Other Substances

The compressibility and coefficient of thermal expansion parameters allow us to construct an equation of state for any substance. Such an equation relates the fundamental properties of the substance: its temperature, pressure, and volume. The partial differential of volume with respect to temperature and pressure is such an equation:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad 2.17$$

Substituting the coefficient of thermal expansion and compressibility for $\partial V/\partial T$ and $\partial V/\partial P$ respectively we have:

$$dV = V(\alpha dT - \beta dP) \qquad 2.18$$

Thus to write an equation of state for a substance, our task becomes to determine its compressibility and coefficient of thermal expansion. Once we know them, we can integrate equation 2.18 to obtain the equation of state. These, however, will generally be complex functions of temperature and pressure, so the task is often not easy.

2.2 Temperature, Absolute Zero, and The Zeroth Law Of Thermodynamics

How do you define temperature? We discussed temperature with respect to the ideal gas law without defining it, though we all have an intuitive sense of what temperature is. We noted above that temperature of a gas is measure of the average (kinetic) energy of its molecules. Another approach might be to use the ideal gas law to construct a *thermometer* and define a temperature scale. A convenient thermometer might be one based on the linear relationship between temperature and the volume of an ideal gas. Such a thermometer is illustrated in Figure 2.3. The equation describing the relationship between the volume of the gas in the thermometer and our temperature, τ, is:

$$V = V_0(1 + \gamma\tau) \qquad 2.19$$

where V_0 is the volume at some reference point where $\tau = 0$ (Figure 2.3a) and γ is a scale factor. For example, we might choose τ=0 to be the freezing point of water and the scale factor such that τ=100 (Figure 2.3b) occurs at the boiling point of water, as is the case in the centigrade scale. Rearranging, we have:

$$\tau = \frac{1}{\gamma}\left(\frac{V}{V_0} - 1\right) \qquad 2.20$$

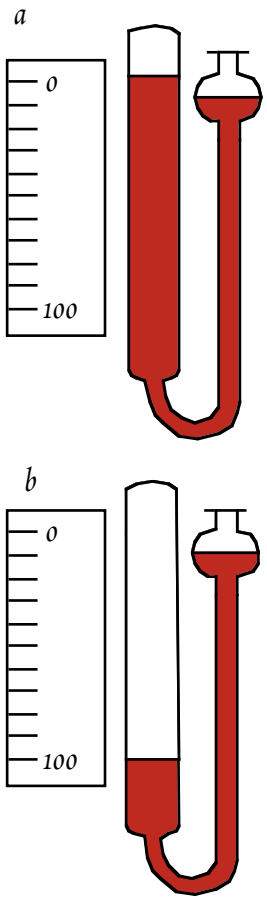


Figure 2.3. An ideal gas thermometer.

Then $\tau = 0$ at $V = V_0$. If V is less than the reference volume, then temperature will be negative on our scale. But notice that while any positive value of temperature is possible on this scale, there is a limit to the range of possible negative values. This is because V can never be negative. The minimum value of temperature on this scale will occur when V is 0. This occurs at:

$$\tau_0 = -\frac{1}{\gamma} \qquad 2.21$$

Thus implicit in the ideal gas law, which we used to make this thermometer, is the idea that there is an absolute minimum value, or an absolute zero, of temperature, which occurs when the volume of an ideal gas is 0. Notice that while the value$(-1/\gamma)$ of this absolute zero will depend on how we designed our thermometer, i.e., on V_0, the result, that a minimum value exists, does not. We should also point out that only an ideal gas will have a volume of 0 at the absolute 0. The molecules of real gases have a finite volume, and such a gas will have a finite volume at absolute 0.

The temperature scale used by convention in thermodynamics is the Kelvin* scale. The magnitude of units, called kelvins (not degrees kelvin) and designated K (not ° K), on this scale are the same as the centigrade scale, i.e., there are exactly 100 kelvins between the freezing and boiling point of water. There is some slight uncertainty (a very much smaller uncertainty than we need to concern ourselves with) concerning the value of absolute zero (i.e., the value of γ in 2.20 and 2.21). The scale has been fixed by choosing 273.16 kelvins to be the triple point of water (0.01° C). On this scale, the absolute zero of temperature occurs at 0±0.01 kelvins. The Kelvin scale should be used wherever temperature occurs in a thermodynamic equation.

Temperature has another fundamental property, and this is embodied in the *zeroth law of thermodynamics*. It is sufficiently obvious from everyday experience that we might overlook it. It concerns thermal equilibrium and may be stated in several ways: *two bodies in thermal equilibrium have the same temperature* and *any two bodies in thermal equilibrium with a third are in equilibrium with each other.*

2.3 Energy and The First Law of Thermodynamics

2.3.1 Energy

The first law may be stated various ways:

- *heat and work are equivalent*
- *energy is conserved in any transformation;*
- *the change of energy of a system is independent of the path taken.*‡

---

* named for Lord Kelvin. Born William Thomson in Scotland in 1824, he was appointed Professor at Glasgow University at the age of 22. Among his many contributions to physics and thermodynamics was the concept of absolute temperature. He died in 1907.

‡This may seem intuitively obvious to us, but it wasn't to James Joule (1818-1889), English brewer and physicist, who postulated it on the basis of experimental results. It wasn't obvious to his contemporaries either. His presentation of the idea of equivalence of heat and work to the British Association in 1843 was received with "entire incredulity" and "general silence". The Royal Society rejected his paper on the subject a year later. If you think

All are restatements of the law of conservation of energy:

Energy can be neither created nor destroyed.

Mathematically: $\mathbf{\Delta U=Q+W}$ or $\mathbf{dU=dQ+dW}$ 2.22

Thermodynamics is concerned only with the internal energy of a system. We don't really care whether the system as a whole is in motion, i.e., whether it has kinetic energy (we do care, however, about the internal kinetic energy, or heat). For the most part, we also don't care whether it has potential energy, i.e., what its position in potential fields is, except to the extent that this influences the state of our system (e.g., pressure in the atmosphere is a function of the altitude, and hence would be of interest to us). In addition, we are almost always concerned *only* with energy *changes*, not with the absolute energy of a system. In thermodynamics ΔU, not U, is the interesting quantity.

Energy may be transferred between a system and it surroundings in several ways: heat, work, radiation, and advection (i.e., energy associated with mass gained or lost by the system). Whenever possible, we will want to chose our system such that it is closed and we don't have to worry about the latter. In most, but not all, instances of geochemical interest, radiation is not important. Thus in geochemical thermodynamics, *heat and work are the forms of energy flow of primary interest*.

2.3.2 Work

We have seen that work is the integral of force applied through a distance. Force times distance has units of energy (mass-velocity^2), thus work is form of energy. The SI (Systeme International) unit of energy is the Joule = 1 kg-m^2/s^2.

There are several kinds of work of interest to thermodynamics, the most important of which is that involved in chemical reactions (later, when we consider oxidation and reduction reactions, we will be concerned with electrochemical work). One of the most important forms of work in classical thermodynamics is 'PV' work: expansion and contraction. Expressing equation 2.4 in differential form:

$$dW = -P_{ext}\, dV \qquad 2.23$$

Pressure is force per unit area and therefore has units of mass-time^{-2}-distance^{-1}, volume has units of distance^3. The product of P and V therefore has units of energy: mass-(distance/time)^2.† The negative sign arises because, *by convention, we define energy flowing into the system as positive*. Work done by the system is thus negative, work done on the system is positive. This conforms to a 1970 I.U.P.A.C. (International Union of Pure and Applied Chemistry) recommendation.

While 'PV' work is not as important in geochemistry as in other applications of thermodynamics, it is nevertheless of significant interest. There is, of course, a great range of pressures within the Earth. Systems rising within the Earth, such a magma or a hydrothermal fluid, will thus do work on their surroundings, and systems sinking, such as sediments being buried or lithosphere being subducted, will have work done on them.

We mentioned the concept of reversible and irreversible reactions, and stated that a reversible reaction is one that occurs in sufficiently small steps that equilibrium is maintained. In an expansion or contraction reaction, equilibrium is maintained and the reaction is reversible if the external pressure is equal to the internal pressure. The work done under these conditions is said to be reversible:

---

about it a bit, it is not so obvious — in fact, there is no good reason why heat and work should be equivalent. This law is simply an empirical observation. The proof is a negative one: experience has found no contradiction of it. German physician Julius Mayer (1814-1878) formulated the idea of conservation of energy in 1842, but his writing attracted little attention. It was Joule's experiments with heat and work that conclusively established the principle of conservation of energy. By 1850, the idea of conservation of energy began to take hold among physicists, thanks to Joule's persistence and the support of a brilliant young physicist named William Thomson, who also had been initially skeptical.

† The pascal, the SI unit of pressure, is equal to 1 kg/m-s^2. Thus if pressure is measured in MPa (megapascals, 1 atm ≈ 1 bar = 0.1 MPa) and volume in cc (= 10^{-6} m^{-3}), the product of pressure times volume will be in joules. This is rather convenient.

$$dW_{rev} = -PdV \qquad 2.24$$

2.3.4 Path Independence, Exact Differentials, State Functions, and the First Law

We said earlier that state functions are those that depend only on the present state of a system. Another way of expressing this is to say that state functions are path independent. Indeed, path independence may be used as a test of whether a variable is a state function or not. This is to say that if Y is a state function, then for any process that results in a change Y1 →Y2, the net change in Y, ΔY, is independent of how one gets from Y1 to Y2. Furthermore, if Y is a state function, then the differential dY is said to be mathematically *exact*.

Let's explore what is meant by an exact differential. An exact differential is the familiar kind, the kind we would obtain by differentiating the function u with respect to x and y, and also the kind we can integrate. But not all differential equations are exact. Let's first consider the mathematical definition of an exact differential, then consider some thermodynamic examples of exact and inexact differentials.

Consider the first order differential expression:

$$Mdx + Ndy \qquad 2.25$$

containing variables M and N, which may or may not be functions of x and y. Equation 2.25 is said to be an *exact differential* if there exists some function u of x and y relating them such that the expression:

$$du = Mdx + Ndy \qquad 2.26$$

is the total differential of u, i.e.,:

$$du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy \qquad 2.27$$

Let's consider what this implies. Comparing 2.26 and 2.27, we see that:

$$\frac{\partial u}{\partial x} = M \quad \text{and} \quad \frac{\partial u}{\partial y} = N \qquad 2.28$$

A necessary, but not sufficient, condition for 2.25 to be an exact differential is that M and N must be functions of x and y.

A general property of partial differentials is the *reciprocity relation* or *cross-differentiation identity*, which that the order of differentiation does not matter, so that:

$$\frac{\partial^2 u}{\partial x \partial y} = \frac{\partial^2 u}{\partial y \partial x} \qquad 2.29$$

(The reciprocity relation is an important and useful property in thermodynamics, as we shall see at the end of this chapter.) If equation 2.26 is the total differential of u, it follows that:

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x} \qquad 2.30$$

which is equivalent to:

$$\left(\frac{dM}{dy}\right)_x = \left(\frac{dN}{dx}\right)_y \qquad 2.31$$

Equation 2.31 is a necessary and sufficient condition for 2.25 to be an exact differential, that is, if the cross differentials are equal, then the differential expression is exact.

Exact differentials have the property that they can be integrated and an exact value obtained. This is true because they depend only on the initial and final values of the independent variables (e.g., x and y in 2.27).

Now let's consider some thermodynamic examples. Volume is a state function and we can express it as an exact differential in terms of other state functions:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \qquad (2.17)$$

Substituting the coefficient of thermal expansion and compressibility for $\partial V/\partial T$ and $\partial V/\partial P$ respectively, equation 2.30 becomes:

$$dV = \alpha V dT + \beta V dP \qquad (2.18)$$

According to equation 2.31, if V is a state function, then:

$$\frac{\partial(\alpha V)}{\partial P} = -\frac{\partial(\beta V)}{\partial T} \qquad 2.32$$

You should satisfy yourself that equation 2.32 indeed holds for ideal gases and therefore that V is a state variable.

Work is not a state function, that is, the work done does not depend only on the initial and final state of a system. We would expect then that dW is not an exact differential, and indeed, this is easily shown for an ideal gas.

For PV work, dW = –PdV. Substituting equation 2.17 for dV and rearranging, we have:

$$dW = -P\left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right] \qquad 2.33$$

Evaluating $\partial V/\partial T$ and $\partial V/\partial P$ for the ideal gas equation and multiplying through by P, this becomes:

$$dW = -NR dT + \frac{NRT}{P} dP \qquad 2.34$$

but

$$\frac{\partial NR}{\partial P} \neq \frac{\partial (NRT/P)}{\partial T} \qquad 2.35$$

We cannot integrate equation 2.34 and obtain a value for the work done without additional knowledge of the variation of T and P because the amount of work done does not depend only on the initial and final values of T and P; it depends on the path taken. Heat is also not a state function, not an exact differential, and also path dependent. Path dependent functions always have inexact differentials; path independent functions always have exact differentials.

On a less mathematical level, let's consider how the work and heat will vary in a transformation of a system, say from state 1 to state 2. Imagine that we burn gasoline in an open container. In this case, in the transformation from state 1 (gasoline) to state 2 (combustion products of gasoline) energy is given up by the system only as heat. Alternatively, we could burn the gasoline in an engine and recover some of the energy as work (expansion of the volume of the cylinder resulting in motion of the piston). The end states of these two transformations are the same, but the amount of heat released and work done varied depending on the path we took. Thus neither work nor heat can be state functions. Energy is a state function, is path independent, and is an exact differential. Whether we burn the gasoline in an open container or an engine, the energy released will be the same. Herein lies the significance for thermodynamics of Joule's discovery: that *the sum of heat and work is independent of the path taken even though, independently, work and heat are not*.

2.4 The Second Law and Entropy

2.4.1 Statement

Imagine a well-insulated box (an isolated system) somewhere in the universe (Figure 2.4). Imagine that within the box are two gases, separated by a removable partition. If we remove the partition, what happens? You know: the two gases mix completely. The process is entirely spontaneous. We have neither added energy to nor taken energy from the system, hence the first law says nothing about this process. Nor did removing the partition "cause" the reaction. This is apparent from the observation that if we reinsert the partition, the gases do not unmix. That you knew that the gases would mix (and

knew as well that they would not unmix upon reinserting the partition) suggests there is something very fundamental and universal about this. We need a physical law that describes it. This is the second law.

The Second Law may be stated in a number of ways:

It is impossible to construct a machine that is able to convey heat by a cyclical process from one reservoir at a lower temperature to another at a higher temperature unless work is done by some outside agency (i.e., air conditioning is never free). §

Heat cannot be entirely extracted from a body and turned into work (i.e., an engine can never run 100% efficiently).

Every system left to itself will, on the average, change toward a condition of maximum probability.

Introducing a new state function **S** called *entropy*, we may state the second law as:

The entropy of the universe always increases.

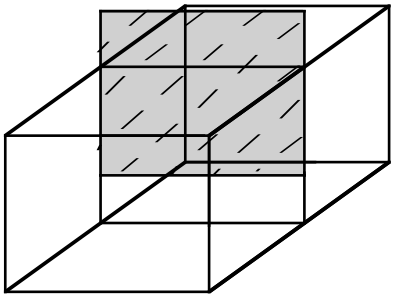


Figure 2.4. A gas-filled box with a removable partition. When the partition is removed, the gases mix. Entropy increases during this process.

In colloquial terms we could say:

You can't shovel manure into the rear end of a horse and expect to get hay out its mouth.

The second law codifies some of our everyday experience. The first law would not prevent us from using a horse to manufacture hay from manure. It only says we can't get more joules worth of hay out than we put in as manure. We would search in vain for any other physical law that prohibited this event. Yet our experience shows that it won't happen. Indeed, this event is so improbable that we find it comical. Similarly, we know that we can convert gasoline and oxygen to carbon dioxide and water in an internal combustion engine and use the resulting energy to drive a vehicle down the road. But adding CO_2 and water to the engine and pushing the car backwards down the street does not produce gasoline and oxygen, although such a result violates no other law of physics. *The second law states that there is a natural direction in which reactions will tend to proceed.* This direction is inevitably that of higher entropy of the system and its surroundings.

2.4.2 Statistical Mechanics: A Microscopic Perspective of Entropy

Whereas energy is a property for which we gain an intuitive feel through every day experience, the concept of entropy is usually more difficult to grasp. Perhaps the best intuitive understanding of entropy can be obtained from the microscopic viewpoint of statistical mechanics. So for that reason, we will make the first of several brief excursions into the world of atoms, molecules, and quanta.

Let's return to our box of gas and consider what happens on a microscopic scale when we remove the partition. To make things tractable, we'll consider that each gas consists of only two molecules, so there are four all together, two red and two black. For this thought experiment, we'll keep track of the individual molecules, so we label them 1red, 2red, 1black, 2 black. Before we removed the partition, the red molecules were on one side and the black ones on the other. Our molecules have some thermal energy, so they are free to move around. So by removing the partition, we are essentially saying that each molecule is equally likely to be found in either side of the box.

---

§Rudolf Clausius (1822-1888), a physicist at the Prussian military engineering academy in Berlin, formulated what we now refer to as the second law and the concept of entropy in a paper published in 1850. Similar ideas were published a year later by William Thomson (Lord Kelvin), who is responsible for the word "entropy". Clausius was a theorist who deserves much of the credit for founding what we now call "thermodynamics" (he was responsible for, among many other things, the virial equation for gases). However, a case can be made that Sadi Carnot (1796-1832) should be given the credit. Carnot was a Parisian military officer (the son of a general in the French revolutionary army) interested in the efficiency of steam engines. The question of credit hinges on whether he was referring to what we now call entropy when he used the word "*calorique*".

Before we removed the partition, there was only one possible arrangement of the system: this is shown in Figure 2.5a. Once we remove the partition, we have 4 molecules and two subvolumes, and a total of $2^4 = 16$ possible configurations (Fig. 2.5b) of the system. The *basic postulate of statistical mechanics* is: *a system is equally likely to be found in any of the states accessible to it*. Thus we postulate that each of these configurations are equally likely. Only one of these states corresponds to the original one (all red molecules on the left). Thus the probability of the system being found in its original state is 1/16. That is not particularly improbable. However, suppose that we had altogether a mole of gas ($\approx 6 \times 10^{23}$ molecules). The probability of the system ever being found again in its original state is then $\approx 2^{-10^{24}}$, which is unlikely indeed.

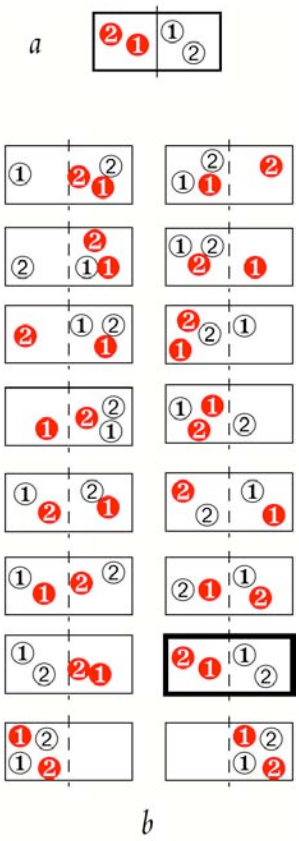


Figure 2.5. Possible distribution of molecules of a red and and a black gas in a box before (a) and after (b) removal of a partition separating them.

Now consider a second example. Suppose that we have two copper blocks of identical mass at different temperatures and separated by a thermally insulating barrier (Figure 2.6). Imagine that our system, which is the two copper blocks, is isolated in space so that the total energy of the system remains constant. What happens if we remove the insulating barrier? Experience tells us that the two copper blocks will eventually come into thermal equilibrium, i.e., their temperatures will eventually be identical.

Now let's look at this process on a microscopic scale. We have already mentioned that temperature is related to internal energy. As we shall see, this relationship will differ depending on the nature and mass of the material of interest, but since our blocks are of identical size and composition, we can assume temperature and energy are directly related in this case. Suppose that before we remove the insulation, the left block has 1 unit of energy and the right one has 5 (we can think of these as quanta, but this is not necessary). The question is, how will energy be distributed after we remove the insulation?

In the statistical mechanical viewpoint, we cannot determine how the energy will be distributed; we can only compute the possible ways it could be distributed. Each of these energy distributions is then equally likely according to the basic postulate. So let's examine how it can be distributed. Since we assume that the distribution is completely random, we proceed by randomly assigning the first unit to either to left or right block, then the second unit to either, etc. With 6 units of energy, there are already more ways of distributing it ($2^6 = 64$) than we have space to enumerate here. For example, there are 6 ways energy can be distributed so that the left block has 1 unit and the right one 5 units. This is illustrated in Figure 2.7. However, since we can't actually distinguish the energy units, all these ways are effectively identical. There are 15 ways, or *combinations*, we can distribute energy so that the left block has 2 units and the right 4 units. Similarly there are 15 combinations where the left block has 4 units and the right has 2 units. For this particular example, the rule is that if there are a total of E units of energy, e of which are assigned to the left block and (E-e) to the right, then there will be $\Omega(e)$ identical combinations where $\Omega(e)$ is calculated as:

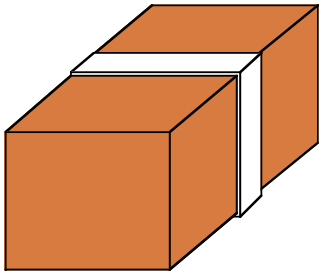


Figure 2.6. Two copper blocks at different temperatures separated by an insulator. When the insulator is removed and the blocks brought in contact, the blocks come to thermal equilibrium. Entropy increases in this process.

$$\Omega(e) = \frac{E!}{e!(E-e)!} \qquad 2.36^{\dagger}$$

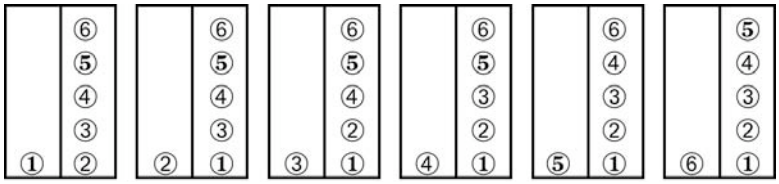


Figure 2.7. There are 6 possible ways to distribute 6 energy units so that the left block has 1 unit and the right block has 5.

Here we use Ω(e) to denote the function that describes the number of states accessible to the system for a given value of *e*. In this particular example, "states accessible to the system" refers to a given distribution of energy units between the two blocks. According to equation 2.36 there are 20 ways of distributing our 6 units of energy so that each block has three. There is, of course, only one way to distribute energy so that the left block has all of the energy and only one combination where the right block has all of it.

According to the basic postulate, any of the 64 possible distributions of energy are equally likely. The key observation, however, is that there are many ways to distribute energy for some values of *e* and only a few for other values. Thus the chances of the system being found in a state where each block has three units is 20/64 = 0.3125, whereas the chances of the system being in the state with the original distribution (1 unit to the left, 5 to the right) are only 6/64 = 0.0938. So it is much more likely that we will find the system in a state where energy is equally divided than in the original state.

Of course, two macroscopic blocks of copper at any reasonable temperature will have far more than 6 quanta of energy. Let's take a just slightly more realistic example and suppose that they have a total of 20 quanta, and compute the distribution. There will be 2^{20} possible distributions, far too many to consider individually, so let's do it the easy way and use equation 2.36 to produce a graph of the probability distribution. Equation 2.36 gives the number of identical states of the system for a given value of *e*. The other thing that we need to know is that the chances of any one of these states occurring, which is simply $(1/2)^{20}$. So to compute the probability of a particular distinguishable distribution of energy occurring, we multiply this probability by Ω. More generally the probability, $\mathcal{P}$, will be:

$$\mathcal{P}(e) = \frac{E!}{e!(E-e)!} p^e q^{E-e} \qquad 2.37$$

where *p* is the probability of an energy unit being in the left block and *q* is the probability of it being in the right. This equation is known as the *binomial distribution*[*]. Since both *p* and *q* are equal to 0.5 in our case (if the blocks were of different mass or of different composition, *p* and *q* would not be equal), the product $p^e q^{E-e}$ is just p^E and 2.37 simplifies to:

$$\mathcal{P}(e) = \frac{E!}{e!(E-e)!} p^E = \Omega(e) p^E \qquad 2.38$$

Since p^E is a constant (for a given value of E and configuration of the system), the probability of the left block having *e* units of energy is directly proportional to Ω(e). It turns out that this is general relationship, so that for any system we may write:

$$\mathcal{P}(f) = C\Omega(f) \qquad 2.39$$

---

† This is the equation when there are two possible outcomes. A more general form for a situation where there are *m* possible outcomes (e.g., copper blocks) would be:

$$\Omega = \frac{N!}{n_1! n_2! \ldots n_m!} \quad \Omega = \frac{N!}{n_1! n_2! \ldots n_m!} \qquad 2.36a$$

where there are n_1 outcomes of the first kind (i.e., objects assigned to the first block), n_2 outcomes of the second, etc. and $N = \sum n_i$ (i.e., N objects to be distributed).

* If you have a spreadsheet program available to you, this equation may be a built-in function, which makes computing graphs such as Figure 2.8 much easier. In Microsoft Excel™, this is the BINOMDIST function.

where f is some property describing the system and C is some constant (in this case 0.5^{20}). Figure 2.8a shows the probability of the left block having e units of energy. Clearly, the most likely situation is that both will have approximately equal energy. The chances of one block having 1 unit and the other 19 units is very small (2×10^{-5} to be exact). In reality of course, the number of quanta of energy available to the two copper blocks will be on the order of Avagadro's number. If one or the other block has 10 or 20 more units or even 10^{10} more quanta than the other, we wouldn't be able to detect it. Thus energy will always appear to be distributed evenly between the two, once the system has had time to adjust.

Figure 2.8b shows Ω as a function of e, the number of energy units in the left block. Comparing the two, as well as equation 2.38, we see that the most probable distribution of energy between the blocks corresponds to the situation where the system has the maximal number of states accessible to it, i.e., to where Ω(e) is maximum.

According to our earlier definition of equilibrium, the state ultimately reached by this system when we removed the constraint (the insulation) is the equilibrium one. We can see here that, unlike the ball on the hill, we cannot determine whether this system is at equilibrium or not simply from its energy: the total energy of the system remained constant. In general for a thermodynamic system, *whether or not the system is at equilibrium depends not on its total energy, but on how that energy is internally distributed*.

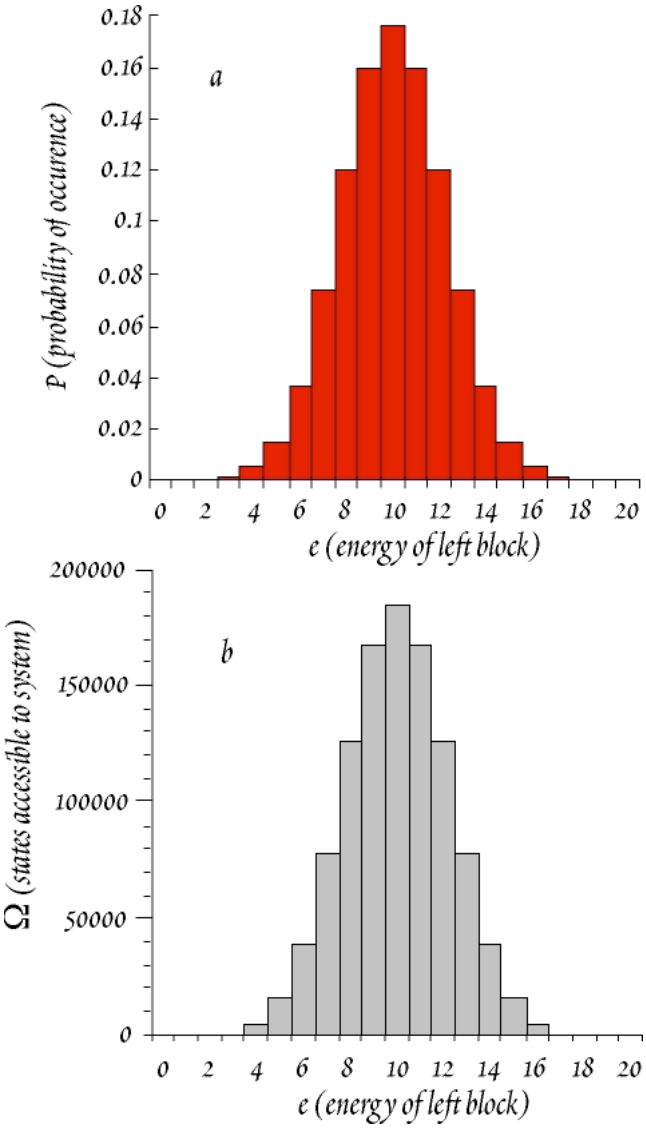


Figure 2.8. (a) Probability of one of two copper blocks of equal mass in thermal equilibrium having e units of energy when the total energy of the two blocks is 20 units. (b) Ω, number of states available to the system (combinations of energy distribution) as a function of ε.

Clearly, it would be useful to have a function that could predict the internal distribution of energy at equilibrium. The function that does this is the *entropy*. To understand this, let's return to our copper blocks. Initially, the two copper blocks are separated by a thermal barrier and we can think of each as an isolated system. We assume that each has an internal energy distribution that is at or close to the most probable one; i.e., each is internally at equilibrium. Each block has its own function Ω (which we denote as Ω_l and Ω_r for the left and right block respectively) that gives the number of states accessible to it at a particular energy distribution. We assume that initial energy distribution is not the final one, so that when we remove the insulation, the energy distribution of system will spontaneously change. In other words:

$$\Omega_l^i \neq \Omega_l^f \qquad \text{and} \qquad \Omega_r^i \neq \Omega_r^f$$

where we use the superscripts i and f to denote initial and final respectively.

When the left block has energy *e*, it can be in any one of $\Omega_l = \Omega(e)$ possible states, and the right block can be in any one of $\Omega_r = \Omega(E\text{-}e)$ states. Both $\mathcal{P}$ and Ω are multiplicative, so the total number of possible states after we remove the insulation, Ω, will be:

$$\Omega(e) = \Omega_l(e) \times \Omega_r(E-e)$$

To make $\mathcal{P}$ and Ω additive we simply take the log:

$$\ln\Omega(e) = \ln\Omega_l(e) + \ln\Omega_r(E-e) \qquad 2.40$$

and

$$\ln \mathcal{P} = \ln C + \ln \Omega \qquad 2.41$$

As additive properties, ln $\mathcal{P}$ and ln Ω are consistent with our other extensive state variables (e.g., E, V).

We want to know which energy distribution, i.e., values of *e* and *E–e*, is the most likely one, because that corresponds to the equilibrium state of the system. This is the same as asking where the probability function, $\mathcal{P}(e)$, is maximum. *Maximum values of functions have the useful property that they occur at points where the derivative of the function is 0*. That is, a maximum of function $f(x)$ will occur where $df(x)/d(x) = 0$[†]. Thus the maximum value of $\mathcal{P}(e)$ in Figure 2.8 occurs where $d\mathcal{P}/de = 0$. The most probably energy distribution will therefore occur at:

$$\frac{\partial \mathcal{P}(e)}{\partial e} = 0 \qquad \text{or equivalently} \qquad \frac{\partial \ln \mathcal{P}(e)}{\partial e} = 0 \qquad 2.42$$

(we use the partial differential notation to indicate that, since the system is isolated, all other state variables are held constant). Substituting equation 2.41 into 2.42, we have:

$$\frac{\partial \ln \mathcal{P}(e)}{\partial e} = \frac{\partial(\ln C + \ln \Omega(e))}{\partial e} = \frac{\partial \ln \Omega(e)}{\partial e} = 0 \qquad 2.43$$

(since C is a constant). Then substituting 2.40 into 2.43 we have:

$$\frac{\partial \ln \Omega(e)}{\partial e} = \frac{\partial \ln \Omega_l}{\partial e} + \frac{\partial \Omega_r(E-e)}{\partial e} = 0 \qquad 2.44$$

so the maximum occurs at:

$$\frac{\partial \ln \Omega_l}{\partial e} = -\frac{\partial \Omega_r(E-e)}{\partial e} \qquad 2.45$$

The maximum then occurs where the function $\partial \ln \Omega / \partial e$ for the two blocks are equal (the negative sign will cancel because we are taking the derivative $\partial f(\text{-}e)/\partial e$). More generally, we may write:

$$\frac{\partial \ln \Omega_l^f(E_l^f)}{\partial E_l^f} = \frac{\partial \ln \Omega_r^f(E_r^f)}{\partial E_r^f} \qquad 2.46$$

Notice two interesting things: *the equilibrium energy distribution is the one where ln Ω is maximum (since it proportional to $\mathcal{P}$) and where the function $\partial \ln\Omega/\partial E$ of the two blocks are equal*. It would appear that both are very useful functions. We define entropy, S, as:

$$\boxed{\mathbf{S = k \ln \Omega}} \qquad 2.47^{\P}$$

and a function β such that:

$$\beta = \frac{\partial \ln \Omega}{\partial E} \qquad 2.48$$

where k is some constant (which turns out to be Boltzmann's constant or the gas constant; the choice depends on whether we work in units of atoms or moles). *The function S then has the property that it is maximum at equilibrium and β has the property that it is the same in every part of the system at equilibrium.*

[†] Either a maximum or minimum can occur where the derivative is 0, and a function may have several of both; so some foreknowledge of the properties of the function of interest is useful in using this property.

[¶] This equation, which relates microscopic and macroscopic variables, is inscribed on the tombstone of Ludwig Boltzmann (1844-1906), the Austrian physicist responsible for it.

Entropy also has the interesting property that in any spontaneous reaction, the total entropy of the system plus its surroundings must increase. In our example, this is a simple consequence of the observation that the final probability, $\mathcal{P}$(E), and therefore also Ω, will be maximum and hence never be less than the original one. Because of that, the final number of accessible states must exceed the initial number and:

$$\ln\Omega_l^f(E_l^f) + \ln\Omega_r^f(E_r^f) \geq \ln\Omega_l^i(E_l^i) + \ln\Omega_r^i(E_r^i) \qquad 2.49$$

rearranging: $$[\ln\Omega_l^f(E_l^f) - \ln\Omega_l^i(E_l^i)] \geq -[\ln\Omega_r^f(E_r^f) - \ln\Omega_r^i(E_r^i)]$$

The quantities in brackets are simply the entropy changes of the two blocks. Hence:

$$\Delta S_l \geq -\Delta S_r \qquad 2.50$$

In other words, *any decrease in entropy in one of the blocks must be at least compensated for by an increase in entropy of the other block*.

For an irreversible process, that is, a spontaneous one such as thermal equilibrium between two copper blocks, we cannot determine exactly the increase in entropy. Experience has shown, however, that the increase in entropy will always exceed the ratio of heat exchanged to temperature. Thus the mathematical formulation of the second law is:

$$\boxed{\frac{\mathbf{dQ}}{\mathbf{T}} \leq \mathbf{dS}} \qquad 2.51$$

Like the first law, equation 2.51 cannot be derived or formally proven; it is simply a postulate that has never been contradicted by experience. For a reversible reaction, i.e., one that is never far from equilibrium and therefore one where dQ is small relative to T,

$$dS = \frac{dQ_{rev}}{T} \qquad 2.52$$

(see the box "the second law in the reversible case"). In thermodynamics, we restrict our attention to systems that are close to equilibrium, so equation 2.52 serves as an operational definition of entropy.

2.4.2.1 Microscopic Interpretation of Temperature

Let's now return to our function β. The macroscopic function having the property of our new function β is temperature. The relation of temperature to β is

$$kT = 1/\beta \qquad 2.53$$

and

$$\frac{1}{kT} = \frac{\partial \ln\Omega}{\partial E} \qquad 2.54$$

Equation 2.53 provides a statistical mechanical definition of temperature. We can easily show that *T is measure of the energy per degree of freedom*. Do to this though, we need one other relationship, which we introduce without proof. This is that Ω increases roughly with E as:

$$\Omega \propto E^f$$

where *f* is the number of degrees of freedom of the system (which in turn is proportional to the number of atoms or molecules in the system times the modes of motion, e.g., vibrational, rotational, translational, available to them). Hence:

$$\beta = \frac{\partial \ln\Omega}{\partial E} \propto \frac{f}{E} \qquad 2.55$$

Substituting $T = 1/\beta$, then

$$T \propto \frac{E}{kf}$$

2.4.2.2 Entropy and Volume

Our discussion of entropy might leave the impression that entropy is associated only with heat and temperature. This is certainly not the case. Our first example, that of the gases in the box, is a good demonstration of how entropy changes can also accompany isothermal processes. When the partition

is removed and the gases mix, there is an increase in the number of states accessible to the system. Before the partition is removed, there is only one state accessible to the system (here "accessible states" means distribution of red and black molecules between the two sides of the box), so $\Omega = 1$. Suppose that after we remove the partition, we find the system in a state is one where there is one molecule of each kind on each side (the most probable case). There are four such possible configurations, so $\Omega = 4$. The entropy change has thus been

$$\Delta S = k(\ln 4 - \ln 1) = k \ln 4 = 2k \ln 2$$

From the macroscopic perspective, we could say that the red gas, initially confined to the left volume, expands into the volume of the entire box, and the black gas expands from the right half to the entire volume. Thus entropy changes accompany volume changes.

2.4.2.3 SUMMARY

It is often said that entropy is a measure of the randomness of a system. From the discussion above, we can understand why. Entropy is a function of the number of states accessible to a system. Because there are more states available to a system when energy or molecules are "evenly" or "randomly" distributed than when we impose a specific constraint on a system (such as the thermal insulation between the blocks or the partition between the gases), there is indeed an association between randomness and entropy. When we remove the insulation between the copper blocks, we allow energy to be randomly distributed between them. In the example of the combustion of gasoline, before combustion all oxygen atoms are constrained to be associated with oxygen molecules. After combustion, oxygen is randomly distributed between water and CO_2 molecules.

More precisely, we may say that an increase in entropy of a system corresponds to a decrease in knowledge of it. In the example of our two gases in the box, before the partition is removed, we know all red molecules are located somewhere in the left half of the box and all black ones somewhere in the right half. After the partition is removed, we know only that the molecules are located somewhere within the combined volume. Thus our knowledge of the location of the molecules decreases in proportion to the change in volume. Molecules in ice are located at specific points in the crystal lattice. When ice melts, or evaporates, molecules are no longer constrained to specific locations: there is an increase in entropy of H_2O and a corresponding decrease in our knowledge of molecular positions. When we allowed the two copper blocks to come to thermal equilibrium, entropy increased. There were more possible ways to distribute energy after the blocks equilibrated than before. As a result, we knew less how energy was distributed after removing the insulation.

As a final point, we emphasize that the second law does not mean we cannot decrease the entropy of a "system". If that were so, the organization of molecules we call life would not be possible. However, if the entropy of a system is to decrease, the entropy of the surroundings must increase. Thus we can air condition a room, but the result is that the surroundings (the "outside") are warmed by more than the air in the room is cooled. Organisms can grow, but in doing so they inevitably, through consumption and respiration, increase the entropy of their environment. Thus we should not be surprised to find that the entropy of the manure is greater than that of hay plus oxygen.

2.4.3 INTEGRATING FACTORS AND EXACT DIFFERENTIALS

A theorem of mathematics states that any inexact differential that is a function of only two variables can be converted to an exact differential. dW is an inexact differential, and dV is an exact differential. Since $dW_{rev} = -PdV$, dW_{rev} can be converted to a state function by dividing by P since

$$\frac{dW_{rev}}{P} = -dV \qquad 2.56$$

and V is a state function. Variables such as P which convert non-state functions to state functions are termed *integrating factor*. Similarly, for a *reversible* reaction, heat can be converted to the state function entropy by dividing by T:

$$\frac{dQ_{rev}}{T} = dS \qquad 2.57$$

Thus temperature is the integrating factor of heat. Entropy is a state function and therefore an exact differential. Therefore equation 2.57 is telling us that although the heat gained or lost in the transformation from state 1 to state 2 will depend on the path taken, *for a reversible reaction the ratio of heat gained or lost to temperature will always be the same, regardless of path.*

If we return to our example of the combustion of gasoline above, the second law also formalizes our experience that we cannot build a 100% efficient engine: the transformation from state 1 to state 2 cannot be made in such a way that all energy is extracted as work; some heat must be given up as well. In this sense, the automobile radiator is necessitated by the second law.

Where P-V work is the only work of interest, we can combine the first and second laws as:

$$dU \leq TdS - PdV$$

The implication of this equation is that equilibrium is approached at prescribed S and V, the energy of the system is minimized. For the specific situation of a reversible reaction where dS = dQ/T, this becomes

$$\boxed{\mathbf{dU_{rev} = TdS_{rev} - PdV}} \qquad 2.58$$

This expresses energy in terms of its natural or *characteristic variables*, S and V. The characteristic variables of a function are those that give the simplest form of the exact differential. Since neither T nor P may have negative values, we can see from this equation that energy will always increase with increasing entropy (at constant volume) and that energy will decrease with increasing volume (at constant entropy). This equation also relates all the primary state variables of thermodynamics, U, S, T, P, and V. For this reason, it is sometimes called the *fundamental equation of thermodynamics*. We will introduce several other state variables derived from these 5, but these will be simply a convenience.

By definition, an adiabatic system is one where dQ = 0. Since $-dQ_{rev}/T = dS_{rev}$ (equation 2.52), it follows that for a reversible process, *an adiabatic change is one carried out at constant entropy, or in other words,*

EXAMPLE 2.1. ENTROPY IN REVERSIBLE AND IRREVERSIBLE REACTIONS

Air conditioners work by allowing freon contained in a closed system of pipes to evaporate in the presence of the air to be cooled, then recondensing the freon (by compressing it) on the warm or exhaust side of the system. Let us define our "system" as only the freon in the pipes. The system is closed since it can exchange heat and do work but not exchange mass. Suppose our system is contained in an air conditioner maintaining a room at 20° C or 293 K and exhausting to outside air at 303 K. Let's assume the heat of evaporation of the coolant (the energy required to transform it from liquid to gas), is 1000 joules. During evaporation, the heat absorbed by the coolant, *dQ*, will be 1000 J. During condensation –1000 J will be given up by the system. For each cycle, the *minimum* entropy change during these transformations is easy to calculate from equation 2.51:

Evaporation: $$dS \geq \frac{dQ}{T} = 1000/293 = 3.413 \text{ J/K}$$

Condensation: $$dS \geq \frac{dQ}{T} = -1000/303 = -3.300 \text{ J/K}$$

The minimum net entropy change in this cycle is the sum of the two or 3.413 - 3.300 = 0.113 J/K. This is a "real" process and irreversible, so the entropy change will be greater than this.

If we performed the evaporation and condensation isothermally at the equilibrium condensation temperature, i.e. reversibly, then this result gives the exact entropy change in each case. In this imaginary reversible reaction, where equilibrium is always maintained, there would be no net entropy change over the cycle. But of course no cooling would be achieved either, so it would be pointless from a practical viewpoint. It is nevertheless useful to assume this sort of reversible reaction for the purposes of thermodynamic calculations, because exact solutions are obtained.

an isoentropic change. For adiabatic expansion or compression therefore, dU = –PdV.

2.5 ENTHALPY

We have now introduced all the fundamental variables of thermodynamics, T, S, U, P and V. Everything else can be developed and derived from these functions. Thermodynamicists have found it *convenient* to define several other state functions, the first of which is called *enthalpy*. *Enthalpy is a composite function and is the sum of the internal energy plus the product PV*:

$$\boxed{\mathbf{H \equiv U + PV}} \qquad 2.59$$

As is the case for most thermodynamic functions, it is enthalpy changes rather than absolute enthalpy that are most often of interest. For a system going from state 1 to state 2, the enthalpy change is:

$$H_2 - H_1 = U_2 - U_1 + P_2V_2 - P_1V_1 \qquad 2.60$$

The First Law states: $U_2 - U_1 = \Delta Q + \Delta W$

so: $H_2 - H_1 = \Delta Q + \Delta W + P_2V_2 - P_1V_1$

If pressure is constant, then: $\Delta H = \Delta Q_P + \Delta W + P\Delta V \qquad 2.61$

(we use the subscript P in ΔQ_P to remind us that pressure is constant). In thermodynamics, PV work is often the only kind of work of interest. *If the change takes place at constant pressure and P-V work is the only work done by the system*, then the last two terms cancel and *enthalpy is simply equal to the heat gained or lost by the system:*

$$\Delta H = \Delta Q_P$$

or in differential form: $\mathbf{dH = dQ_p} \qquad 2.62$

H is a state function because it is defined in terms of state functions U, P, and V. Because enthalpy is a state function, dQ must also be a state function under the conditions of constant pressure and the only work done being PV work.

More generally, the enthalpy change of a system may be expressed as:

$$dH = dU + VdP + PdV$$

or at constant pressure as:

$$dH = dU + PdV \qquad 2.63$$

In terms of its characteristic variables, it may also be expressed as:

$$dH \le TdS + VdP \qquad 2.64$$

From this it can be show that H will be at a minimum at equilibrium when S and P are prescribed:

$$\boxed{\mathbf{dH_{rev} = TdS_{rev} + VdP}} \qquad 2.65$$

The primary value of enthalpy is measuring the energy consumed or released in changes of state of a system. For example, how much energy is given off by the reaction:

$$2H_2 + O_2 \rightleftarrows 2H_2O$$

To determine the answer we could place hydrogen and oxygen in a well-insulated piston-cylinder maintaining constant pressure. We would design it such that we could easily measure the temperature before and after reaction. Such an apparatus is known as a *calorimeter*. By measuring the temperature before and after the reaction, and knowing the *heat capacity* of the reactants and our calorimeter, we could determine the enthalpy of this reaction. This enthalpy value is often also called the *heat of reaction* or *heat of formation* and is designated ΔH_r (or ΔH_f). Similarly, we might wish to know how much heat is given off when NaCl is dissolved in water. Measuring temperature before and after reaction would allow us to calculate the *heat of solution*. The enthalpy change of a system that undergoes melting is known as the heat of fusion or heat of melting, ΔH_m (this quantity is sometimes denoted ΔH_f; we will use the subscript *m* to avoid confusion with heat of formation); that of a system undergoing boiling is known as the heat of vaporization, ΔH_v. As equation 2.65 suggests, measuring enthalpy change is also a convenient way of determining the entropy change.

At this point, it might seem that we have wandered rather far from geochemistry. However, we shall shortly see that functions such as entropy and enthalpy and measurements of such things as heats of solutions and heats of melting are essential to predicting equilibrium geochemical systems.

2.6 HEAT CAPACITY

It is a matter of every day experience that the addition of heat to a body will raise its temperature. We also know that if we bring two bodies in contact, they will eventually reach the same temperature. In that state, the bodies are said to be in thermal equilibrium. However, thermal energy will not necessarily be partitioned equally between the 2 bodies. It would require half again as much heat to increase the temperature of 1g of quartz by 1° C as it would to increase the temperature of 1g of iron metal by 1° C. (We saw that temperature is a measure of the energy per degree of freedom. It would appear then that quartz and iron have different degrees of freedom per gram, something we will explore below.) *Heat capacity* is the amount of heat (in joules or calories) required to raise the temperature of a given amount (usually a mole) of a substance by 1 K. Mathematically, we would say:

$$C = \frac{dQ}{dT} \qquad 2.66$$

However, the heat capacity of a substance will depend on whether heat is added at constant volume or constant pressure, because some of the heat will be consumed as work if the volume changes. Thus a substance will have two values of heat capacity: one for constant volume and one for constant pressure.

2.6.1 CONSTANT VOLUME HEAT CAPACITY

Recall that the first law states: $dU = dQ + dW$

If we restrict work to PV work, this may be rewritten as:

$$dU = dQ - PdV$$

If the heating is carried out at constant volume, i.e., $dV = 0$, then $dU = dQ$ (all energy change takes the form of heat) and:

$$\boxed{C_v = \left(\frac{\partial U}{\partial T}\right)_V} \qquad 2.67$$

The value of C_V for an ideal gas is $^3/_2R$ where R is the gas constant, as is shown in the boxed discussion below. Molecular gases, however, are not ideal. Vibrational and rotation modes also come into play, and heat capacity of real gases, as well as solids and liquids, is a function of temperature.

For solids, motion is vibrational and heat capacities depend on vibrational frequencies, which in turn depend on temperature and bond strength (for stronger bonds there is less energy stored as potential energy, hence less energy is required to raise temperature), for reasons discussed below. For incompressible substances such as solids, the difference between C_V and C_P is generally small.

2.6.2 CONSTANT PRESSURE HEAT CAPACITY

In geochemistry, constant volume situations are rare and temperature changes at constant pressure are of greater interest. Equation 2.61 states that $\Delta H = \Delta Q_p$. Substituting this expression in equation 2.66 we have:

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P} \qquad 2.68$$

Thus enthalpy change at constant pressure may also be expressed as:

$$dH = C_P dT \qquad 2.69$$

In geochemistry, it will be mainly constant pressure heat capacity that will be of primary interest to us, because in natural situations, volumes do not usually remain fixed.

2.6.3 Energy Associated with Volume and the Relationship between C_V and C_P

Constant pressure and constant temperature heat capacities are different because there is energy associated (work done) with expansion and contraction. Thus how much energy we must transfer to a substance to raise its temperature will depend on whether some of this energy will be consumed in this process of expansion. These energy changes are due to potential energy changes associated with changing the position of an atom or molecule in the electrostatic fields of its neighbors. The difference between C_v and C_p reflects this energy associated with volume. Let's now determine what this difference is.

We can combine relations 2.67 and 2.68 as:

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \qquad 2.70$$

From this, we may derive the following relationship:

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P \qquad 2.71$$

and further:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad 2.72$$

It can also be shown that, for a reversible process:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\beta} - P \qquad 2.73$$

$(\partial U/\partial V)_T$ is the energy associated with the volume occupied by a substance and is known as the *internal pressure* (P_{int}, which we introduced earlier in our discussion of the van der Waals law, e.g., equation 2.17). It is a measure of the energy associated with the forces holding molecules or atoms together. For real substances, energy changes associated with volume changes reflect potential energy increases associated with increase separation between charged molecules and/or atoms; there are no such forces in an ideal gas, so this term is 0 for an ideal gas. Substituting 2.73 into 2.72, we obtain:

$$C_P - C_v = T\bar{V}\frac{\alpha^2}{\beta} \qquad 2.74$$

Thus the difference between C_p and C_v will depend on temperature and pressure for real substances. The terms on the right will always be positive, so that C_p will always be greater than C_v. This accords with our expectation, since energy will be consumed in expansion when a substance is heated at con-

Example 2.2: Measuring Enthalpies of Reaction

Sodium reacts spontaneously and vigorously with oxygen to form Na_2O. The heat given off by this reaction is the enthalpy of formation ΔH_f of Na_2O. Suppose that you react 23 g of Na metal with oxygen in a calorimeter that has the effective heat capacity of 5 kg of water. The heat capacity of water is 75.3 J/mol K. If the calorimeter has a temperature of 20°C before the reaction and a temperature of 29.9°C after the reaction, what is ΔH_f of Na_2O? Assume that the Na_2O contributes negligibly to the heat capacity of the system.

Answer: The heat capacity of the calorimeter is

$$75.3\text{J/mol K} \times 5000\text{g} \div 18\text{g/mol} = 20917\text{ J/K.}$$

The heat required to raise its temperature by 9.9 K is then

$$9.9 \times 20917 = 207.08\text{ kJ}$$

which is the enthaply of this reaction. Our experiment created 0.5 moles of Na_2O, so ΔH is –414.16 kJ/mol.

stant pressure, whereas this will not be the case for heating at constant volume. For an ideal gas, C_p–C_v = R.

For gases, it is fairly straightforward to measure either C_p or C_v. It is impractical to measure C_v for solids and liquids. Thus only experimentally determined values of C_p are available for solids and liquids, and values of C_v must be obtained from equation 2.74 when required.

We found earlier that C_p is the variation of heat with temperature at constant pressure. How does this differ from the variation of energy with temperature at constant volume? To answer this question, we rearrange equation 2.71 and substitute C_v for $(\partial U/\partial T)_V$ and $V\alpha$ for $(\partial V/\partial T)_P$. After simplifying the result, we obtain (on a molar basis):

$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - P\bar{V}\alpha \qquad 2.75$$

For an ideal gas, the term $PV\alpha$ reduces to R, so that $(\partial U/\partial T)_P = C_p - R$. $C_p - R$ may be shown to be equal to C_V, so the energy change with temperature for an ideal gas is the same for both constant pressure and constant volume conditions. This is consistent with the notion that the difference between C_p and C_v reflects the energy associated with and changing distances between atoms and molecules in the presence of attractive forces between them. In an ideal gas, there are no such forces, hence $(\partial U/\partial T)_P = (\partial U/\partial T)_V$.

2.6.4 Heat Capacity of Solids: A Problem in Quantum Physics

As we shall see, knowledge of the heat capacity of substances turns out to be critical to determining properties such as enthalpy and entropy, and, ultimately, to predicting chemical equilibrium. The heat capacity of a substance reflects the internal motion of its atoms. There are 3 kinds of motion available to atoms and molecules: translational, vibrational and rotational[£], but often one or more of these modes will not be available and not contribute to the energy of a substance. For gases at low temperature, only rotational and translational motions are important (for a monatomic gas, only translational modes are available), while only vibrational motions are important for solids (translational modes are available to solids, which is why solids have finite vapor pressures, but they are extremely improbable, which is why vapor pressures of solids are very small and can usually be neglected). Twice as much energy is typically required to raise the temperature of a vibrational mode by 1 K as for a translational mode. This is because vibration involves both kinetic and potential energy of two or more atoms. Also, vibrational modes do not accept much energy at low temperature. This latter phenomenon is not predicted by classical physics; as a result 19th century physicists were puzzled by the temperature dependence of heat capacity. In 1869 James Maxwell referred to the problem as "the greatest difficulty yet encountered in molecular theory." The solution required a more radical revision to physics than Maxwell imagined: the heat capacity problem turned out to be one of the first indications of the inadequacy of classical physics. An understanding of the dependence of heat capacity on temperature was only achieved in the 20th century with the aid of quantum physics. A complete theoretical treatment of heat capacity of real substances is beyond the scope of this book. However, even the few statements we will make will require us to make another excursion into statistical mechanics, a closely related field to discover the Boltzmann Distribution Law. What we learn will be of considerable use in subsequent chapters.

2.6.4.1 The Boltzmann Distribution Law

Consider a mineral sample, A, in a heat bath, B (B having much more mass than A), and assume they are perfectly isolated from their surroundings. The total energy of the system is fixed, but the energy of A and B will oscillate about their most probable values. The question we ask is *what is the probability that system A is in* a *state such that it has energy* E_A*?*

[£] R. Clausius recognized the possibility that molecules might have these three kinds of motion in 1855.

We assume that the number of states accessible to A when it has energy E_A is some function of energy, i.e.,

$$\Omega(a) = \Omega(E_A) \qquad 2.76$$

Following the basic postulate, we also assume that all states are equally probable and that the probability of a system having a given energy is simply proportional to the number of states the system can assume when it has that energy:

$$\mathcal{P} = C\,\Omega \qquad (2.39)$$

where C is a constant. Thus the probability of A being in state *a* with energy E_A is:

$$\mathcal{P}_a = C_A\Omega(E_A) \qquad 2.77$$

Since the total energy of the two system is fixed, system B will have some fixed energy E_B when A is in state *a* with energy E_A, and:

$$E_B = E - E_A$$

where E is the total energy of the system. As we mentioned earlier, Ω is multiplicative, so the number of states available to the total system, A + B, is the product of the number of states available to A times the states available to B:

$$\Omega_{Total} = \Omega_A\Omega_B$$

If we stipulate that A is in state *a*, then Ω_A is 1 and the total number of states available to the system in that situation is just Ω_B:

$$\Omega_{Total} = 1 \times \Omega_B = \Omega(E_B)$$

Thus the probability of finding A in state *a* is equal to the probability of finding B in one of the states associated with energy E_B, so that:

$$\mathcal{P}_a = C_B\Omega(E_B) = C_B\Omega(E - E_A) = C_B\exp[\ln\Omega\,(E - E_A)] \qquad 2.78$$

where E is the total energy of the system (i.e., $E = E_A + E_B$). We can expand ln Ω ($E\text{-}E_A$) as a Taylor Series about E:

$$\ln\Omega(E - E_A) = \ln\Omega(E) - E_A\left(\frac{d\ln\Omega(E)}{dE}\right) + \ldots \qquad 2.79$$

and since B is much larger than A, $E >> E_A$, higher order terms may be neglected.

Substituting β for $\partial\ln\Omega(E)/dE$ (Equ 2.48), we have:

$$\Omega(E - E_A) = \exp(\ln\Omega(E) - E_A\beta) = \Omega(E)e^{-\beta E_A}$$

and

$$\mathcal{P}_a = C_B\Omega(E)e^{-\beta E_A} \qquad 2.80$$

Since the total energy of the system, E, is fixed, Ω(E) must also be fixed, i.e., constant, so:

$$\mathcal{P}_a = Ce^{-\beta E_A} \qquad 2.81$$

Substituting 1/kT for β (Equ. 2.53), we have:

$$\mathcal{P}_a = Ce^{-E_A/kT}$$

We can deduce the value of the constant C by noting that $\sum\mathcal{P}_i = 1$, i.e., the probabilities over all energy levels must sum to one (because the system *must always* be in one of these states). Therefore:

$$\sum\mathcal{P}_i = C\sum e^{-\beta E_i} = 1 \qquad 2.82$$

so that

$$C = 1/\sum e^{-\beta E_i} \qquad 2.83$$

Generalizing our result, the probability of the system being in state *i* corresponding to energy ε_i is:

$$\mathcal{P}_i = \frac{e^{-\epsilon_i / kT}}{\sum_n e^{-\epsilon_n / kT}} \qquad 2.84$$

This equation is the *Boltzmann distribution law**, and one of the most important equations in statistical mechanics. Though we derived it for a specific situation and introduced an approximation (the Taylor Series expansion), these were merely conveniences; the result is very general. If we define our "system" as an atom or molecule, then this equation tells us the probability of an atom having a given energy value, ε_i. This is the statistical mechanical interpretation of this equation. The basic tenet of quantum physics is that energy is quantized: only discrete values are possible. The Boltzmann distribution law tells the probability of an atom having the energy associated with quantum level *i*.

The Boltzmann distribution law says that the population of energy levels decreases exponentially as the energy of that level increases (*energy among atoms is like money among men: the poor are many and the rich few*). A hypothetical example is shown in Figure 2.9.

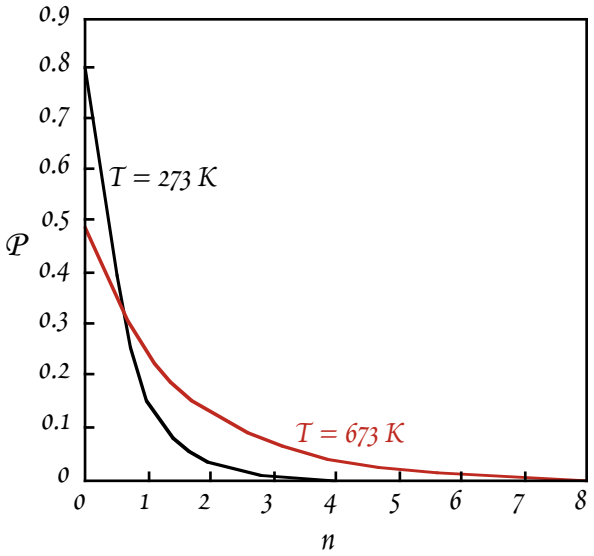


Figure 2.9. Occupation of vibrational energy levels calculated from the Boltzmann distribution. The probability of an energy level associated with the vibrational quantum number *n* is shown as a function of *n* for a hypothetical diatomic molecule at 273 K and 673 K.

2.6.4.2 The Partition Function

The denominator of Equ. 2.84, which is the probability normalizing factor or the *sum of the energy distribution over all accessible states*, is called the *partition function* and is denoted Q:

$$Q = \sum_i e^{-\epsilon_i / kT} \qquad 2.85$$

The partition function is a key variable in statistical mechanics and quantum physics. It is related to macroscopic variables with which we are already familiar, namely energy and entropy. Let's examine these relationships.

We can compute the total internal energy of a system, U, as the average energy of the atoms times the number of atoms, *n*. To do this we need to know how energy is distributed among atoms. Macroscopic systems have a very large number of atoms (~10^{23}, give or take a few in the exponent). In this case, the number of atoms having some energy ε_i is proportional to the probability of one atom having this energy. So to find the average, we take the sum over all possible energies of the product of energy times the possibility of an atom having that energy. Thus the internal energy of the system is just:

* We now understand and interpret this law in terms of quantum physics, but Boltzmann formulated it 30 years before Planck and Einstein laid the foundations of quantum theory. Ludwig Boltzmann's work in the second half of the nineteenth century laid the foundations of statistical mechanics and paved the way for quantum theory in the next century. His work was heavily attacked by other physicists of the time, who felt physics should deal only with macroscopic observable quantities and not with atoms, which were then purely hypothetical constructs. These attacks contributed to increasingly frequent bouts of depression, which ultimately led to Boltzmann's suicide in 1906. Ironically and sadly, this was about the time that Perrin's experiments with Brownian motion, Millikan's oil drop experiment, and Einstein's work on the photoelectric effect confirmed the discrete nature of mass, charge, and energy, and thereby the enduring value of Boltzmann's work.

$$U = n\sum_i \varepsilon_i \mathcal{P}_i = \frac{n\sum \varepsilon_i e^{-\varepsilon_i/kT}}{Q} \qquad 2.86$$

The derivative of Q with respect to temperature (at constant volume) can be obtained from 2.85:

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{kT}\sum \varepsilon_i e^{-\varepsilon_i/kT} \qquad 2.87$$

Comparing this with equation 2.86, we see that this is equivalent to:

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{Q}{nkT^2}U \qquad 2.88$$

It is also easy to show that $\partial \ln Q/\partial T = 1/Q\,\partial Q/\partial T$, so the internal energy of the system is:

$$U = nkT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \qquad 2.89$$

For 1 mole of substance, n is equal to Avagadro's number, N_0. Since $R = N_0 k$, equation 2.89, when expressed on a molar basis, becomes:

$$U = RT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \qquad 2.90$$

We should not be surprised to find that entropy is also related to Q. This relationship, the derivation of which is left to you (Problem 2.12), is:

$$S = \frac{\bar{U}}{T} + R\ln Q \qquad 2.91$$

Since the partition function is a sum over all possible states, it might appear that computing it would be a formidable, if not impossible, task. As we shall see, however, *the partition function can very often be approximated to a high degree of accuracy by quite simple functions*. The partition function and Boltzmann distribution will prove useful to us in subsequent chapters in discussing several geologically important phenomena such as diffusion and the distribution of stable isotopes between phases, as well as in understanding heat capacities.

2.6.4.3 Energy Distribution in Solids

According to quantum theory, all modes of motion are quantized. Consider, for example, vibrations of atoms in a hydrogen molecule. Even at absolute zero temperature, the atoms will vibrate at a ground state frequency. The energy associated with this vibration will be:

$$\varepsilon_0 = \tfrac{1}{2}\, h\nu_0 \qquad 2.92$$

where h is Planck's constant and ν_0 is the vibrational frequency of the ground state. Higher quantum levels have higher frequencies (and hence higher energies) that are multiples of this ground state:

$$\varepsilon_n = (n+\tfrac{1}{2})h\nu_0 \qquad 2.93$$

where n is the quantum number (an integer ≥ 0).

Now consider a monatomic solid, such as diamond, composed of N identical atoms arranged in a crystal lattice. For each vibration of each atom, we may write an atomic partition function, q. Since vibrational motion is the only form of energy available to atoms in a lattice, the atomic partition function may be written as:

$$q = \sum_m e^{-\varepsilon_m/kT} = \sum_n^{\infty} e^{-(n+\frac{1}{2})h\nu_0/kT} \qquad 2.94$$

We can rewrite 2.94 as: $$q = e^{-h\nu_0/2kT} \sum_{n}^{\infty} e^{-nh\nu_0/kT} \quad 2.95$$

The summation term can be expressed as geometric series, $1 + x + x^2 + x^3 + ...$, where $x = e^{-h\nu_0/kT}$. Such a series is equal to $1/(1 - x)$ if $x<1$. Thus 2.95 may be rewritten in simpler form as:

$$q = \frac{e^{-h\nu_0/2kT}}{1-e^{-h\nu_0/kT}} \quad 2.96$$

At high temperature, $h\nu_0/kT << 1$, and we may approximate $e^{-h\nu_0/kT}$ in the denominator of Equ. 2.96 by $1 - h\nu_0/kT$, so that at high temperature:

$$q \cong \frac{kTe^{-h\nu_0/2kT}}{h\nu_0} \quad 2.97$$

Using this relationship, and those between constant volume heat capacity and energy and between energy and the partition function it is possible to show that:

$$C_V = 3R \quad 2.98$$

This is called the *Dulong-Petit Limit* and it holds only where the temperature is high enough that the approximation $e^{-h\nu_0/kT} = 1-h\nu_0/kT$ holds. For a solid consisting of N different kinds of atoms, the predicted heat capacity is 3NR. Observations bear out these predictions. For example, at 25°C the observed heat capacity for NaCl, for which N is 2, is 49.7 J/K, whereas the predicted value is 49.9 J/K. Substances whose heat capacity agrees with that predicted in this manner are said to be *fully activated*. The temperature at which this occurs, called the *characteristic* or *Einstein temperature*, varies considerably from substance to substance (for reasons explained below). For most metals, it is in the range of 100 to 600 K. For diamond, however, the Einstein temperature is in excess of 2000 K.

Now consider the case where the temperature is very low. In this case, the $h\nu_0/kT >> 1$ and the denominator of equation 2.99 therefore tends to 1, so that 2.99 reduces to:

$$q \cong e^{-h\nu_0/2kT} \quad 2.99$$

The differential with respect to temperature of $\ln q$ is then simply:

$$\left(\frac{\partial q}{\partial T}\right)_V = \frac{h\nu_0}{2kT} \quad 2.100$$

If we insert this into equation 2.90 and then into 2.80 and differentiate U with respect to temperature, we find that the predicted heat capacity is 0! In actuality, only a perfectly crystalline solid would have 0 heat capacity near absolute 0. Real solids have a small but finite heat capacity.

On a less mathematical level, the heat capacities of solids at low temperature are small because the spacings between the first few vibrational energy levels are large. As a result, energy transitions are large and therefore improbable. Thus at low temperature, relatively little energy will go into vibrational motions.

We can also see from equation 2.93 that the gaps between energy levels depend on the fundamental frequency ν_0. The larger the gap in vibrational frequency, the less likely will be the transition to higher energy states. The ground state frequency in turn depends on bond strength. Strong bonds have higher vibrational frequencies and as a result, energy is less readily stored in atomic vibrations. In general, covalent bonds will be stronger than ionic ones, which in turn are stronger than metallic bonds. Thus diamond, which has strong covalent bonds, has a low heat capacity until it is fully activated, and full activation occurs at very high temperatures. The bonds in quartz and alumina (Al_2O_3) are also largely covalent, and these substances also have low heat capacities until fully activated. Metals, on the other hand, tend to have weaker bonds and high heat capacities.

Heat capacities are more difficult to predict at intermediate temperatures and require some knowledge of the vibrational frequencies. One simple assumption, used by Einstein‡, is that all vibrations have the same frequency. The Einstein model provides reasonable predictions of C_V at intermediate and high temperatures, but does not work well at low temperatures. A somewhat more sophisticated assumption was used by Debye§, who assumed a range of frequencies up to a maximum value, ν_D, now called the *Debye frequency*, and then integrated the frequency spectrum. The procedure is too complex for us to treat here. At low temperature, the Debye theory predicts:

$$C_V = \frac{12\pi^4}{5} NR\left(\frac{T}{\theta_D}\right)^3 \qquad 2.101$$

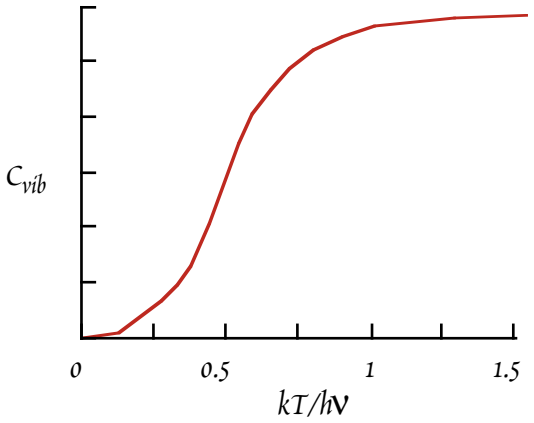


Figure 2.10. Vibrational contribution to heat capacity as a function of kT/hν.

where $\theta_D = h\nu_D/k$ and is called the *Debye temperature*.

Nevertheless, geochemists generally use empirically determined heat capacities. Constant pressure heat capacities are easier to determine, and therefore more generally available and used. For minerals, which are relatively incompressible, the difference between C_v and C_p is small and can often be neglected. Empirical heat capacity data is generally in the form of the coefficients of polynomial expressions of temperature. The *Maier-Kelley formulation* is:

$$C_P = a + bT - \frac{c}{T^2} \qquad 2.102$$

where *a*, *b*, and *c* are the empirically determined coefficients. The *Haas-Fisher* formulation is:

$$C_P = a + bT + \frac{c}{T^2} + fT^2 + gT^{-1/2} \qquad 2.103$$

with *a*, *b*, *c*, *f*, and *g* as empirically determined constants.

Since these formulae and there associated constants are purely empirical (i.e., neither the equations nor constants have a theoretical basis), they should not be extrapolated beyond the calibrated rang.

2.6.5 Relationship of Entropy to Other State Variables

We can now use heat capacity to define the temperature dependency of entropy:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \qquad 2.104 \qquad\qquad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \qquad 2.105$$

The dependencies on pressure and volume (at constant temperature) are:

---

‡ Albert Einstein, though best know for his relativity theories, was also the founder, along with Max Planck, of quantum physics. His work on the quantum basis of heat capacity of solids was published in 1907. Einstein was born in 1879 in Ulm, Germany, and published some of his most significant papers while working as a patent clerk in Bern, Switzerland. He later joined the Prussian Academy of Sciences in Berlin. A dedicated and active pacifist, Einstein left Germany when Hitler came to power in 1933. He later joined the Center for Advanced Studies in Princeton, New Jersey. He died in Princeton in 1955.

§ Peter Debye (1884-1966) was born in Maastricht, Netherlands (as Petrus Debije), but spent much of his early career in Germany, eventually become director of the Kaiser-Wilhelm-Institut in Berlin. While he was visiting Cornell University in 1940, Germany invaded Holland and Debye simply remained at Cornell, eventually becoming chairman of the Chemistry Department. Debye made numerous contributions to physics and physical chemistry; we shall encounter his work again in the next chapter.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\alpha V \qquad 2.106 \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta} \qquad 2.107$$

2.6.6 Additive Nature of Silicate Heat Capacities

For many oxides and silicates, heat capacities are approximately additive at room temperature. Thus, for example, the heat capacity of enstatite, $MgSiO_3$, may be approximated by adding the heat capacities of its oxide components, quartz (SiO_2) and periclase (MgO). In other words since:

$$SiO_2 + MgO \rightarrow MgSiO_3$$

then $$C_{p\text{-En}} \approx C_{p\text{-Qz}} + C_{p\text{-Pe}}$$

Substituting values: $C_{p\text{-En}} \approx 10.62 + 9.03 = 19.65$ cal/mol-K

The observed value for the heat capacity of enstatite at 300 K is 19.62 cal/mol-K, which differs from our estimate by only 0.1%. For most silicates and oxides, this approach will yield estimates of heat capacities that are within 5% of the observed values. However, this is not true at low temperature. The same calculation for $C_{p\text{-En}}$ carried out using heat capacities at 50 K differs from the observed value by 20%.

The explanation for the additive nature of oxide and silicate heat capacities has to do with the nature of bonding and atomic vibrations. The vibrations that are not fully activated at room temperature are largely dependent on the nature of the individual cation-oxygen bonds and not on the atomic arrangement in complex solids.

2.7 The Third Law and Absolute Entropy

2.7.1 Statement of the Third Law

The entropies of substances tend toward zero as absolute zero temperature is approached. Or as Lewis and Randall expressed it:

> *If the entropy of each element in some crystalline state may be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy, but at absolute zero, the entropy may become zero, and does so become in the case of perfectly crystalline substances.*

2.7.2 Absolute Entropy

We recall that entropy is proportional to the number of possible arrangements of a system: $S = k \ln \Omega$. At absolute zero, a perfectly crystalline substance has only one possible arrangement, namely the ground state. Hence $S = k \ln 1 = 0$.

The implication of this seemingly trivial statement is that we can determine the absolute entropy of substances. We can write the complete differential for S in terms of T and P as:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad 2.108$$

Substituting equations 2.106 and 2.107, we have:

$$dS = \frac{C_P}{T} dT - \alpha V dP \qquad 2.108$$

The coefficient of thermal expansion is 0 at absolute 0; the choice of 1 atm for the heat capacity integration is a matter of convenience because C_P measurements are made at 1 atm.

Actually, the absolute entropies of real substances tend not to be zero at absolute zero, which is to say they are not 'perfectly crystalline' in the third law sense. A residual entropy, S_0, which reflects such things as mixing of two or more kinds of atoms (elements or even isotopes of the same element) at crystallographically equivalent sites, must also be considered. This *configurational entropy* is important for some geologically important substances such as feldspars and amphiboles. Configurational entropy can be calculated as

$$S_{conf} = -R\sum_j m_j \sum_i X_{ij} \ln X_{ij} \qquad 2.110$$

where m_j is the total number of atoms in the *jth crystallographic* site (in atoms per formula unit) and $X_{i,j}$ is the mole fraction of the i^{th} atom (element) in the j^{th} site. We will return to this equation when we consider multicomponent systems.

2.8 Calculating Enthalpy and Entropy Changes

Example 2.3: Configurational Entropy

Olivine is an example of a solid solution, which we will discuss at length in Chapter 3. Fe and Mg may substitute for each other in the octahedral site. Assuming that the distribution of Fe and Mg within this site is purely random, what is the configurational entropy of olivine of the composition $(Mg_{0.8},Fe_{0.2})_2SiO_4$?

Answer: To solve this problem, we need to apply equation 2.110. We need only consider the octahedral site containing Fe and Mg, because O and Si are the only kinds of atoms occupying the tetrahedral and anion sites. The values for X for these 2 sites will therefore be 1, and ln (1) = 0, so there is no contribution to configurational entropy.

For the octahedral site, $m = 2$, $X_1 = X_{Mg} = 0.8$ and $X_2 = X_{Fe} = 0.2$. Therefore, the configurational entropy will be:

$$S_{conf} = -8.314 \times 2\,(0.8\ln(0.8) + 0.2\ln(0.2)) = 8.32 \text{ J mol}^{-1}\text{K}^{-1}$$

2.8.1 Enthalpy Changes due to Changes in Temperature and Pressure

From equation 2.62, we can see that the temperature derivative of enthalpy is simply the isobaric heat capacity:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

and hence:

$$dH = C_P\, dT \qquad 2.111$$

Thus the change in enthalpy over some temperature interval may be found as:

$$\Delta H = \int_{T_1}^{T_2} C_P dT \qquad 2.112$$

C_p is often a complex function of temperature, so the integration is essential. Example 2.4 below illustrates how this is done.

Isothermal enthalpy changes refer are those occurring at constant temperature, for example, changes in enthalpy due to isothermal pressure changes. Though pressure changes at constant temperature are relatively rare in nature, hypothetical isothermal paths are useful in calculating energy changes. Since enthalpy is a state property, the net change in the enthalpy of a system depends only on the starting and ending state, i.e., the enthalpy change is path-independent. Imagine a system consisting of a quartz crystal that undergoes a change in state from 25°C and 1 atm to 500° and 400 atm. How will the enthalpy of this system change? Though in actuality the pressure and temperature changes may have occurred simultaneously, because the enthalpy change is path-independent, we can treat the problem as an isobaric temperature change followed by an isothermal temperature change, as illustrated in Figure 2.11. Knowing how to calculate isothermal enthalpy

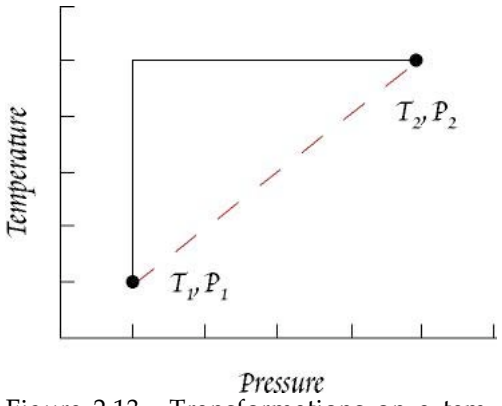


Figure 2.13. Transformations on a temperature-pressure diagram. Changes in state variables such as entropy and enthalpy are path independent. For such variables, the transformation paths shown by the solid line and dashed line are equivalent.

changes is useful for this reason.

We want to know how enthalpy changes as a function of pressure at constant temperature. We begin from equation 2.76, which expresses the enthalpy change as a function of volume and pressure:

$$dH = dU + VdP + PdV \qquad (2.63)$$

By making appropriate substitutions for dU, we can derive the following of enthalpy on pressure:

$$dH = V(1 - \alpha T)dP \qquad 2.112$$

If changes are large, α, β, and V must be considered functions of T and P and and integration performed over the pressure change. The isothermal enthalpy change due to pressure change is thus given by:

$$\Delta H = \int_{P_1}^{P_2} V(1 - \alpha T)dP \qquad 2.113$$

Example 2.4: Calculating Isobaric Enthalpy Changes

How does the enthalpy of a 1 mol quartz crystal change if it is heated from 25° C to 300° C if the temperature dependence of heat capacity can be expressed as $C_p = a + bT - cT^{-2}$ J/K-mol, and a = 46.94, b = 0.0343, and c = 1129680? Assume pressure is constant.

The first step is to convert temperature to kelvins: all thermodynamic formulae assume temperature is in kelvins. So T_1 = 298 K and T_2 = 573 K. To solve this problem, we need to use equation 2.112. Substituting the expression for heat capacity into Equ. 2.112, we have:

$$\Delta H = \int_{298}^{573}\left(a + bT - cT^{-2}\right)dT = a\int_{298}^{573} dT + b\int_{298}^{573} TdT - c\int_{298}^{573} T^{-2}dT$$

Performing the integral, we have:

$$\Delta H = \left[aT + \frac{b}{2}T^2 + \frac{c}{T}\right]_{298}^{573} = \left[46.94 \times T + \frac{0.0343}{2}T^2 + \frac{1129680}{T}\right]_{298}^{573}$$

Now that we have done the math, all that is left is arithmetic. This is most easily done using a spreadsheet. Among other things, it is much easier to avoid arithmetical errors. In addition, we have a permanent record of what we have done. We might set up a spreadsheet to calculate this problem as follows:

	Values			Formulae & Results	
a	46.94		H	(a*Temp)+(b*Temp^2/2)+(c_/Temp)	
b	0.0343		H1	19301.98	J/mol
c	1129680		H2	34498.98	J/mol
Temp1	298		**ΔH=**	**15.20**	**kJ/Mol**
Temp2	573				

This example is from Microsoft Excel™. One the left, we have written down the names for the various constants in one column, and their values in an adjacent one. Using the Create Names command, we assigned the names in the first column to the values in the second (to avoid confusion with row names, we have named T_1 and T_2 Temp1 and Temp2 respectively; Excel automatically added an underline to 'c', so this constant appears as c_ in our formula). In the column on the right, we have written the formula out in the second row, then evaluated it at T_1 and T_2 in the third and forth rows respectively. The last row, in bold, contains our answer, 15.2 kJ/mole, determined simply by subtracting 'H1' from 'H2' (and dividing by 1000). *Hint*: we need to keep track of units. Excel won't do this for us.

2.8.3 Changes in Enthalpy due to Reactions and Change of State

We cannot measure the absolute enthalpy of substances, but we can determine the enthalpy *changes* resulting from transformations of a system, and they are of great interest in thermodynamics. For this purpose, a system of relative enthalpies of substances has been established. Since enthalpy is a function of both temperature and pressure, the first problem is to establish standard conditions of temperature

and pressure to which these enthalpies apply. These conditions, by convention, are 298.15 K and 0.1 MPa (25° C and 1 bar). Under these conditions the elements are assigned enthalpies of 0. *Standard state enthalpy of formation*, or heat of formation, from the elements, $\Delta H°$, can then be determined for compounds by measuring the heat evolved in the reactions that form them from the elements (e.g., Example 2.2). For example, the heat of formation of water is determined from the energy released at constant pressure in the reaction: $H_2 + {}^1/_2 O_2 \rightarrow H_2O$, which yields a $\Delta H°$ of -285.83 kJ/mol, where water is in the liquid state. *The minus sign indicates heat is liberated in the reaction*, i.e., the reaction is *exothermic* (a reaction that consumes heat is said to be *endothermic*).

Having established such a system, the enthalpy associated with a chemical reaction is easily calculated using Hess's Law, which is:

$$\boxed{\Delta H_r = \sum_i \nu_i \Delta H^0_{f,i}} \qquad 2.114$$

where ν_i is the stoichiometric coefficient for the i^{th} species. In other words, the enthalpy of reaction is just the total enthalpy of the products less the total enthalpy of the reactants. The use of Hess's Law is illustrated in Example 2.5 below.

The *heat of vaporization* of a substance is the energy required to convert that substance from liquid to gas, i.e., to boil it. If the reaction $H_2 + {}^1/_2 O_2 \rightarrow H_2O$ is run to produce water vapor, the $\Delta H°$ turns out to be -241.81 kJ/mol. The difference between the enthalpy of formation of water and vapor, 44.02 kJ/mol, is the heat consumed in going from liquid water to water vapor, or This is exactly the amount of energy that would be required to boil 1 mole of water, i.e., convert it from liquid to gas. Analogously, the *heat of melting* (or fusion) is the enthalpy change in the melting of a substance. Because reaction rates are often very slow, and some compounds are not stable at 298 K and 1 MPa, it is not possible to measure the enthalpy for every compound. However, the enthalpies of formation for these compounds can generally be calculated indirectly.

Example 2.4: Enthalpies (or Heats) of Reaction and Hess's Law

What is the energy consumed or evolved in the hydration of corundum (Al_2O_3) to form gibbsite ($Al(OH)_3$)? The reaction is:

$$\frac{1}{2}\,Al_2O_3 + \frac{3}{2}\,H_2O \rightarrow Al(OH)_3$$

Answer: We use *Hess's Law*. To use Hess's Law we need the standard state enthalpies for water, corundum, and gibbsite. These are: Al_2O_3: -1675.70 kJ/mol, H_2O: -285.83 and $Al(OH)_3$: -1293.13. The enthalpy of reaction is $\Delta H_r = -1293.13 - (0.5 \times -1675.70) - (1.5 \times -285.83) = -26.53$ kJ

This is the enthalpy of reaction at 1 bar and 298° K. Suppose you were interested in this reaction under metamorphic conditions such as 300° C and 50 MPa. How would you calculate the enthalpy of reaction then?

2.8.4 Entropies of Reaction

Since $dH = dQ_p$ (2.62) and $dS_{rev} = \frac{dQ}{T}$ (2.57)

then at constant pressure: $$dS_{rev} = \frac{dH}{T} \qquad 2.115$$

Thus at constant pressure, the entropy change in a reversible reaction is simply the ratio of enthalpy change to temperature.

Entropies are additive properties and entropies of reaction can be calculated in the same manner as for enthalpies, i.e., Hess's Law applies:

$$\Delta S_r = \sum_i \nu_i \Delta S^0_{f,i} \qquad 2.116$$

The total entropy of a substance can be calculated as:

$$S_{298} = \int_0^{298} \frac{C_P dT}{T} + S_0 + \Delta S_\phi \qquad 2.117$$

where S_0 is the entropy at 0 K (configurational, or 'third law' entropy) and ΔS_Φ is the entropy change associated with any phase change. Compilations for S_{298} are available for many minerals. Table 2.2 lists some heat capacity constants for the power series formula as well as other thermodynamic data for a few geologically important minerals.

2.9 FREE ENERGY

We can now introduce two free energy functions, the Helmholtz Free Energy and the Gibbs Free En-

TABLE 2.2: STANDARD STATE THERMODYNAMIC DATA FOR SOME IMPORTANT MINERALS

Phase/ Compound	Formula	ΔH_f^o (kJ/mol)	S° (J/K-mol)	ΔG_f^o (kJ/mol)	$\overline{V}$ (cc/mol)*	C_p a	b	c
H_2O_g	H_2O(gas)	-241.81	188.74	-228.57	24789.00	30.54	0.01029	0
H_2O_l	H_2O(liquid)	-285.84	69.92	-237.18	18.10	29.75	0.03448	0
CO_2	CO_2	-393.51	213.64	-394.39	24465.10	44.22	0.00879	861904
Calcite	$CaCO_3$	-1207.30	92.68	-1130.10	36.93	104.52	0.02192	2594080
Graphite	C	0	5.740		5.298			
Diamond	C	1.86	2.37		3.417			
Aragonite	$CaCO_3$	-1207.21	90.21	-1129.16	34.15	84.22	0.04284	1397456
α-Qz	SiO_2	-910.65	41.34	-856.24	22.69	46.94	0.03431	1129680
β-Qz	SiO_2	-910.25	41.82	-856.24		60.29	0.00812	0
Cristobal.	SiO_2	-853.10	43.40	-853.10	25.74	58.49	0.01397	1594104
Coesite	SiO_2	-851.62	40.38	-851.62	20.64	46.02	0.00351	1129680
Periclase	MgO	-601.66	26.94	-569.38	11.25	42.59	0.00728	619232
Magnetite	Fe_3O_4	-1118.17	145.73	-1014.93	44.52	91.55	0.20167	0
Spinel	$MgAl_2O_4$	-2288.01	80.63	-2163.15	39.71	153.86	0.02684	4062246
Hem	Fe_2O_3	-827.26	87.61	-745.40	30.27	98.28	0.07782	1485320
Corundum	Al_2O_3	-1661.65	50.96	-1568.26	25.58	11.80	0.03506	3506192
Kyanite	Al_2SiO_5	-2581.10	83.68	-2426.91	44.09	173.18	0.02853	5389871
Andalusite	Al_2SiO_5	-2576.78	92.88	-2429.18	51.53	172.84	0.02633	5184855
Sillimanite	Al_2SiO_5	-2573.57	96.78	-2427.10	49.90	167.46	0.03092	4884443
Almandine	$Fe_3Al_2Si_3O_{12}$	-5265.5	339.93	-4941.73	115.28	408.15	0.14075	7836623
Grossular	$Ca_3Al_2Si_3O_{12}$	-6624.93	254.68	-6263.31	125.30	435.21	0.07117	11429851
Albite	$NaAlSi_3O_8$	-3921.02	210.04	-3708.31	100.07	258.15	0.05816	6280184
K-feldspar	$KAlSi_3O_8$	-3971.04	213.93	-3971.4	108.87	320.57	0.01804	12528988
Anorthite	$CaAl_2Si_2O_8$	-4215.60	205.43	-3991.86	100.79	264.89	0.06190	7112800
Jadeite	$NaAlSi_2O_6$	-3011.94	133.47	-2842.80	60.44	201.67	0.04770	4966408
Diospide	$CaMgSi_2O_6$	-3202.34	143.09	-3029.22	66.09	221.21	0.03280	6585616
Enstatite	$MgSiO_3$	-1546.77	67.86	-1459.92	31.28	102.72	0.01983	2627552
Forsterite	Mg_2SiO_4	-2175.68	95.19	-2056.70	43.79	149.83	0.02736	3564768
Clinozo	$Ca_2Al_3Si_3O_{12}(OH)$	-68798.42	295.56	-6482.02	136.2	787.52	0.10550	11357468
Tremolite	$Ca_2MgSi_8O_{22}(OH)_2$	-12319.70	548.90	-11590.71	272.92	188.22	0.05729	4482200
Chlorite	$MgAl(AlSi_3)O_{10}(OH)_8$	-8857.38	465.26	-8207.77	207.11	696.64	0.17614	15677448
Pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	-12623.40	669.44	-11950.58	273.5	861.07	0.17431	21007864
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	-6226.07	287.86	-5841.65	149.66	420.95	0.01204	8995600
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	-5972.28	287.86	-5591.08	140.71	408.19	0.110374	10644096
Gibbsite	$Al(OH)_3$	-1293.13	70.08	-1155.49	31.96	36.19	0.19079	0
Boehmite	AlO(OH)	-983.57	48.45	-908.97	19.54	60.40	0.01757	0
Brucite	$Mg(OH)_2$	-926.30	63.14	-835.32	24.63	101.03	0.01678	2556424

Data for the standard state of 298.15 K and 0.1 MPa. ΔH_f^o is the molar heat (enthalpy) of formation from the elements ; S° is the standard state entropy; V is the molar volume; a, b and c are constants for the heat capacity (C_p) computed as: $C_p = a + bT - cT^{-2}$ J/K-mol. Modified from Helgeson et al. (1978).
*cc/mol = J/MPa/mol.

ergy. The Gibbs Free Energy is one of the most useful functions in thermodynamics.

2.9.1 Helmholtz Free Energy

We can rearrange equation 2.58 to read dU - TdS = -PdV. The -PdV term is the work term and the TdS term is the heat function. TdS is the energy unavailable for work. Therefore *dU - TdS is the amount of internal energy available for work*, or the *Free Energy*. We define it as A, the *Helmholtz Free Energy:*

$$A \equiv U - TS \qquad 2.118$$

As usual, we are interested in the differential form (since we are more interested in changes than in absolutes):

$$dA = dU - d(TS) = dU - SdT - TdS \qquad 2.119$$

Example 2.6: Calculating Enthalpy and Entropy Changes

If the heat capacity of steam can be represented by a three-term power series:

$$C_p = a + bT + cT^2$$

with constants a = 36.37 J/K-mol, $b = -7.84\times10^{-3}$ J/K^2-mol, and $c = 9.08\times10^{-6}$ J/K^3-mol, and the enthaply of vaporization at 100°C is 40.6 kJ/mol, calculate the S and H changes when 1 mol of liquid water at 100° C and 1 atm is converted to steam and brought to 200° C and 3 atm. Assume that with respect to volume, steam behaves as an ideal gas (which, in reality, it is certainly not).

Answer: We need to calculate entropy and enthalpy associated with three changes: the conversion of water to steam, raising the steam from 100° C to 200° C, and increasing the pressure from 1 atm to 3 atm. Since both S and H are state variables, we can treat these three processes separately; our answer will be the sum of the result for each of these processes and will be independent of the order in which we do these calculations.

1. Conversion of water to steam. This process will result in ΔH of 40.6 kJ. For entropy, ΔS = ΔH/T = 40.6/373 = 109 J/K. We converted centigrade to Kelvin, or absolute, temperature.

2. Raising the steam from 100°C to 200°C (from 373 K to 473 K) isobarically. Since heat capacity is a function of temperature, we will have to integrate equation 2.81 over the temperature interval:

$$\int_{T_1}^{T_2} C_P\,dT = \int_{373}^{473}\left(a + bT + cT^2\right)dT = a\int_{373}^{473} dT + b\int_{373}^{473} TdT + c\int_{373}^{473} T^2 dT = \left[aT + \frac{b}{2}T^2 + \frac{c}{3}T^3\right]_{373}^{473}$$

Evaluating this, we find that ΔH = (17.20 – 0.88 + 0.32) – (13.57 – 0.55 + 0.16) = 3.469 kJ. The entropy change is given by:

$$\Delta S = \int_{T_1}^{T_2}\frac{C_P}{T}dT = \int_{373}^{473}\frac{a}{T}dT + \int_{373}^{473} bdT + \int_{373}^{473} cTdT = \left[a\ln T + bT + \frac{c}{2}T^2\right]_{373}^{473}$$

Evaluating this, we find that ΔS = (224.01-3.71+1.02)– (215.37-2.93+.63) = 8.24 J/K.

3. Increasing pressure from 1 atm to 3 atm (0.1 MPa to 0.3 MPa) isothermally. We can use equation 2.116 to determine the enthalpy change associated with the pressure change. On the assumption of ideal gas behavior, we can substitute 1/T for α. Doing so, we find the equation goes to 0; thus there is no enthalpy change associated with a pressure change for an ideal gas. This is in accord with assumption about an ideal gas: namely that there are no forces between molecules, hence no energy is stored as potential energy of attraction between molecules.

The isothermal pressure dependence of entropy is given by equation 2.106. We substitute 1/T for α and RT/P for V and integrate from P_1 to P_2:

$$\Delta S = \int_{P_1}^{P_2} -\frac{1}{T}\frac{RT}{P}dP = \int_{P_1}^{P_2} -\frac{R}{P}dP = -R\left[\ln P\right]_{0.1}^{0.3} = -8.315\left[\ln\frac{0.3}{0.1}\right]\text{J/K} = -9.13\text{J/K}$$

The whole enthalpy and entropy changes are the sum the changes in these three steps:

ΔH = 40.6 + 3.5 + 0 = 44.1 kJ ΔS = 108.8 + 8.2 – 9.1 = 107.9 J/K

or substituting 2.58 into 2.119: $dA = -SdT - PdV$ 2.120

2.9.2 Gibbs Free Energy

2.9.2.1 Derivation

The Gibbs Free Energy is perhaps misnamed. By analogy to the Helmholtz Free Energy, it should be called the Free Enthalpy (but enthalpy is an energy), because it is derived as follows:

$$\boxed{G \equiv H - TS} \quad 2.121$$

and $$dG = d(H - TS) = dH - d(TS) \quad 2.122$$

or $$dG = TdS + VdP - d(TS) = TdS + VdP - SdT - TdS$$

which reduces to: $$\boxed{dG = VdP - SdT} \quad 2.123$$

Notice the similarity to the Helmholtz Free Energy; in that case we subtracted the TS term from the internal energy; in this case we subtracted the TS term from the enthalpy. *The Gibbs Free Energy is the energy available for non-PV work (such as chemical work).* It has two other important properties: its independent variables are T and P, generally the ones in which we are most interested in geochemistry, and it contains the entropy term (as does the Helmholtz free energy), and hence can be used as an indication of the direction in which spontaneous reactions will occur.

2.9.2.2 Gibbs Free Energy Change in Reactions

For a finite change at *constant temperature*, the Gibbs Free Energy change is:

$$\boxed{\Delta G = \Delta H - T\Delta S} \quad 2.124$$

The free energy change of formation, ΔG_f, is related to the enthalpy and entropy change of reaction:

$$\Delta G_f^o = \Delta H_f^o - T\Delta S_f^o \quad 2.125$$

Like other properties of state, the Gibbs free energy is additive. Therefore:

$$\Delta G_r = \sum_i \nu_i \Delta G_{f,i} \quad 2.126$$

In other words, we can use Hess's Law to calculate the free energy change of reaction. Values for ΔG_f at the standard state are available in compilations.

2.9.3 Criteria for Equilibrium and Spontaneity

The Gibbs Free Energy is perhaps the single most important thermodynamic variable in geochemistry because it provides this criterion for recognizing equilibrium. This criterion is:

Products and reactants are in equilibrium when their Gibbs free energies are equal.

Another important quality of the Gibbs Free Energy is closely related:

At fixed temperature and pressure, a chemical reaction will proceed in the direction of lower Gibbs free energy (i.e., $\Delta G_r < 0$).

The reverse is also true: a reaction will not proceed if it produces an increase in the Gibbs Free Energy.

On an intuitive level, we can understand the Gibbs Free Energy as follows. We know that transformations tend to go in the direction of the lowest energy state (e.g., a ball rolls down hill). We also have learned that transformations go in the direction of increased entropy (if you drop a glass it breaks into pieces; if you drop the pieces they don't re-assemble into a glass). We must consider both the tendency for energy to decrease and the tendency for entropy to increase in order to predict the direction of a chemical reaction. This is what the Gibbs Free Energy does.

EXAMPLE 2.7: USING GIBBS FREE ENERGY TO PREDICT EQUILIBRIUM

Using the thermodynamic data given in Table 2.2 calculate ΔG_r for the reaction:

$$CaAl_2Si_2O_8 + 2Mg_2SiO_4 \rightleftarrows CaMgSi_2O_6 + MgAl_2O_4 + 2MgSiO_3$$

(Anorthite + 2 Forsterite $\rightleftarrows$ Diopside + Spinel + 2 Enstatite)

at 298K and 0.1 MPa. Which mineral assemblage is more stable under these conditions (i.e., which side of the reaction is favored)? Which assemblage will be favored by increasing pressure? Why? Which side will be favored by increasing temperature? Why?

Answer: Since the data in Table 2.2 are listed in terms of ΔH_f and ΔS_f, it is most convenient to use equation 2.124, to calculate our answer:

$$\Delta G = \Delta H - T\Delta S$$

ΔH is calculated as: $\Delta H_{f,Di} + \Delta H_{f,Sp} + 2\times\Delta H_{f,En} - (\Delta H_{f,An} + 2\times\Delta H_{f,Fo})$. ΔS is calculated in a similar manner. Our result is –6.08 kJ/mol. Because ΔG_r is negative, the reaction will proceed to the right, so that the assemblage on the right is more stable under the conditions of 298 K and 1 atm.

To find out which side will be favored by increasing pressure and temperature, we use equations 2.127 and 2.128 to see how ΔG will change. For temperature, $\partial\partial G/\partial T = -\Delta S$. ΔS for the reaction is -36.37 J/K-mol, and $\partial\partial G/\partial T = 36.37$. The result is positive, so that ΔG will increase with increasing T. Hence the left side will be favored by increasing temperature. Had we carried out the calculation at 1000° C and 0.1 MPa, a temperature appropriate for crystallization from magma, we would have found that the anorthite-forsterite assemblage is stable. For pressure, $\partial\partial G/\partial P = \Delta V$. ΔV for the reaction is -20.01 cc/mol (=J/MPa-mol). Thus ΔG will decrease with increasing pressure, so that the right side of the reaction will be favored.

Reassuringly, our thermodynamic result is consistent with geologic observation. The assemblage on the left, which could be called 'plagioclase peridotite' transforms to the assemblage on the right, 'spinel peridotite' as pressure increases in the mantle.

2.9.4 TEMPERATURE AND PRESSURE DEPENDENCE OF THE GIBBS FREE ENERGY

One reason the Gibbs Free Energy is particularly useful is that its characteristic variables are temperature and pressure, which are the 'external' variables of greatest interest in geochemistry. Since the Gibbs Free Energy is a state variable, we can deduce its temperature and pressure dependencies from equation 2.123, which are:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \qquad 2.127 \qquad\qquad \left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \qquad 2.128$$

Equations 2.127 and 2.128 allow us to predict how the Gibbs Free Energy of reaction will change with changing temperature and pressure. *Thus we can predict how the direction of a reaction will change if we change temperature and pressure.* To obtain the Gibbs Free Energy of Reaction at some temperature T´ and pressure P´, we integrate:

$$\Delta G_{T',P'} = \Delta G_{T_{ref},P_{ref}} + \int_{P_{ref}}^{P'} \Delta V_r dP - \int_{T_{ref}}^{T'} \Delta S_r dT \qquad 2.129$$

where ΔG° is the 'standard state' Gibbs Free Energy change. For liquids, and particularly for gases, effects of pressure and temperature of the volume change are important and cannot be ignored. The reference pressure is generally 0.1 MPa. For solids, however, we can often ignore the effects of temperature and pressure on ΔV so the first integral reduces to: $\Delta V(P-P_{ref})$. On the other hand, we usually cannot ignore the temperature dependence of entropy. Hence we need to express ΔS_{rr} as a function of temperature. The temperature dependence of entropy is given by equation 2.105. Writing this in integral form, we have:

$$\Delta S(T) = \Delta S_{T_{ref}} + \int_{T_{ref}}^{T} \frac{\Delta C_p}{T} dT \qquad 2.130$$

Substituting this into 2.129, the second integral becomes:

$$\Delta G_{T'} = -\Delta S_{ref}(T' - T_{ref}) - \int_{T_{ref}}^{T'} \int_{T_{ref}}^{T} \frac{\Delta C_p}{T} dT dT \qquad 2.131$$

EXAMPLE 2.8. PREDICTING THE EQUILIBRIUM PRESSURE OF A MINERAL ASSEMBLAGE

Using the thermodynamic reaction and data as in Example 2.7:

$$CaAl_2Si_2O_8 + 2Mg_2SiO_4 \rightleftarrows CaMgSi_2O_6 + MgAl_2O_4 + 2MgSiO_3$$

(Anorthite + Forsterite $\rightleftarrows$ Diopside + Spinel + 2 Enstatite)

determine the pressure at which these two assemblages will be in equilibrium at 1000° C. Assume that the volume change of the reaction is independent of pressure and temperature (i.e., α and $\beta = 0$).

Answer: These two assemblages will be in equilibrium if and only if the Gibbs Free Energy of reaction is 0. Mathematically, our problem is to solve equation 2.129 for P such that $\Delta G_{1273,P} = 0$.

Our first step is to find ΔG_r for this reaction at 1000°C (1273 K) using equation 2.131. Heat capacity data in Table 2.2 is in the form: $C_p = a + bT - cT^{-2}$. Substituting for ΔC_p, we have:

$$\Delta G_T = -\Delta S_{T_{ref}}(T' - T_{ref}) - \int_{T_{ref}}^{T'} \int_{T_{ref}}^{T} \left(\frac{\Delta a}{T} + \Delta b - \frac{\Delta c}{T^3} \right) dT dT \qquad 2.132$$

Performing the double integral and collecting terms, substituting ΔT for $T' - T_{ref}$, this simplifies to:

$$\Delta G_{T'} = -\Delta T \left[\Delta S_{T_{ref}} - \Delta a + \frac{\Delta b}{2} \Delta T - \frac{\Delta c \Delta T}{2T' T_{ref}^2} \right] - \Delta a T' \ln \frac{T'}{T_{ref}} \qquad 2.133$$

Equation 2.133 is a general solution to equation 2.131 when the Maier-Kelley heat capacity is used.

We found ΔS_{Tref} to be –36.37 J/K-mol in Example 2.7. Computing Δa as $(a_{Di} + a_{Sp} + 2a_{En}) - (a_{An} + 2a_{Fo})$, we find Δa = 15.96 J/mol. Computing Δb and Δc similarly, they are -0.01732 J/K-mol and 1.66×10^6 J-K^2/mol respectively. Substituting values into equation 2.135, we find ΔG_T = 36.74 kJ/mol.

Since we may assume the phases are incompressible, the solution to the pressure integral is:

$$\Delta G_P = \int_{P_{ref}}^{P'} \Delta V_r dP = \Delta V_r (P' - P_{ref}) \qquad 2.134$$

Equation 2.129 may now be written as:

$$\Delta G_{T',P'} = 0 = \Delta G° + \Delta G_T + \Delta V_r (P' - P_{ref})$$

Let $\Delta G_{1273,0.1} = \Delta G° + \Delta G_T$. $\Delta G°$ is -6.95 kJ/mol (calculated from values in Table 2.2), so $\Delta G_{1273,0.1}$ =29.86kJ/mol. $\Delta G_{1273,0.1}$ is positive, meaning that the left side of the reaction is favored at 1000° C and atmospheric pressure, consistent with our prediction based on $\partial G/\partial T$.

Solving for pressure, we have

$$P' = \frac{-\Delta G_{T' P_{ref}}}{\Delta V_r} + P_{ref} \qquad 2.135$$

With ΔV = -20.01cc/mol, we obtain a value of 1.49 GPa (14.9 kbar). Thus assemblages on the right and left will be in equilibrium at 1.49 GPa and 1000°C. Below that pressure, the left is stable, above that pressure, the right side is the stable assemblage, according to our calculation.

The transformation from 'plagioclase peridotite' to 'spinel peridotite' actually occurs around 1.0 GPa in the mantle. The difference between our result and the real world primarily reflects differences in mineral composition: mantle forsterite, enstatite and diopside are solids solutions containing Fe and other elements. The difference does not reflect our assumption that the volume change is independent of pressure. When available data for pressure and temperature dependence of the volume change is included in the solution, the pressure obtained is only marginally different: 1.54 GPa.

EXAMPLE 2.9: VOLUME AND FREE ENERGY CHANGES FOR FINITE COMPRESSIBILITY

The compressibility (β) of forsterite (Mg_2SiO_4) is 8.33 x 10^{-6} MPa^{-1}. Using this and the data given in Table 2.2, what is the change in molar volume and Gibbs Free Energy of forsterite at 100 MPa and 298K?
Answer: Let's deal with volume first. We want to know how the molar volume (43.79 cc/mol) changes as the pressure increases from the reference value (0.1 MPa) to 1GPa. The compressibility is defined as:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (2.12)$$

So the change in volume for an incremental increase in pressure is given by:

$$dV = -V\beta dP \qquad 2.136$$

To find the change in volume over a finite pressure interval, we rearrange and integrate:

$$\int_{V^o}^{V} \frac{dV}{V} = -\int_{P^o}^{P} \beta dP$$

Performing the integral, we have:

$$\ln\frac{V}{V^o} = -\beta(P - P^o) \qquad 2.137$$

where P is the pressure interval, P'-P^o. This may be rewritten as:

$$V = V^o e^{-\beta(P-P^o)} \qquad 2.138$$

However, te value of β□□ is of the order of 10^{-2}, and in this case, the approximation $e^x \approx x + 1$ holds, so that 2.138 may be written as:

$$V \cong V^o(1 - \beta(P - P^o)) \qquad 2.139$$

Equation 2.139 is a general expression that expresses volume as a function of pressure when β is known and is independent of temperature and pressure. Furthermore, in situations where $P >> P^o$, this can be simplified to:

$$V \cong V^o(1 - \beta P) \qquad 2.140$$

Using equation 2.140, we calculate a molar volume of 43.54 cc/mol (identical to the value obtained using 2.138). The volume change, ΔV is 0.04 cc/mol.

The change in Free Energy with volume is given by:

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

so that the free energy change as a consequence of a finite change is pressure can be obtained by integrating:

$$\Delta G = \int_{P^o}^{P} V dP$$

Into this we may substitute equation 2.140:

$$\Delta G = \int_{V^o}^{V'} V^o(1 - \beta P) dP = V^o\left[P - \beta P^2\right]_{P^o}^{P} \qquad 2.141$$

Using 2.141 we calculate a value of ΔG of 4.37 kJ/ mol.

2.10 The Maxwell Relations

The reciprocity relationship, which we discussed earlier, leads to a number of useful relationships. These relationships are known as the Maxwell Relations*. Consider the equation:

$$dU = TdS - PdV \tag{2.58}$$

If we write the partial differential of U in terms of S and V we have:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{2.142}$$

From a comparison of these two equations, we see that:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \tag{2.137}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \tag{2.143}$$

And since the cross differentials are equal, it follows that:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \tag{2.144}$$

The other Maxwell Relations can be derived in an exactly analogous way from other state functions. They are:

from dH (Equ. 2.65)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{2.145}$$

from dA (Equ. 2.120)

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{2.146}$$

from dG (Equ. 2.123)

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{2.147}$$

References and Suggestions for Further Reading

Anderson, G. M. and D. A. Crerar. 1993, *Thermodynamics in Geochemistry*, New York: Oxford Univ. Press.

Broecker, W. S. and V. M. Oversby, 1971. *Chemical Equilibria in the Earth.* New York: McGraw-Hill.

Castellan, G. W. 1964. *Physcial Chemistry*. Reading: Addison-Wesley.

Chandler, D. 1987. *Introduction to Modern Statistical Mechanics*. New York: Oxford.

Denbigh, K. G., 1981. *The Principles of Chemical Equilibrium*, Cambridge: Cambridge Univ. Press.

Feynman, R., R. B. Leighton, and M. L. Sands, 1989. *The Feynman Lectures on Physics, Vol. I*. Pasadena: Calif. Inst. Tech.

Fletcher, P. 1993. *Chemical Thermodynamics for Earth Scientists*, Essex: Logman Scientific and Technical.

Haas, J. L. and J. R. Fisher, 1976. Simultaneous evaluation and correlation of thermodynamic data, *Am. J. Sci.* 276: 525-545.

Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D. K. Bird. 1978. Summary and critique of the thermodynamic properties of rock-forming minerals. *Am. J. Sci.* 278A: 1-229.

Nordstrom, D. K. and J. L. Munoz, 1986. *Geochemical Thermodynamics,* Palo Alto: Blackwell Scientific.

Reif, F. 1965. *Fundamentals of Statistical and Thermal Physics*. New York: McGraw-Hill.

Swalin, R. A. 1962. *Thermodynamics of Solids*. New York: John Wiley and Sons.

* The Maxwell Relations are named for Scottish physicist James Clerk Maxwell (1831-1879), perhaps the most important figure in 19th century physics. He is best known for his work on electromagnetic radiation, but he also made very important contributions to statistical mechanics and thermodynamics.

Chapter 2: Fundamental Concepts of Thermodynamics

Problems

1. For a pure olivine mantle, calculate the adiabatic temperature gradient $(\partial T/\partial P)_S$ at 0.1 MPa (1 atm) and 1000°C. Use the thermodynamic data in Table 2.2 for forsterite (Mg-olivine, Mg_2SiO_4) and $\alpha = 44 \times 10^{-6}$ K^{-1}, and $\beta = 8 \times 10^{-6}$ MPa^{-1}.
Note that: 1 cc/mol = 1 J/MPa/mol.

2. For an ideal gas, show that:

$$\frac{\partial \alpha V}{\partial P} = -\frac{\partial \beta V}{\partial T}$$

3. A quartz crystal has a volume of 7.5 ml at 298 K and 0.1 MPa. What is the volume of the crystal at 840K and 12.3 MPa if
a.) $\alpha = 1.4654 \times 10^{-5}$ K^{-1} and $\beta = 2.276 \times 10^{-11}$ Pa^{-1} and α and β are independent of T and P.
b.) $\alpha = 1.4310 \times 10^{-5}$ K^{-1} + 1.1587×10^{-9} K^{-2}T
$\beta = 1.8553 \times 10^{-11}$Pa^{-1} + 7.9453×10^{-8} P^{-1}

4. One mole of an ideal gas is allowed to expand against a piston at constant temperature of 0°C. The initial pressure is 1 MPa and the final pressure is 0.04 MPa. Assuming the reaction is reversible,
a. What is the work done by the gas during the expansion?
b. What is the change in the internal energy and enthalpy of the gas?
c. How much heat is gained/lost during the expansion?

5. Lava lakes generally have a temperature of about 1100°C. Assuming that basaltic magma travels from its place of origin quickly enough so that negligible heat is lost to wall rocks, calculate the temperature of the magma at a depth of 40 km. The density of basaltic magma at 1200°C is 2.61 g/cc; coefficient of thermal expansion is about 1×10^{-4}/K. Assume a heat capacity of 0.2 cal/g-deg and that pressure is related to depth as 1km = 0.33kb (kb is kilobars; assume 1bar = 1 atm.).
(HINT: "negligible heat loss" means the system may be treated as adiabatic.)

6 Show that the C_p of an ideal monatomic gas is 5/2 R.

7. Show that:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$$

8. Show that for a reversible process:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\alpha}{\beta} - P \qquad \text{(equ. 2.73)}$$

(Hint: begin with the statement of the first law (equation 2.58), make use of the Maxwell relations, and your proof in problem 7.)

9. Imagine that there are 30 units of energy to distribute among 3 copper blocks.
a.) If the energy is distributed completely randomly, what is the probability of the first block having all the energy?
b.) If n_1 is the number of units of energy of the first block, construct a graph (a histogram) showing the probability of a given value of n_1 occurring as a function of n_1. (*HINT: use equation 2.37, but modify it for the case where there are 3 blocks*).

9. Consider a box partitioned into equal volumes, with the left half containing 1 mole of Ne and the right half containing 1 mole of He. When the partition is removed, the gases mix. Show, using a classi-

cal thermodynamic approach (i.e., macroscopic) that the entropy change of this process is $\Delta S = 2R \ln 2$. Assume that He and Ne are ideal gases and that temperature is constant.

10. Find expressions for C_p and C_v for a van der Waals gas.

11. Show that β (the compressibility, defined in equation 2.12) of an ideal gas is equal to $1/P$.

12. Show that $$S = \frac{\overline{U}}{T} + R \ln Q$$

Hint: Start with equations 2.47 and 2.36a using the approximation that ln N! = N ln N – N.

13. Show that $$\Delta H = \int_{P_1}^{P_2} V(1 - \alpha T) dP$$

Hint: Begin with equation 2.63 and express dU as a function of temperature and volume change.

14. Helium at 298K and 1 atm has S° = 30.13 cal/K-mole. Assume He is an ideal gas.
a. Calculate V, H, G, α, ß, Cp, Cv, for He at 298K and 1 atm.
b. What are the values for these functions at 600K and 100 atm?
c. What is the entropy at 600 K and 100 atm?

15. Given the following standard data:

$$Mg + 3/2\ O_2 + Si \rightarrow MgSiO_3 \qquad \Delta H = -1497.4 \text{ kJ/mol}$$
$$Si + O_2 \rightarrow SiO_2 \qquad \Delta H = -859.4 \text{ kJ/mol}$$
$$2Mg + 2O_2 + Si \rightarrow Mg_2SiO_4 \qquad \Delta H = -2042.6 \text{ kJ/mol}$$

find ΔH in Joules for: $Mg_2SiO_4 + SiO_2 \rightarrow 2MgSiO_3$

16. Using the data in Table 2.2, calculate the enthalpy and entropy change of diopside as it is heated at constant pressure from 600 K to 1000 K.

17. Calculate the total enthalpy upon heating of 100g of quartz from 25° C to 900° C. Quartz undergoes a phase transition from α-quartz to β-quartz at 575° C. The enthalpy of this phase transition is ΔH_{tr} = 0.411 kJ/mol. Use the Maier-Kelly heat capacity data in Table 2.2.

18. Calcite and aragonite are two forms of $CaCO_3$ that differ only their crystal lattice structure. The reaction between them is thus simply:

$$\text{Calcite} \rightleftarrows \text{Aragonite}$$

Using the data in Table 2.2,
a.) Determine which of these forms is stable at the surface of the earth (25° C and 0.1 MPa).
b.) Which form is favored by increasing temperature?
c.) Which form is favored by increasing pressure?

19. Use the data in Table 2.2 to determine the pressure at which calcite and aragonite are in equilibrium at 300°C.

20. Suppose you found kyanite and andalusite coexisting in the same rock, that you had reason to believe this was an equilibrium assemblage, and that you could independently determine the temperature of equilibrium to be 400°C. Use the data in Table 2.2 to determine the pressure at which this rock equilibrated.