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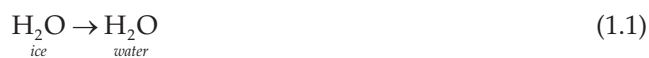
ENERGY IN GEOCHEMICAL PROCESSES

Introduction

The purpose of this book is to introduce the average Earth science student to chemical principles that are fundamental to the sciences of geology and environmental geoscience. There can be no more fundamental place to begin than with the topic of energy (Box 1.1), which lies at the heart of both geology and chemistry. Energy plays a role in every geological process, from the atom-by-atom growth of a mineral crystal to the elevation and subsequent erosion of entire mountain chains. Consideration of energy provides an incisive intellectual tool for analysing the workings of the complex geological world, making it possible to extract from this complexity a few simple underlying principles upon which an orderly understanding of Earth processes can be based.

Many natural processes involve a flow of energy. The spontaneous melting of an ice crystal, for example,

requires energy to be transferred by means of heat into the crystal from the 'surroundings' (the air or water surrounding the crystal). The crystal experiences an increase in its internal energy, which transforms it into liquid water. The process can be symbolized by writing down a formal reaction:



in which molecules of water (H₂O) are represented as migrating from the solid state (left-hand side) into the liquid state (right-hand side). Even at 0°C, ice and water both possess internal energy associated with the individual motions of their constituent atoms and molecules. This energy content, which we loosely visualize as heat 'stored' in each of the substances, is more correctly called the **enthalpy**¹ (symbol *H*). Because the

¹ Words in **bold** type indicate terms that are defined in the Glossary.

Box 1.1 What is energy?

The concept of energy is fundamental to all branches of science, yet to many people the meaning of the term remains elusive. In everyday usage it has many shades of meaning, from the personal to the physical to the mystical. Its scientific meaning, on the other hand, is very precise.

To understand what a scientist means by energy, the best place to begin is with a related – but more tangible – scientific concept that we call *work*. Work is defined most simply as *motion against an opposing force* (Atkins, 2010, p. 23). Work is done, for example, when a heavy object is lifted a certain distance above the ground against the force of gravity (Figure 1.1.1). The amount of work this involves will clearly depend upon how heavy the object is, the vertical distance through which its centre of gravity is lifted (Figure 1.1.1b), and the strength of the gravitational field acting on the object. The work done in this operation can be calculated using a simple formula:

$$\begin{array}{l} \text{Work} = m \times h \times g \\ \text{J} \quad \text{kg m ms}^{-2} \end{array} \quad (1.1.1)$$

where m represents the mass of the object (in kg), h is the distance through which its centre of gravity is raised (in m – see footnote)², and g , known as the *acceleration due to gravity* (metres per second per second = m s^{-2}), is a measure of the strength of the gravitational field where the experiment is being carried out; at the Earth's surface, the value of g is 9.81 m s^{-2} . The scientific unit that we use to measure work is called the joule (J), which as

² m in italics represents mass (a variable in this equation); m in regular type is the abbreviation for metres (units).

Equation 1.1.1 shows is equivalent to $\text{kg} \times \text{m} \times \text{m s}^{-2} = \text{kg m}^2 \text{ s}^{-2}$ (see Table A2, Appendix A). Alternative forms of work, such as cycling along a road against a strong opposing wind, or passing an electric current through a resistor, can be quantified using comparably simple equations, but whichever equation we use, work is always expressed in joules.

The weight suspended in its elevated position (Figure 1.1.1b) can itself do work. When connected to suitable apparatus and allowed to fall, it could drive a pile into the ground (this is how a pile-driver works), hammer a nail into a piece of wood, or generate electricity (by driving a dynamo) to illuminate a light bulb. The work ideally recoverable from the elevated weight in these circumstances is given by Equation 1.1.1. If we were to raise the object twice as far above the ground (Figure 1.1.1c), we double its capacity for doing work:

$$\text{Work} = m \times 2h \times g \quad (1.1.2)$$

Alternatively if we raise an object three times as heavy to a distance h above the ground (Figure 1.1.1d), the amount of work that this new object could perform would be three times that of the original object in Figure 1.1.1b:

$$\text{Work} = 3m \times h \times g \quad (1.1.3)$$

The simple mechanical example in Figure 1.1.1 shows only one, simply understood way of doing work. Mechanical work can also be done by an object's motion, as a demolition crew's 'wrecking ball' illustrates. Electric current heating the element of an electric fire represents another form of work, as does an explosive charge used to blast a rock face in a mine.

molecules in liquid water are more mobile than those in ice – that is, they have higher **kinetic energy** – the enthalpy of water (H_{water}) is greater than that of an equivalent amount of ice (H_{ice}) at the same temperature. The difference can be written:

$$\Delta H = H_{\text{water}} - H_{\text{ice}} \quad (1.2)$$

The Δ symbol (the Greek capital letter 'delta'), when written in front of H , signifies the *difference* in enthalpy

between the initial (solid) and final (liquid) states of the compound the H_2O . It represents the work (Box 1.1) that must be done in disrupting the chemical bonds that hold the crystal together. ΔH symbolizes the amount of heat that must be supplied from the surroundings for the crystal to melt completely; this is called the **latent heat of fusion**, or more correctly the *enthalpy of fusion*, a quantity that can be measured experimentally or looked up in tables.

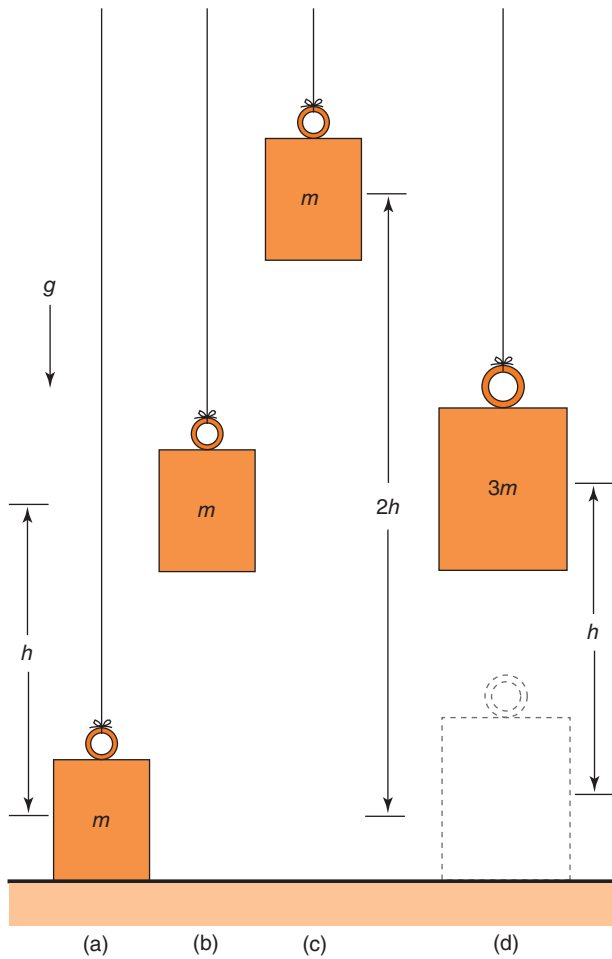


Figure 1.1.1 Work done in raising an object: (a) an object of mass m resting on the ground; (b) the same object elevated to height h ; (c) the object elevated to height $2h$; (d) another object of mass $3m$ elevated to height h . Note: elevation is measured between each object's *centre of gravity* in its initial and final positions (note the centre of gravity of the larger weight is slightly higher than the smaller one).

This simple example illustrates how one can go about documenting the energy changes that accompany geological reactions and processes, as a means of understanding why and when those reactions occur. This is the purpose of *thermodynamics*, a science that documents and explains quantitatively the energy changes in natural processes, just as economics analyses the exchange of money in international trade. Thermodynamics provides a fundamental theoretical

Energy is simply the term that we use to describe a system's *capacity for doing work*. Just as we recognize different forms of work (mechanical, electrical, chemical ...), so energy exists in a number of alternative forms, as will be illustrated in the following pages. The energy stored in an electrical battery, for example, represents the amount of work that it can generate before becoming exhausted. A system's capacity for doing work is necessarily expressed in the units of work (just as the capacity of a bucket is expressed as the number of litres of water it can contain), so it follows that energy is also expressed in joules= $\text{kgm}^2\text{s}^{-1}$. When discussing large amounts of energy, we use larger units such as kilojoules ($\text{kJ}=10^3\text{J}$) or megajoules ($\text{MJ}=10^6\text{J}$).

framework for documenting and interpreting energy changes in processes of all kinds, not only in geology but in a host of other scientific disciplines ranging from chemical engineering to cosmology.

Thermodynamics, because it deals with very abstract concepts, has acquired an aura of impenetrability in the eyes of many Earth science students, particularly those less at home in the realm of mathematics. With this in mind, one objective of these opening chapters

will be to show that thermodynamics, even at a simple and approachable level, can contribute a lot to our understanding of *chemical reactions* and *equilibrium* in the geological world.

Energy changes in chemical systems are most easily introduced (as in Box 1.1) through analogy with mechanical forms of energy, which should be familiar from school physics.

Energy in mechanical systems

The energy of a body is defined as its capacity for doing work (Box 1.1). As we have discovered, ‘work’ can take various forms, but in simple mechanical systems it usually implies the movement of a body from one position to another against some form of physical resistance (friction, gravity, electrostatic forces, etc.). Then:

$$\begin{array}{l} \text{work done} = \text{force required to move body} \\ \text{J (joules)} \qquad \qquad \text{N (newtons)} = \text{kg m s}^{-2} \\ \qquad \qquad \qquad \qquad \times \text{distance body is moved} \\ \qquad \qquad \qquad \qquad \qquad \qquad \text{m (metres)} \end{array} \quad (1.3)$$

So, for example, the work done in transporting a train-load of iron ore from *A* to *B* is the mechanical force required to keep the train rolling multiplied by the distance by rail from *A* to *B*. The energy required to do this is generated by the combustion of fuel in the engine.

One can distinguish two kinds of mechanical energy. Firstly, an object can do work by means of its motion. A simple example is the use of a hammer to drive a nail into wood. Work is involved because the wood resists the penetration of the nail. The energy is provided by the downward-moving hammer-head which, because of its motion, possesses **kinetic energy** (a name derived from the Greek *kinetikos*, meaning ‘setting in motion’). The kinetic energy E_k possessed by a body of mass m travelling with velocity v is given by:

$$\begin{array}{l} E_k = \frac{1}{2} m v^2 \\ \text{(J)} \quad \text{(kg)(m s}^{-1}\text{)}^2 \end{array} \quad (1.4)$$

Thus the heavier the hammer (m) and/or the faster it moves (v), the more kinetic energy it possesses and the further it will drive in the nail. For similar reasons, a fast-moving stream can carry a greater load of sediment than a slow-moving one.

Secondly, an object in a gravitational field possesses energy (i.e. can do work) by virtue of its position in that field, a property known as **potential energy**. The water held behind a hydroelectric dam has a high potential energy: under the influence of the Earth’s gravitational field it would normally flow downhill until it reached sea-level, but the dam prevents this from happening. The fact that the *controlled* downward flow of this water under gravity can be made to drive turbines and generate electricity indicates that the water held behind the dam has the potential for doing work, and therefore possesses energy.

The potential energy E_p of an object of mass m at a height h above the ground is given by:

$$\begin{array}{l} E_p = m \times g \times h \\ \text{(J)} \quad \text{(kg)(m s}^{-2}\text{)(m)} \end{array} \quad (1.5)$$

where g is the acceleration due to gravity (9.81 m s^{-2}). Similar equations can be written representing the potential energies of bodies in other types of force field, such as those in electric and nuclear fields.

An important aspect of potential energy is that its value as calculated from Equation 1.5 depends upon the baseline chosen for the measurement of height h . The potential energy calculated for an object in a second-floor laboratory, for example, will differ according to whether its height is measured from the laboratory floor, from the ground level outside, or from sea-level. The last of these alternatives seems at first sight to be the most widely applicable standard to adopt, but even that reference point fails to provide a baseline that can be used for the measurement of height and potential energy down a deep mine (where both quantities might have negative values measured relative to sea-level). This ambiguity forces us to recognize that potential energy is not something we can express on an absolute scale having a universal zero-point, as we do in the case of temperature or electric charge. The value depends upon the ‘frame of reference’ we choose to adopt. We shall discover that this characteristic applies to chemical energy as well. It seldom presents practical difficulties because in thermodynamics one is concerned with energy *changes*, from which the baseline-dependent element cancels out (provided that the energy values used have been chosen to relate to the same frame of reference).

In general, a body possesses kinetic *and* potential energy by virtue of its overall motion and position.

There is also an internal contribution to its total energy from the individual motions of its constituent atoms and molecules, which are continually vibrating, rotating and – in liquids and gases – migrating about. This internal component, the aggregate of the kinetic energies of all the atoms and molecules present, is what we mean by the **enthalpy** of the body. Enthalpy is closely related to the concept of heat (and was at one time referred to, rather misleadingly, as ‘heat content’). Heat is one of the mechanisms by which enthalpy can be transferred from one body to another. The effect of heating a body is simply to increase the kinetic energy of the constituent atoms and molecules, and therefore to increase the enthalpy of the body as a whole.

Natural processes continually convert energy from one form into another. One of the fundamental axioms of thermodynamics, known as the First Law, is that *energy can never be created, destroyed or ‘lost’* in such processes, but merely changes its form (Box 1.2). Thus the energy given out by a reaction is matched exactly by the amount of energy gained by the surroundings.

Box 1.2 The First Law of Thermodynamics

The most fundamental principle of thermodynamics is that energy is never created, lost or destroyed. It can be transmitted from one body to another, or one place to another, and it can change its identity between a number of forms (as for example when the potential energy of a falling body is transformed into kinetic energy, or when a wind turbine converts the kinetic energy of moving air into electrical energy). But we never observe new energy being created from scratch, nor does it ever just disappear. Accurate energy bookkeeping will always show that *in all known processes total energy is always conserved*. This cardinal principle is called the *First Law of Thermodynamics*. The energy given out by a reaction or process is matched exactly by the amount of energy gained by the surroundings.

Implicit in the First Law is the recognition that work is equivalent to energy, and must be accounted for in energy calculations. When a compressed gas at room temperature escapes from a cylinder, it undergoes a pronounced cooling, often to the extent that frost forms around the valve. (A smaller cooling effect occurs when you blow on

Energy in chemical and mineral systems: free energy

Experience tells us that mechanical systems in the everyday world tend to evolve in the direction that leads to a *net reduction in total potential energy*. Water runs downhill, electrons are drawn toward atomic nuclei, electric current flows from ‘live’ to ‘neutral’, and so on. The potential energy released by such changes reappears as other forms of energy or work: for example, the kinetic energy of running water, the light energy radiated by electronic transitions in atoms (Chapter 6), or the heat generated by an electric fire.

Thermodynamics visualizes chemical processes in a similar way. Reactions in chemical or geological systems arise from differences in what is called **free energy**, G , between products and reactants. The significance of free energy in chemical systems can be compared to that of potential energy in mechanical systems. A chemical reaction proceeds in the direction which leads to a *net reduction in free energy*, and the chemical energy so released reappears as energy in some other form – the

your hand through pursed lips.) The cause of the cooling is that the gas has had to do work during escaping: it occupies more space outside the cylinder than when compressed inside it, and it must make room for itself by displacing the surrounding atmosphere. Displacing something against a resisting force (in this case atmospheric pressure) constitutes work, which the gas can only accomplish at the expense of its enthalpy. This is related directly to temperature, so that a drain on the gas’s internal energy reserves becomes apparent as a fall in temperature.

A similar cooling effect may operate when certain gas-rich magmas reach high crustal levels or erupt at the surface. An example is kimberlite, a type of magma that commonly carries diamonds up from the mantle. Kimberlite penetrates to the surface from depths where the associated gases are greatly compressed, and the work that they do in expanding as the magma–gas system bursts through to the surface reduces its temperature; kimberlites found in subvolcanic pipes (diatremes) appear to have been emplaced in a relatively cool state.

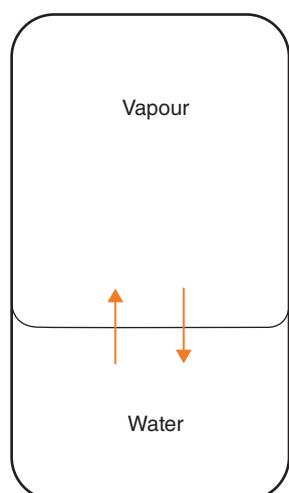
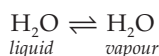


Figure 1.1 A simple model of chemical equilibrium between two coexisting phases, water and its vapour. The equilibrium can be symbolized by a simple equation.



At equilibrium, the migration of water molecules from the liquid to the vapour (evaporation, upward arrow) is balanced exactly by the condensation of molecules from vapour to liquid (downward arrow).

electrical energy obtained from a battery, the light and heat emitted by burning wood, and so on.

What form does free energy take? How can it be calculated and used? These questions are best tackled through a simple example. Imagine a sealed container partly filled with water (Figure 1.1). The space not filled by the liquid takes up water vapour (a gas) until a certain pressure of vapour is achieved, called the *equilibrium vapour pressure* of water, which is dependent only upon the temperature (assumed to be constant). H_2O is now present in two stable forms, each one having physical properties and structure distinct from the other: these two states of matter are called **phases**. From this moment on, unless circumstances change, the system will maintain a constant state, called *equilibrium*, in which the rate of evaporation from the liquid phase is matched exactly by the rate of condensation from the vapour phase: the relative volumes of the two phases will therefore remain constant.

In this state of equilibrium, the free energies associated with a given amount of water in each of these two phases must be equal. If that were not the case, a net

flow of water molecules would begin from the high- G phase to the low- G phase, allowing the total free energy of the system to fall in keeping with the general tendency of chemical systems to minimize free energy. Any such flow, which would alter the relative proportions of the two phases, is inconsistent with the steady state observed. Clearly, at equilibrium, equivalent amounts of the two phases must have identical free energies:

$$G_{\text{vapour}} = G_{\text{liquid}} \quad (1.6)$$

This statement is in fact the thermodynamic definition of ‘equilibrium’ in such a system.

But here we seem to have stumbled upon a paradox. Common sense tells us that to turn liquid water into vapour we have to supply energy, in the form of heat. The amount required is called the **latent heat of evaporation** (more correctly, the *enthalpy* of evaporation). This indicates that the vapour has a greater enthalpy (H_{vapour}) than an equivalent amount of the liquid (H_{liquid}):

$$H_{\text{vapour}} > H_{\text{liquid}} \quad (1.7)$$

The difference reflects the fact that water molecules in the vapour state have (a) greater potential energy, having escaped from the intermolecular forces that hold liquid water together, and (b) greater kinetic energy (owing to the much greater mobility of molecules in the gaseous state).

How can we reconcile Equations 1.6 and 1.7? Is it not common sense to expect the liquid state, in which the water molecules have much lower energies, to be intrinsically more stable than the vapour? What is it that sustains the vapour, in spite of its higher enthalpy, as a stable phase *in equilibrium with* the liquid?

The answer lies in the highly disordered state characteristic of the vapour. Molecules in the gas phase fly around in random directions, occasionally colliding but, unlike molecules in a liquid, free to disperse throughout the available volume. The vapour is said to possess a high **entropy** (S). Entropy is a parameter that quantifies the degree of internal disorder of a substance (Box 1.3). Entropy has immense significance in thermodynamics, owing to Nature’s adherence to the *Second Law of Thermodynamics*. This states that *all spontaneous processes result in an increase of entropy*. The everyday consequences of the Second Law – so familiar that we

often take them for granted – are discussed further in Box 1.3. In the present context, Nature’s preference for disordered, high-entropy states of matter is what makes it possible for vapour to coexist with liquid. In a sense, the higher entropy of the vapour ‘stabilizes’ it in relation to the liquid state, compensating for the higher enthalpy required to sustain it.

Clearly, any analysis in energy terms, even of this simple example, will succeed only if the entropy difference (ΔS) between liquid and vapour is taken into account. This is why the definition of the free energy (alternatively called the ‘Gibbs energy’) of each phase therefore incorporates an entropy term:

$$G_{\text{liquid}} = H_{\text{liquid}} - T.S_{\text{liquid}} \quad (1.8)$$

$$G_{\text{vapour}} = H_{\text{vapour}} - T.S_{\text{vapour}} \quad (1.9)$$

H_{liquid} and H_{vapour} are the enthalpies of the liquid and vapour respectively. S_{liquid} and S_{vapour} are the corresponding entropies. (Take care not to confuse the similar-sounding terms ‘enthalpy’ and ‘entropy’.) The absolute temperature T (measured in kelvins) is assumed to be uniform in a system in equilibrium (Chapter 2), and therefore requires no subscript.

The important feature of these equations is the negative sign. It means that the vapour can have higher enthalpy (H) and higher entropy (S) than the liquid, and yet have the same free energy value (G), which must be true if the two phases are to be in equilibrium. Perhaps a more fundamental understanding of the minus sign can be gained by rearranging Equations 1.8 and 1.9 into this form:

$$H = G + T.S \quad (1.10)$$

The enthalpy of a phase can thus be seen as consisting of two contributions:

- G The part that potentially can be released by the operation of a chemical reaction, which is logically called ‘free’ energy. This therefore provides a measure of the instability of a system (just as the potential energy of the water in a reservoir reflects its gravitational instability).
- $T.S$ The part that is irretrievably bound up in the internal disorder of a phase at temperature T , and that is therefore not recoverable through chemical reactions.

Equations 1.8 and 1.9 express the fundamental contribution that disorder makes to the energetics of chemical and geological reactions, a question we shall take up again in the following sections.

Units

Enthalpy, entropy and free energy, like mass and volume, are classified as **extensive** properties. This means that their values depend on the amount of material present. On the other hand, temperature, density, viscosity, pressure and similar properties are said to be **intensive** properties, because their values are unrelated to the size of the system being considered.

In published tables of enthalpy and entropy (Chapter 2), the values given are those for one **mole** – abbreviated in the SI system to ‘mol’ – of the substance concerned (18 g in the case of water). One therefore speaks of **molar** enthalpy and entropy, and of molar free energy and molar volume as well. The units of molar enthalpy and molar free energy are joules per mole (J mol^{-1}); those of molar entropy are joules per kelvin per mole ($\text{J K}^{-1} \text{mol}^{-1}$). The most convenient units for expressing molar volume are $10^{-6} \text{m}^3 \text{mol}^{-1}$ (which are the same as $\text{cm}^3 \text{mol}^{-1}$, the units used in older literature).

In thermodynamic equations like 1.8, temperature is always expressed in *kelvins* (K). One kelvin is equal in magnitude to one $^{\circ}\text{C}$ but the scale begins at the absolute zero of temperature (-273.15°C), not at the freezing point of water (0°C). Therefore:

$$T \text{ in K} = T \text{ in } ^{\circ}\text{C} + 273.15 \quad (1.11)$$

The SI units for pressure are pascals (Pa; see Appendix A).

Free-energy changes

For the reasons discussed above in relation to potential energy, the numerical values of G_{liquid} and G_{vapour} have no *absolute* significance. In considering whether water will evaporate or vapour will condense in specific circumstances, what concerns us is the *change* in free energy ΔG arising from the liquid-to-vapour ‘reaction’. The first step in calculating free-energy changes is to write down the process concerned in the form of a

Box 1.3 Some properties of entropy

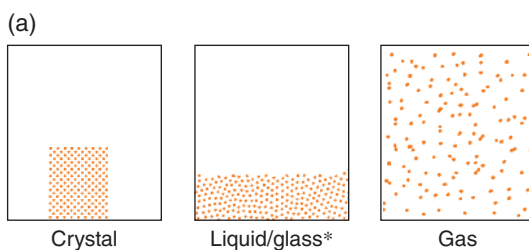
The concept of disorder is of fundamental importance in thermodynamics, because it allows us to distinguish those processes and changes that occur naturally – ‘spontaneous’ processes – from those that do not. We are accustomed to seeing a cup shattering when it falls to the floor, but we never see the fragments reassemble themselves spontaneously to form a cup hanging on the dresser hook. Nor is it a natural experience for the air in a cold room to heat up a warm radiator. The direction of change that we accept as natural always leads to a more disordered state than we began with.

To apply such reasoning to the direction of chemical change, we need a variable that quantifies the degree of disorder in a chemical system. In thermodynamics this is defined by the **entropy** of the system. To define entropy rigorously lies beyond the scope of this book, but it is worth identifying the processes that lead to an increase of entropy. The entropy of a system depends upon:

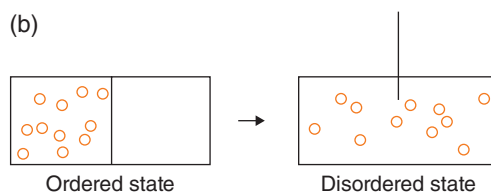
- (i) the distribution of *matter* or of individual chemical species in the system; and
- (ii) the distribution of *energy*.

Entropy and the distribution of matter

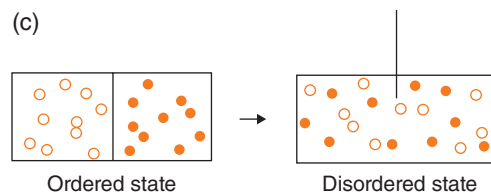
(a) Entropy increases as a substance passes from the solid state to the liquid state to the gaseous state.*



(b) Entropy increases when a gas expands.



(c) Entropy increases when pure substances are mixed together.



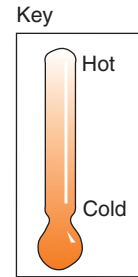
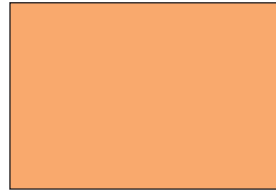
* A glass is a solid having the disordered structure of a liquid, but deprived of atomic mobility (no flow). Its entropy is intermediate between liquid and crystalline solid.

Entropy and the distribution of energy

The entropy of a system increases

(d)

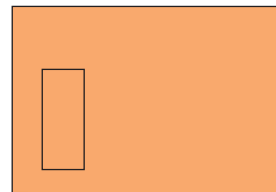
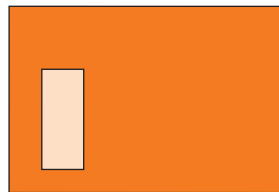
when a substance is heated:



because raising the temperature makes the random thermal motions of atoms and molecules more vigorous.

(e)

when heat flows from a hot body (e.g. a radiator) to a cold body (the surrounding air):

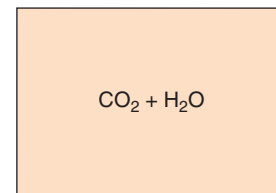
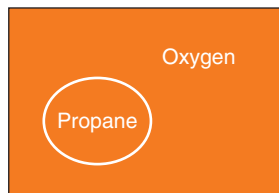


Heat concentrated in one place
Ordered state

Heat uniformly distributed
Disordered state

(f)

when chemical energy (fuel + oxidant) is transformed into heat:



Chemical energy of
fuel/oxidant mixture
Ordered state

Hot combustion products
Disordered state

(g)

when mechanical energy is transformed into heat (e.g. friction).

The Second Law of Thermodynamics

The Second Law states that *the operation of any spontaneous process leads to an (overall) increase of entropy*. Our experience of this law is so intricately woven into the fabric of everyday life that we are scarcely aware of its existence, but its impact on science is nonetheless profound. The expansion of a gas is a spontaneous process involving an increase of entropy: a gas never spontaneously contracts into a smaller volume. Water never runs uphill. Applying heat to an electric fire will never generate electricity. All of these impossible events, were they to occur, would bring about a reduction of entropy and therefore violate the Second Law.

Entropy is lowest when energy is concentrated in one part of a system. This is a characteristic of all of the energy resources that we exploit: water retained behind a hydroelectric dam, chemical energy stored in a tank of gasoline or in a charged battery, nuclear energy in a uranium fuel rod, etc. Entropy is highest when energy is evenly distributed throughout the system being considered, and in such circumstances it cannot be put to good use. Spontaneous (entropy-increasing) changes are always accompanied by a degradation in the 'quality' of energy, in the sense that it becomes dispersed more widely and uniformly.

chemical reaction, as in Equation 1.1. For the water/vapour equilibrium:



The equilibrium symbol (\rightleftharpoons) represents a balance between two competing opposed ‘reactions’ taking place at the same time:

‘Forward’ reaction: liquid \rightarrow vapour (evaporation)
reactant product

‘Reverse’ reaction: liquid \leftarrow vapour (condensation)
product reactant

By convention, the free-energy *change* for the forward reaction (ΔG) is written:

$$\begin{aligned} \Delta G &= G_{\text{products}} - G_{\text{reactants}} \\ &= G_{\text{vapour}} - G_{\text{liquid}} \end{aligned} \quad (1.13)$$

Each G can be expressed in terms of molar enthalpy and entropy values obtained from published tables (Equations 1.8 and 1.9). Thus

$$\begin{aligned} \Delta G &= (H_{\text{vapour}} - T.S_{\text{vapour}}) - (H_{\text{liquid}} - T.S_{\text{liquid}}) \\ &= (H_{\text{vapour}} - H_{\text{liquid}}) - T(S_{\text{vapour}} - S_{\text{liquid}}) \\ &= \Delta H - T.\Delta S \end{aligned} \quad (1.14)$$

In this equation ΔH is the heat input per mole required to generate vapour from liquid (the latent heat of evaporation). In the context of a true chemical reaction, it would represent the *heat of reaction* (strictly the *enthalpy* of reaction). If ΔH for the forward reactions is negative, heat must be given out by the reaction, which is then said to be **exothermic** (‘giving out heat’). A positive value implies that the reaction will proceed only if heat is drawn in from the surroundings. Reactions that absorb heat in this way are said to be **endothermic** (‘taking in heat’). ΔS represents the corresponding entropy change between liquid and vapour states.

The values of H_{vapour} , H_{liquid} , S_{vapour} and S_{liquid} can be looked up as molar quantities for the temperature of interest (e.g. room temperature ≈ 298 K) in published tables. In this case, ΔH and ΔS can be calculated by simple difference, leading to a value for ΔG (taking care to enter the value of T in kelvins, not $^{\circ}\text{C}$). From the sign obtained for ΔG , it is possible to predict in

which direction the reaction will proceed under the conditions being considered. A negative value of ΔG indicates that the products are more stable – have a lower free energy – than the reactants, so that the reaction can be expected to proceed in the forward direction. If ΔG is positive, on the other hand, the ‘reactants’ will be more stable than the ‘products’, and the reverse reaction will predominate. In either case, reaction will lead eventually to a condition where $\Delta G=0$, signifying that equilibrium has been reached.

Now let us see how these principles apply to minerals and rocks.

Stable, unstable and metastable minerals

The terms ‘stable’ and ‘unstable’ have a more precise connotation in thermodynamics than in everyday usage. In order to grasp their meaning in the context of minerals and rocks, it will be helpful to begin by considering a simple physical analogue. Figure 1.2a shows a rectangular block of wood in a series of different positions relative to some reference surface, such as a table top upon which the block stands. These configurations differ in their potential energy, represented by the vertical height of the *centre of gravity* of the block – shown as a dot – above the table top. Several general principles can be drawn from this physical system which will later help to illuminate some essentials of mineral equilibrium:

- Within this frame of reference, configuration D has the lowest potential energy possible, and one calls this the *stable* position. At the other extreme, configurations A and C are evidently *unstable*, because in these positions the block will immediately fall over, ending up in a position like D. Both clearly have higher potential energy than D.
- In discussing stable and unstable configurations, one need not consider all forms of energy possessed by the wooden block, some of which (for example, the total electronic energy) would be difficult to quantify. Mechanical stability depends solely upon the relative potential energies of – or energy differences between – the several configurations, and not on their absolute energy values.

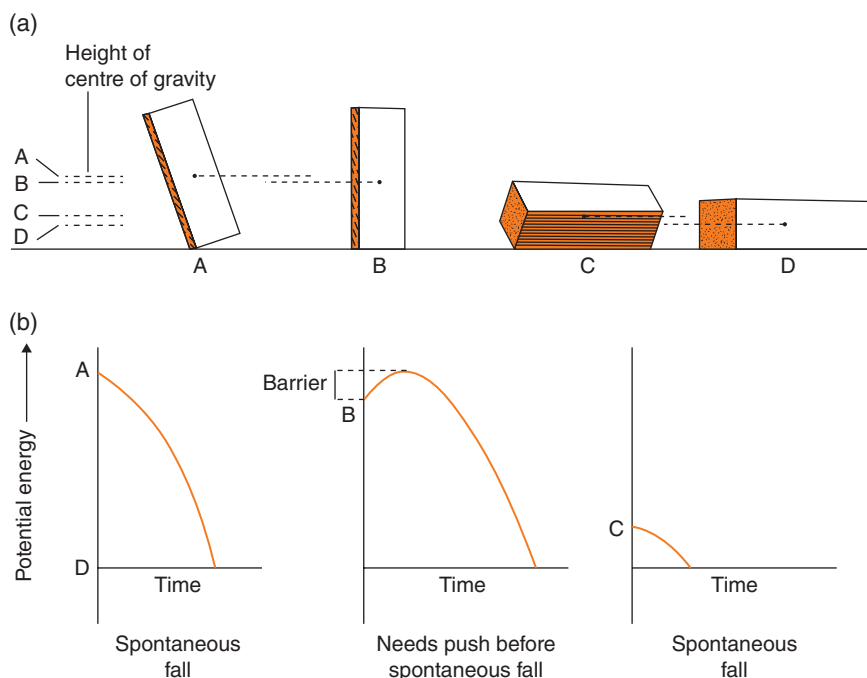


Figure 1.2 Potential energy of a rectangular wooden block in various positions on a planar surface. (a) Four positions of the block, showing the height of its centre of gravity (dot) in each case. (b) The pattern of potential-energy change as the block topples, for the unstable (A, C) and **metastable** (B) configurations.

(c) Configuration B presents something of a paradox. It has a potential energy greater than the unstable state C, yet, if left undisturbed, it will persist indefinitely, maintaining the appearance of being stable. The introduction of a small amount of energy, such as a person bumping into the table, may however be sufficient to knock it over. The character of configuration B can be clarified by sketching a graph of potential energy against time as the block topples over (Figure 1.2b). For both unstable positions A and C, the potential energy falls continuously to the value of position D; but in the case of position B the potential energy must first *rise* slightly, before falling to the minimum value. The reason is that the block has to be raised on to its corner (position A) before it can fall over, and the work involved in so raising its centre of gravity constitutes a potential energy 'hurdle' which has to be surmounted before the block can topple. By inhibiting the spontaneous toppling of the block, this hurdle stabilizes configuration B. One uses the term **metastable** to describe any high-potential-energy state that is stabilized by such an energy hurdle.

The application of this reasoning to mineral stability can be illustrated by the minerals calcite and aragonite, whose ranges of stability in pressure–temperature space are shown in the form of a *phase diagram* in Figure 1.3a. These minerals are alternative crystallographic forms of calcium carbonate (CaCO_3), stable under different physical conditions. The phase diagram shown in Figure 1.3a is divided into two areas called *stability fields*, one representing the range of applied pressure and temperature under which calcite is the stable mineral; the other – at higher pressures – indicating the range of conditions favouring aragonite. The stability fields are separated by a line, called a **phase boundary**, which defines the restricted set of circumstances under which calcite *and* aragonite can coexist together *in equilibrium* with each other.

The energetics of the calcite–aragonite system are illustrated in Figure 1.3b, which shows how the molar free energies of the two minerals vary along the line X–Y in Figure 1.3a. At high pressure (Y), deep within the crust, the molar free energy of aragonite is less than that of calcite, and thus aragonite is the stable mineral under these conditions, analogous to configuration D

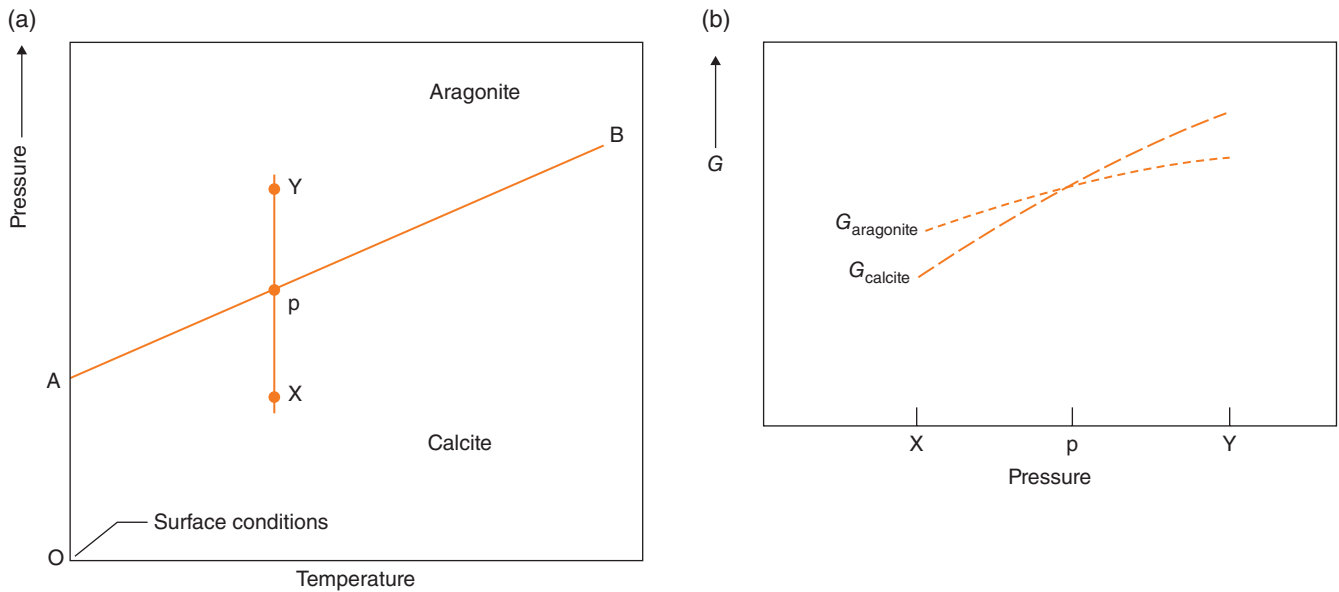


Figure 1.3 Stability of CaCO_3 polymorphs. (a) Pressure–temperature phase diagram showing the stability fields of calcite and aragonite. The line A–B is the phase boundary, indicating the P – T conditions under which calcite and aragonite are able to coexist in stable equilibrium. (b) Variation of free energy (G) of calcite and aragonite over a range of pressures along the isothermal line X–Y in (a).

of the wooden block in Figure 1.2a. At a lower pressure (X) nearer to the surface, however, the position is reversed: calcite has the lower free energy and is therefore the stable mineral. The lines representing the free energy of calcite and aragonite as a function of pressure cross over in Figure 1.3b at a point marked p. Here the two minerals have equal molar free energies, and are therefore in chemical equilibrium with each other. Point p therefore marks the position in Figure 1.3b of the phase boundary appearing in Figure 1.3a.

Imagine transporting a sample of aragonite from the conditions represented by point Y to a new location (at a shallower depth in the Earth’s crust) having the pressure and temperature coordinates of point X. Under the new conditions aragonite will no longer be the stable mineral and it will *tend* to achieve a state of lower free energy by recrystallizing to calcite. This transformation may not occur immediately, however, because the status of aragonite is similar to the wooden block in position B. The same three points made above in relation to Figure 1.2 can be reiterated for the calcite–aragonite system:

(a) Calcite, having the lower free energy, will be the *stable* form of calcium carbonate under the lower pressure conditions defined by X.

(b) Many other forms of energy are associated with calcite and aragonite under such conditions, but in discussing thermodynamic stability we are concerned only with *free-energy differences* between alternative states. This has the important consequence that free energy needs only to be expressed in relative terms, referred to a convenient but arbitrary common point, a sort of thermodynamic ‘sea-level’. All important applications of thermodynamics involve the calculation of free-energy differences between the various states of the system being considered, and the notion of an absolute scale of free-energy values, analogous to the absolute temperature scale, is unnecessary and inappropriate.

(c) In spite of not being stable under near-surface conditions (Figure 1.3), aragonite is quite a common mineral, and may survive for long periods of geological time on the surface of the Earth. Like configuration B in Figure 1.2a, aragonite may give the appearance of being in a stable state in such circumstances, even though its free energy clearly exceeds that of calcite. (Under certain circumstances, aragonite may actually crystallize under near-surface conditions: for example, the shells of

planktonic gastropods (pteropods) are constructed of aragonite precipitated directly from seawater.) The explanation for this appearance of stability is that aragonite is stabilized by a free-energy 'hurdle', just like its mechanical analogue.

The free-energy path followed by aragonite (under the conditions shown by X in Figure 1.3a), as it undergoes transformation into calcite, is shown Figure 1.4. The energy hurdle exists because rearranging the crystal structure of aragonite into that of calcite involves some work being done in breaking bonds and moving atoms about. Although this energy investment is recovered several times over in the net release of free energy as the reaction proceeds, its importance in determining whether the reaction can begin is considerable. In recognition of this influence, the height of the energy hurdle is called the *activation energy* of the reaction (symbol E_a).

Figure 1.4 illustrates an important distinction between two major domains of geochemical science. *Thermodynamics* is concerned with the free-energy changes associated with chemical equilibrium between phases, and provides the tools for working out which mineral assemblages will be stable under which conditions. Only the initial and final states are of interest in thermodynamics, and attention is confined to *net* energy differences between reactants and products (ΔG , ΔH , ΔS), as Chapter 2 will show. The science of *chemical kinetics* deals with the mechanics of the reactions that lead to equilibrium and the rates at which they occur. In this area, as we shall see in Chapter 3, the

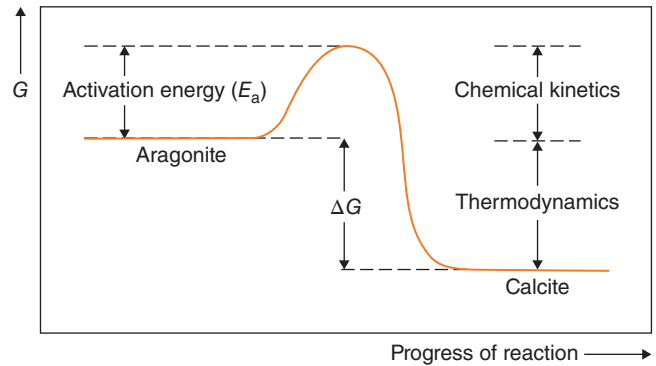


Figure 1.4 The free-energy path during the recrystallization of aragonite into calcite at the P - T conditions shown by X in Figure 1.3.

activation energy asserts a dominant role, accounting for the strong influence of temperature on many geological processes.

Further reading

- Atkins, P. (2010) *The Laws of Thermodynamics: A Very Short Introduction*. Oxford: Oxford University Press (especially chapters 1 and 2).
- Goldberg, D. (2010) *Beginning Chemistry*. 2nd edn. New York: McGraw Hill.
- Pauken, M. (2011) *Thermodynamics for Dummies*. Chichester: John Wiley and Sons, Ltd.
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