# 1 Review of Fundamentals

The following brief notes cover some of the more important points which students have met in previous courses on thermodynamics.

A principal objective of thermodynamics is to provide relations between certain equilibrium properties of matter. These relations lead to predictions about unmeasured properties. Thus, redundant measurements can be avoided, as the following sketch illustrates.
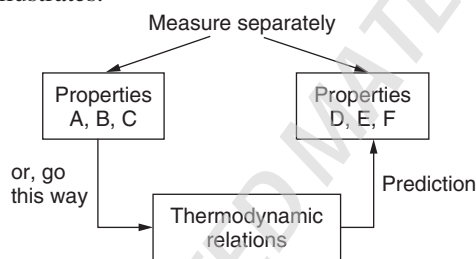
These thermodynamic relations sometimes connect quantities which might not appear to be related at first glance. An important example in regard to the subject of this book is illustrated in the following sketch:
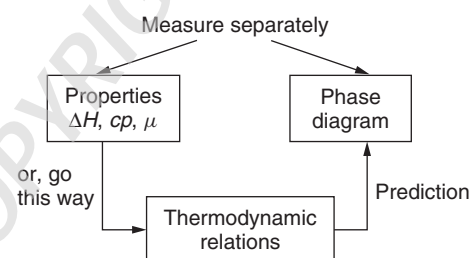
It is not immediately obvious that the phase diagram shown in the second sketch, traditionally obtained from thermal analysis measurements, can be calculated, in principle, from appropriate thermochemical measurements: Thermodynamics is concerned with the *macroscopic* properties of substances and systems *at equilibrium* (the definition of equilibrium is given later). Statistical mechanics is concerned with interpreting the equilibrium macroscopic properties in terms of *microscopic* properties, that is, in terms of atoms, electrons, bonds

between atoms, and so on. Specification of a microscopic state requires $\approx 10^{23}$ independent variables, usually called degrees of freedom in thermodynamics, whereas specification of a macroscopic state requires only a few independent variables (two in the case of a pure substance undergoing $p-V$ work only). The reason for this enormous reduction in the number of independent variables is that the macroscopic properties are determined by the time average of the many possible microscopic states.

Most of this course is concerned with macroscopic thermodynamics, but we will also cover some elementary aspects of statistical mechanics.

Historical Perspective   Newton (1687) quantified the concepts of force and physical work (= force × distance) but never mentioned energy. This concept came much later from Thomas Young (1807) and Lord Kelvin (1851), the latter appreciating that energy was the primary principle of physics. The science of mechanics is concerned with applying the conservation of energy to physical work problems.

Energy is the capacity to do work, potential energy being the form by virtue of position and kinetic energy being the form by virtue of motion.

There is no mention of heat in mechanics. The early calorific theory of heat had to be discarded following the experiments of Count Rumford (1798) and Joule (ca. 1850), who showed the equivalence of work transfer and heat transfer; that is, they are simply different forms of energy transfer. Work is energy transferred such that it can, in principle, be used to raise a weight, while heat is energy transferred as a result of a temperature difference. Atomistically, in work transfer, the atoms move in a uniform fashion while in heat transfer the atoms are moving in a disorganized fashion.

The equivalence of work transfer and heat transfer led to a broadening of the meaning of the conservation of energy and this became the first law in the new science of thermodynamics.

Later developments came from Carnot, Lord Kelvin, Clausius, and Boltzmann with the realization that there are some limitations in the heat transfer–work transfer process. This led to the idea of the *quality* of energy and the introduction of a new quantity, entropy. The limitations on different processes could be understood in terms of whether there is an overall increase in the thermal and/or positional disorder.

1.1   SYSTEMS, SURROUNDINGS, AND WORK

In thermodynamics we consider the system and its surroundings. It is up to the thermodynamicist to define the system and the surroundings. The two might be

  (i) isolated from one another, an *isolated* system;
 (ii) in mechanical contact only, an *adiabatic* system;
(iii) in mechanical and thermal contact, a *closed* system; or
 (iv) also able to exchange matter, an *open* system.

By mechanical contact we mean that work can be exchanged between the system and the surroundings. As is illustrated schematically in Figure 1.1, *work is always measured in the surroundings* and not in the system. For the moment, we consider only mechanical work; other types of work are consider later in Section 1.5.2.

Convention   Work done *by* the system on the surroundings is taken as *positive*. Mechanical work is defined as the product of a generalized force f and its *conjugate* displacement variable dX:

$$\delta w = f_{\text{surr}} \, dX \tag{1.1}$$

The subscript surr refers to the surroundings.

Note that we write δw and not dw because work exchanged between system and surroundings is a *path-dependent* quantity. Paths may be drawn in state space (the space spanned by the chosen independent variables) with many different paths being possible in the joining of two points. Consider, for example, the two paths in going from A to B in Figure 1.2. Clearly, if we go along the path ACB the work done ($\int p \, dV$) is different from when we go along the path ADB. No work is done along the paths AC and BD (the volume is constant) with these transitions being made possible by heat transfer. This path dependence demonstrates that work is not a state function. which is defined as one which is path independent when considering movement between two points in state space.

Any state function Y, being path independent, is zero when a system is put through a cyclic path or loop, that is, for a state function,

$$\oint dY = 0$$

Especially important is the path where equilibrium is maintained, between system and surroundings, at all points as the path is traversed—a *quasi-static* or *reversible* path. Although impossible to achieve in practice, since we would have to go infinitely slowly, it is a very useful concept. When $f_{\text{surr}} = f$, the latter being
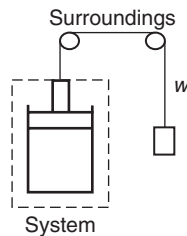

Figure 1.1   Work is measured in the surroundings and not in the system. On our convention, work done *by the system* is taken as positive.
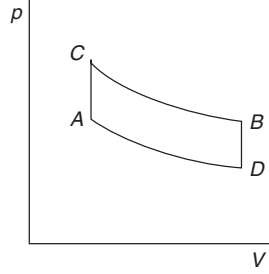
Figure 1.2 Work is not a state function; it depends on the path taken. The work done on going from A to B via ACB is different from that along the path ADB.

the value in the system, we can write

$$\delta w_{\text{rev}} = f \, dX \tag{1.2}$$

An *equation of state* (EOS) is a relation between conjugate (defined later) work variables for a body in equilibrium. Some well-known examples of approximate EOS are

$$\sigma = k\epsilon \quad \text{(Hooke's law)}$$
$$pV = nRT \quad \text{(perfect gas law)}$$
$$p = -\frac{B_T}{V_0}\Delta V \quad \text{(solid compression)}$$

Given an EOS, we can then evaluate $w_{\text{rev}} = \int \delta w_{\text{rev}}$ along quasi-static or reversible paths. For the above EOS examples

$$w_{\text{rev}} = \int \sigma \, d\epsilon = \int k\epsilon \, d\epsilon = \frac{1}{2}k\epsilon^2$$
$$(w_{\text{rev}})_T = -\int p \, dV = nRT \, \log_e\left(\frac{V_2}{V_1}\right)$$
$$w_{\text{rev}} = -\int p \, dV = \frac{1}{2}\frac{B_T}{V_0}(\Delta V)^2$$

1.2   THERMODYNAMIC PROPERTIES

Thermodynamic properties may be classified into being either *extensive* or *intensive*.

1. The meaning of extensive is clear. If M is mass and k a constant, then, in the case of volume, for example,

$$V(kM) = kV(M) \tag{1.3}$$

Mathematically, extensive properties like V are said to be homogenous functions of the first degree.

2. Intensive properties can be divided into two types and it is important to distinguish between the two:

   (a) *Field*: T, p, μ (much more later about this function)

   (b) *Density*: $V_m = V/N_{\text{total}}$, $H_m = H/N_{\text{total}}$, and mole fraction $x_i = N_i/N_{\text{total}}$

There is an important distinction between these two kinds of intensive variables in that a field variable takes on identical values in any coexisting phases at equilibrium, a density variable does not.

1.3 THE LAWS OF THERMODYNAMICS

The laws of thermodynamics can be introduced historically via experimental observations and many equivalent statements are possible. Alternatively, they may be stated as postulates, axiomatic statements, or assumptions based on experience. In this approach, the existence of some new state functions (bulk properties) is postulated with a recipe given for how to measure each of them. This latter approach is adopted here.

(a) *Zeroth Law*   Thermodynamic temperature T is a state function.

  Recipe   The thermodynamic temperature is equal to the ideal gas temperature, pV_m/R. It is possible, therefore, to define T in terms of mechanical ideas only, with no mention of heat. Note, however, that the thermodynamic temperature is selected as a primary quantity in the SI system.

(b) *First Law*   The internal energy U is a state function.

  Recipe   If we proceed along an adiabatic path in state space, then

$$dU = -\delta w_{\text{adiabatic}} \tag{1.4}$$

  The negative sign here arises since, if work is done by the system, its energy is lowered. Note that only changes in U can be measured. This applies to all energy-based extensive thermodynamic quantities.

  The first law leads to the definition of heat. Heat should only be referred to as an energy *transfer* and not as an energy or heat *content*; that is, heat is not a noun, heat flow is a process.

  For a nonadiabatic process, the change in U is no longer given by the work done on the system. The missing contribution defines the heat transferred:

$$\boxed{dU = \delta q - \delta w} \quad \text{(first law)} \tag{1.5}$$

Just as δw is path dependent, δq is also path dependent; that is, q is not a state function, whereas U is.

Equation (1.5) is the differential form of the conservation of energy or first law for any system. Note that there is no specific mention of p–V work in this statement. It is generally valid.

Convention   Heat flow *into* the system is taken to be *positive* (Fig. 1.3). Since both work and heat flow are measured in the surroundings, where the field variables are taken to be constant, any changes in state in the surroundings are always considered to be made quasi-statically.

(c) *Second Law*   while the first law is concerned with the conservation of energy, the second law is concerned with how energy is spread. Any spontaneous process occurs in a way so as to *maximize the spread of energy between accessible states of the system and its surroundings*. Entropy is the property which is the measure of this spread.

The second law is usually stated in two parts:

1. Entropy S of the system is a state function.
   Recipe   If the state of a system is changed reversibly by heat flow, then the entropy change is given by

$$\boxed{dS = \frac{\delta q_{\text{rev}}}{T}}\quad\text{(second law, part 1)}\tag{1.6}$$

2. In a spontaneous process, entropy in the system plus surroundings, sometimes called the universe, is created (energy is spread).

   The total entropy change of the system plus surroundings is then given by

$$dS_{\text{univ}} = dS + dS_{\text{surr}} \geq 0\tag{1.7}$$

In an isolated system there is no external creation of entropy so that

$$dS_{\text{surr}} = 0\quad\text{and}\quad dS \geq 0$$
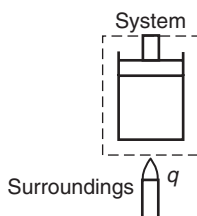

Figure 1.3   Heat flow is measured in the surroundings. In our convention, heat flow *into the system* is taken as positive.

(d) *Third Law*   The third law is not really a law of macroscopic thermody-
namics since its formulation requires some microscopic information. The
word law is too strong for a rule which is known to have exceptions. In a
form due originally to Planck, it can be stated as:

For any pure substance in a stable, perfectly crystalline form at 0 K, S can
be taken to be zero.

Note that:

   (i) This is not to say that the entropy has an absolute value of zero.
   Given time enough, all systems would undergo intranuclear and
   isotopic changes. These are so slow, however, that they may be
   considered to make a time-independent contribution; that is, they
   contribute an additive constant to the entropy so that it is satisfac-
   tory to take this as zero.

   (ii) Mixtures are specifically excluded from the defining statement.
   Thus glasses, solid solutions, and asymmetric molecules may have
   residual entropies at 0 K.

   (iii) Pressure is not mentioned in the defining statement. This is because
   $dS/dp = -dV/dT$ and the thermal expansivity $\alpha = (1/V)\, dV/dT$
   is also zero at 0 K [see (1.28) for the relation between dS/dp and
   β].

This wording of the third law means that the entropy of every pure crystalline
substance (element or compound) in its lowest energy state is taken to be zero
at 0 K. This wording does not preclude, for example, that $S(C(\text{diamond})) =
S(C(\text{graphite})) = 0$ at $T = 0$ K. Although there is an energy difference between
these two allotropes, the lower energy graphite states are not accessible to dia-
mond at low temperature: Only excitations to other diamond states are possible.
This is why both C(graphite) and C(diamond) can be given zero entropies at 0 K.

It is clear that microscopic (crystallographic) information about the substance
is needed in order to be sure that the substance is in its lowest energy state.
Specifying the composition of the substance alone is not sufficient. This is why
the third law cannot be regarded on the same macroscopic footing as the zeroth,
first, and second laws.

Example 1.1 State Functions
The changes in H (or any other state function) when a system is put through a
cycle is given by

$$\oint dH = 0$$

Consider the cycle shown in Figure 1.4. Each stage in the cycle is carried out
at a total pressure of 1 bar. We place no restriction on the steps that take place
(they do not have to be carried out quasi-statically) as long as the system at the
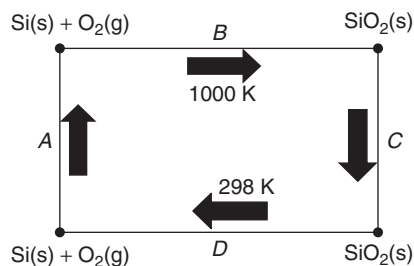start and end points of each step is in internal equilibrium:

Figure 1.4   Enthalpy is a state function.

(A) $\left[H^\circ(1000) - H^\circ(298)\right]_{\text{Si(s)}} + \left[H^\circ(1000) - H^\circ(298)\right]_{\text{O}_2\text{(g)}}$

$\qquad = \displaystyle\int_{298}^{1000} [C_p(\text{Si}) + C_p(\text{O}_2)]\,dT = 17{,}075 + 22{,}694 \text{ J}$

(B) $-\Delta_f H^\circ(\text{SiO}_2(\text{s}), 1000) = -857{,}493 \text{ J}$

(C) $\left[H^\circ(298) - H^\circ(1000)\right]_{\text{SiO}_2}$

$\qquad = \displaystyle\int_{1000}^{298} C_p(\text{SiO}_2)\,dT = -43{,}611 \text{ J}$

(D) $\Delta_f H^\circ(\text{SiO}_2(\text{s}), 298.15) = +861{,}335 \text{ J}$

from which, for the cycle

$$\oint (A - B - C - D) = 17{,}075 + 22{,}694 - 857{,}493 - 43{,}611 + 861{,}335 = 0$$

The same procedure may be followed for the state properties U, S, A, and G. For all of these state functions, $\oint dY = 0$.

1.4   THE FUNDAMENTAL EQUATION

The combined statement of the first and second laws comes by first expressing the first law for *any* process,

$$\delta q = dU + \delta w \tag{1.8}$$

and then introducing the second law for a *reversible* process, $\delta q_{\text{rev}} = T\,dS$, to obtain

$$T\,dS = dU + \delta w_{\text{rev}} \tag{1.9}$$

For a *closed system of fixed amounts of substances doing p–V work only* we can write $\delta w_{\text{rev}} = p\,dV$ so that

$$\boxed{dU = T\,dS - p\,dV} \quad (p\text{–}V \text{ work only, fixed amounts}) \tag{1.10}$$

Although we have derived this equation by considering reversible processes, it is applicable to any process as long as the initial and final states are in internal equilibrium, since it involves state functions only. It is called the fundamental equation or Gibbs's first equation and we consider its application later.

It can be seen from (1) that the natural independent variables of the state function U are S and V.

1.5   OTHER THERMODYNAMIC FUNCTIONS

For systems undergoing p–V work only, we have seen that the primary functions of thermodynamics are the mechanical variables p and V together with the variables T, U, and S. For convenience, however, many other state functions are defined since it is usually not convenient for the natural variables of a system to be S and V; that is, we do not usually hold these variables constant when carrying out experiments. The introduction of new state functions enable us to change the natural variables to anything desired (in mathematical terms, we perform Legendre transformations).

The most important of these new derived functions are as follows:

1. Enthalpy H is defined as

$$H = U + pV \tag{1.11}$$

   Its usefulness comes from the fact that, at constant p,

$$dH|_p = dU + p\,dV \tag{1.12}$$

   and, if this equation is compared with

$$dU = \delta q - p\,dV \tag{1.13}$$

   then we see that

$$dH|_p = \delta q \tag{1.14}$$

   Note that there is nothing in this last equation about maintaining constant T or carrying out the process reversibly. An enthalpy change can be obtained from the measured heat flow required to bring about the change at constant p. This is the basis of *calorimetry*.

2. Heat capacities C_p and C_V are two response functions (partial derivatives of other functions):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

3. Helmholtz energy A is defined as $A = U - TS$. For an isothermal process $dA = dU - T\,dS$, but for a reversible process $\delta w_{\text{rev}} = -dU + T\,dS$, so

that, for a reversible, isothermal process,

$$-dA|_T = \delta w_{rev} \tag{1.15}$$

that is, in an isothermal process, the decrease in A measures the maximum work performed by the system.

4. Entropy change has already been defined: $\delta q_{rev} = T\,dS$, where δq_{rev} can be expressed in terms of the heat capacity at constant pressure. This then gives

$$dS|_p = \frac{\delta q_{rev}|_p}{T} = \frac{C_p}{T}dT \tag{1.16}$$

and, when this is integrated, advantage is taken of the third law to obtain absolute entropies:

$$S|_p(T) = \int_0^T \frac{C_p}{T}dT \tag{1.17}$$

In practice, it is more useful to do the integration in two stages:

$$S|_p(T) - S|_p(298\ \mathrm{K}) = \int_{298K}^T \frac{C_p}{T}dT \tag{1.18}$$

5. Gibbs energy G is defined as $G = U + pV - TS$. For an isothermal, isobaric process

$$dG = dU + p\,dV - T\,dS \tag{1.19}$$

For a reversible isothermal, isobaric process (combine with $\delta w_{rev} = -dU + T\,dS$),

$$-dG|_{p,T} = \delta w_{rev} - p\,dV \tag{1.20}$$

This is the total reversible work less the $p-V$ work so that, in an isothermal, isobaric process, the decrease in G measures *the maximum non$-p-V$ work performed*. It is the most widely used derived function in materials thermodynamics. The non$-p-V$ work of most interest to us is chemical work.

By using the definitions of the derived functions H, A, G, we can derive the other three Gibbs equations for $p-V$ work only, fixed amounts:

$$\boxed{dH = T\,dS + V\,dp} \tag{1.21}$$

$$\boxed{dA = -S\,dT - p\,dV} \tag{1.22}$$

$$\boxed{G = -S\,dT + V\,dp} \tag{1.23}$$

The natural variables of G are p, T, which are the ones usually controlled in experiments and this accounts for the importance of this particular state function.

1.5.1   Maxwell's Equations

Return to (1.10), which is the total differential of $U = U(S, V)$. We can rewrite this equation in terms of partial derivatives as follows:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad (1.24)$$

If we compare (1.10) with (1.24), we see that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad (1.25)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \qquad (1.26)$$

Application of standard partial differentiation theory like this to the other Gibbs equations leads to similar relations and further relations can be obtained from the cross-derivatives, for example,

$$\left(\frac{\partial^2 U}{\partial S\, \partial V}\right)_V = \left(\frac{\partial^2 U}{\partial V\, \partial S}\right)_S \qquad (1.27)$$

which, using (1.25), gives

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \qquad (1.28)$$

Such relations are called Maxwell's equations. Their importance lies in the fact that they can point to the recognition of redundant measurements and offer the possibility of obtaining difficult-to-measure property variations from variations in properties which are easier to measure.

All the equations in this section apply to systems performing $p–V$ work only and are of fixed composition. We must now consider the modifications brought about by the inclusion of other types of work and the effect of changes in the amounts of substances which comprise the system.

1.5.2   Defining Other Forms of Work

With the conservation of energy as the fundamental principle, it is possible to invent other forms of thermodynamic work which can then be incorporated into the conservation-of-energy equation. By doing this, force and displacement are used in a much broader sense than they are in mechanical work. Any form of work which brings about a change in internal energy is to be considered. It may be a potential times a capacity factor or a field times a polarization.

Most notably in the present context is the invention, made by Gibbs, of chemical work. Chemical work can, of course, be considered as originating in the potential and kinetic energies of the atoms and electrons, but Gibbs realized that it is more useful to regard it as a separate form of work. In doing so, he introduced a most important new state function, the *chemical potential*, and also extended the fundamental equations to incorporate this new form of work.

The fundamental equations previously given apply to *closed* systems, that is, of fixed amounts of substance. They can be extended to include varying amounts, either for the case of a closed system, in which the amounts of substances are varying due to chemical reactions occurring within the system, or to *open* systems, where substances are being exchanged with the surroundings and in which reactions may or may not be occurring. In both cases chemical work is involved; that is, changes in internal energy are occurring.

If the amounts of substances can vary in a system, then, clearly, the state functions will depend on the n_i. In the case of U, for example, we now have $U = U(S, V, n_1, n_2 \ldots)$. Equation (1.24) will be modified to

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_j} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_j} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} dn_i \qquad (1.29)$$

where n_j means all the others except i.

In order to be able to write this in a manner similar to (1.10), we need a symbol for the partial derivative of U with respect to n_i. The usual symbol is μ_i and its name is the *chemical potential* (p–V and chemical work only):

$$\boxed{dU = T\,dS - p\,dV + \sum_i \mu_i\,dn_i} \qquad (1.30)$$

The other Gibbs equations may be modified in a similar fashion (p–V and chemical work only):

$$\boxed{dH = T\,dS + V\,dp + \sum_i \mu_i\,dn_i} \qquad (1.31)$$

$$\boxed{dA = -S\,dT - p\,dV + \sum_i \mu_i\,dn_i} \qquad (1.32)$$

$$\boxed{dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i} \qquad (1.33)$$

Note that the definition of μ_i varies depending on which function is being used:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad (1.34)$$

This extension of thermodynamics from a study of heat engines to its application to phase and chemical equilibrium by Gibbs represents one of the greatest achievements in nineteenth-century science. Recall that, in the application of thermodynamics to heat engines, the nature of the fluid of the engine is unimportant, but in introducing chemical work, the nature of the material constituting the system becomes all important.

Chemical work is not the only possible form of work which might have to be considered. Some examples of different types of thermodynamic work are given in the accompanying table. In order to emphasize the fact that (1.10) is a restricted form of the fundamental equation, let us write down a more complete statement which takes into account some other possible types of work:

$$dU = T\,dS - p\,dV + \sum_{i=1}^{N} \mu_i\,dn_i + \phi\,dm$$

$$+ \sum_{i=1}^{N} \psi_i\,dQ_i + \sigma\,d\epsilon + \gamma\,dA_s + \cdots \tag{1.35}$$

In writing the equation in this form it is assumed that the various types of work are independent of one another. This may not always be the case; often, two or more work terms are *coupled*.

A complete new set of Maxwell's equations can also be obtained from the fundamental equations for systems undergoing these various forms of work.

Type of Work	Field Variable	Extensive Variable	Differential Work in dU
Mechanical			
Pressure–volume	$-p$	V	$-p\,dV$
Elastic	τ_{ij}	$V\eta_{ij}$	$V\sum \tau_{ij}\,d\eta_{ij}$
Gravitational	$\phi = gh$	$m = \sum M_i n_i$	$\phi\,dm = \sum ghM_i\,dn_i$
Surface	γ	A_s	$\gamma\,dA_s$
Electromagnetic			
Charge transfer	ψ_i	Q_i	$\psi_i\,dQ_i$
Electric polarization	$\mathbf{E}$	p	$\mathbf{E}\cdot dp_i$
Magnetic polarization	$\mathbf{B}$	m	$\mathbf{B}\cdot dm$
Chemical			
No reactions	μ_i	n_i species	$\sum_i \mu_i\,dn_i$
With reactions	μ_i	ξ extent of reaction	$\sum_i \nu_i \mu_i\,d\xi$

1.6   EQUILIBRIUM STATE

A precise definition of a system in equilibrium is not straightforward. To define a system as being in equilibrium when its properties are not changing with time is unacceptable—the state which involves a steady flow of heat or matter through a system is a time-independent state but systems in which these processes are occurring are not in equilibrium; there are field gradients. We need a better definition and one is discussed below.

The second law, part 2, states that $dS_{univ} \geq 0$, with the inequality referring to spontaneous processes and the equality to reversible processes, the latter corresponding with the system being in equilibrium.

If we consider an isolated system (no work or heat flow and, therefore, constant U and V), then $dS_{surr} = 0$ so that

$$dS|_{U,V} = dS_{univ} \geq 0 \qquad (1.36)$$

In other words, for an isolated system, S reaches a maximum at the equilibrium state, making this state function the appropriate *thermodynamic potential* for isolated systems. The important point here is that, under certain constraints, we have replaced a property of the universe (system + surroundings) by a property of the system alone.

Of more practical interest is to obtain the appropriate thermodynamic potential for constant p and T conditions and the nature of the extrema conditions. We can do this as follows:

$$G = U + pV - TS \qquad (1.37)$$

$$dG = dU + p\,dV + V\,dp - T\,dS - S\,dT \qquad (1.38)$$

$$= \delta q - p_{surr}\,dV + p\,dV + V\,dp - T\,dS - S\,dT \qquad (1.39)$$

and at constant p and T where $p_{surr} = p$ we have

$$dG|_{p,T} = -T\,dS_{surr} - T\,dS$$

$$= -T\,dS_{univ} \leq 0 \qquad (1.40)$$

From the general statement of the second law, dS_{univ} is a maximum at equilibrium, it follows from (1.40) that *the appropriate thermodynamic potential for conditions of constant p and T is the Gibbs energy and G evolves to a minimum at equilibrium*. Since these conditions are the most frequently met, the Gibbs energy is usually the most important thermodynamic potential of interest. Note that, again, a property of the universe has been replaced by a property of the system alone.

For small excursions from an equilibrium state, we can expand any function for G as a Taylor series in the state space variables. As illustrated in Figure 1.5, which shows G as a function of only two state space variables, the extrema in
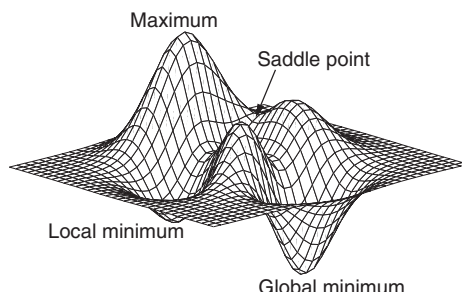
Figure 1.5 Local and global equilibrium, drawn using Matlab®.

multidimensional space can be maxima, minima, or saddle points (a maximum in some directions, a minimum in others). The required conditions for the extremum to be a minimum when there are two such variables, x and y, can be written as

$$\frac{\partial^2 G}{\partial x^2} \quad \text{and} \quad \frac{\partial^2 G}{\partial y^2} > 0 \tag{1.41}$$

$$\frac{\partial^2 G}{\partial x^2}\frac{\partial^2 G}{\partial y^2} > \left(\frac{\partial^2 G}{\partial x\,\partial y}\right)^2 \tag{1.42}$$

Failure of the condition given in (1.40) implies a saddle point.

These conditions only apply, however, for small excursions from the equilibrium point. As shown in Figure 1.5, it is possible to have a local minimum which fulfils the above conditions, but it is not the global minimum which we seek in our thermodynamic calculation.

For both the local and global minima, a small fluctuation from the equilibrium point will result in $dG|_{p,T} > 0$ and the system will wish to return to its equilibrium point. In both cases also the field variables (T, p, μ_A) are constant throughout the system. This means that we can apply the equations of thermodynamics equally well to the metastable local equilibrium and the stable global equilibrium situations if we ensure that there are no large-scale fluctuations which will take us from the local to the global equilibrium.

The global equilibrium, that is, *the true equilibrium state, is when* $\Delta G|_{p,T} > 0$ *for any excursions from that state*, providing the start and end states are maintained in internal equilibrium by the imposition of extra constraints. It is this definition of the equilibrium state which is mainly used throughout these chapters, but, as has been indicated previously, other thermodynamic potentials fulfil the same role as G for other conditions.

EXERCISES

1.1 Starting from Al(s) and O_2(g) at 298 K and 1 bar, use the data given below and the cycle illustrated in Figure 1.6 to confirm that $\oint dS = 0$:
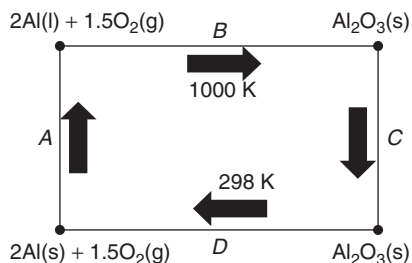
Figure 1.6   Cycle to be considered.

$$T_{\text{fus}}(\text{Al}) = 933 \text{ K} \qquad \Delta_{\text{fus}}H_m = 10460 \text{ J mol}^{-1}$$

$$C_p = a + bT + cT^2 + dT^{-2}$$

	a	$b/10^3$	$c/10^6$	$d/10^{-5}$	$S^{\circ}(298)/\text{J K}^{-1} \text{ mol}^{-1}$
Al(s)	20.7	12.4	0	0	28.3
Al(l)	31.8	0	0	0	0
O_2(g)	30	4.184	0	−1.67	205.0
Al_2O_3(s)	106.6	17.78	0	−28.53	51.0

1.2   Starting with $CaCO_3$(s) at 298 K and 1 bar:

(a) Calculate the heat transferred in producing 1 mol of CaO(s) at 1200 K and 1 mol of CO_2(g) at 500 K.

(b) Calculate the standard entropy change for this process.

1.3   (a) Write down the full equations required for evaluation of the standard enthalpy and Gibbs energy for the reaction equation

$$CaCO_3(s) = CaO(s) + CO_2(g)$$

(b) Determine the temperature at which $\Delta G^{\circ} = 0$ for this reaction equation.

(c) Calculate the enthalpy of reaction at the temperature for which the equilibrium pressure of CO_2 is 1 bar.

			$C_p = a + bT + cT^2 + dT^{-2}/\text{J K}^{-1} \text{ mol}^{-1}$			
Substance	$\Delta_f H^{\circ}(298\text{K})/$ kJ mol^{-1}	$S^{\circ}(1000K)/$ J K^{-1} mol^{-1}	a	$b \times 10^3$	$c \times 10^5$	$d \times 10^{-5}$
CaO(s)	−634.92	96.96	57.75	−107.79	0.53	−11.51
CO_2(g)	−393.51	269.19	44.14	9.04	0	−8.54
$CaCO_3$(s)	−1206.60	220.21	99.55	27.14	0	−21.48

1.4 Given the following data:
Note that $\langle C_p^\circ \rangle$ refers to the average values of C_p° over the range 298–1000 K. Calculate:

(a) The standard entropy of oxidation of Si(s) to SiO_2(s) at 1000 K.
(b) The same using the values of $\langle C_p^\circ \rangle$. Compare with the result from (a).

Substance	S°(s, 298 K)/ J K^{-1} mol^{-1}	$(S^\circ_{1000} - S^\circ_{298})$/ J K^{-1} mol^{-1}	$\langle C_p^\circ \rangle$/ J K^{-1} mol^{-1}
Si(s)	18.81	28.69	23.23
O_2(g)	209.15	38.43	32.10
SiO_2(s)	27.78	72.15	56.02

(c) $\Delta_f H^\circ(SiO_2, 1000\,\text{K})$ using the value of $\Delta_f H^\circ(SiO_2, 298\,\text{K})$ in the text.

1.5 Derive (1.21), (1.22), and (1.23) from (1.10) and the definitions of the functions H, A and G.

1.6 (a) If the entropy of transition of a pure substance A, $\Delta_\alpha^\beta S^\circ(A)$, at constant p is constant, show that the corresponding enthalpy change, $\Delta_\alpha^\beta H^\circ(A)$, is also constant.

(b) If the phase transition of a pure substance is a function of T and p and the value of $\Delta_\alpha^\beta S^\circ(A)$ is independent of the change in conditions, show that the value of $\Delta_\alpha^\beta H^\circ(A)$ is no longer constant, as was the case for the constraint of constant p. (*Hint*: Use the Maxwell relationships.)