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This chapter introduces some of the basic concepts of thermodynamics. It concentrates on the conservation of energy—the experimental observation that energy can be neither created nor destroyed—and shows how the principle of the conservation of energy can be used to assess the energy changes that accompany physical and chemical processes. Much of this chapter examines the means by which a system can exchange energy with its surroundings in terms of the work it may do or the heat that it may produce. The target concept of the chapter is enthalpy, which is a very useful book-keeping property for keeping track of the heat output (or requirements) of physical processes and chemical reactions at constant pressure. We also begin to unfold some of the power of thermodynamics by showing how to establish relations between different properties of a system. We shall see that one very useful aspect of thermodynamics is that a property can be measured indirectly by measuring others and then combining their values. The relations we derive also enable us to discuss the liquefaction of gases and to establish the relation between the heat capacities of a substance under different conditions.

The release of energy can be used to provide heat when a fuel burns in a furnace, to produce mechanical work when a fuel burns in an engine, and to generate electrical work when a chemical reaction pumps electrons through a circuit. In chemistry, we encounter reactions that can be harnessed to provide heat and work, reactions that liberate energy which is squandered (often to the detriment of the environment) but which give products we require, and reactions that constitute the processes of life. **Thermodynamics**, the study of the transformations of energy, enables us to discuss all these matters quantitatively and to make useful predictions.

The basic concepts

For the purposes of physical chemistry, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where we make our measurements. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 2.1). If matter can be transferred through the boundary between the system and its surroundings the system is classified as **open**. If matter cannot pass through the boundary the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings. For example, a closed system can expand and thereby raise a weight in the surroundings; it may also transfer energy to them if they are at a lower temperature.

An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

2.1 Work, heat, and energy

The fundamental physical property in thermodynamics is work: **work** is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

The **energy** of a system is its capacity to do work. When work is done on an otherwise isolated system (for instance, by compressing a gas or winding a spring), the capacity of the system to do work is increased; in other words, the energy of the system is increased. When the system does work (when the piston moves out or the spring unwinds), the energy of the system is reduced and it can do less work than before.

Experiments have shown that the energy of a system may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between the system and its surroundings we say that energy has been transferred as **heat**. When a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than the same amount of cold water. Not all boundaries permit the transfer of energy even though there is a temperature difference between the system and its surroundings.

An **exothermic process** is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic. An **endothermic process** is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water. To avoid a lot of awkward circumlocution, we say that in an exothermic process energy is transferred ‘as heat’ to the surroundings and in an endothermic process energy is transferred ‘as heat’ from the surroundings into the system. However, it must never be forgotten that heat is a process (the transfer of energy as a result of a temperature difference), not an entity. An endothermic process in a diathermic container results in energy flowing into the system as heat. An exothermic process in a similar diathermic container results in a release of energy as heat into the surroundings. When an endothermic process takes place in an adiabatic container, it results in a lowering of temperature of the system; an exothermic process results in a rise of temperature. These features are summarized in Fig. 2.2.

Molecular interpretation 2.1 Heat and work

In molecular terms, heating is the transfer of energy that makes use of *disorderly molecular motion*. The disorderly motion of molecules is called **thermal motion**. The thermal motion of the molecules in the hot surroundings stimulates the molecules in the cooler system to move more vigorously and, as a result, the energy of the system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings (Fig. 2.3).

In contrast, *work is the transfer of energy that makes use of organized motion* (Fig. 2.4). When a weight is raised or lowered, its atoms move in an organized way (up or down). The atoms in a spring move in an orderly way when it is wound; the

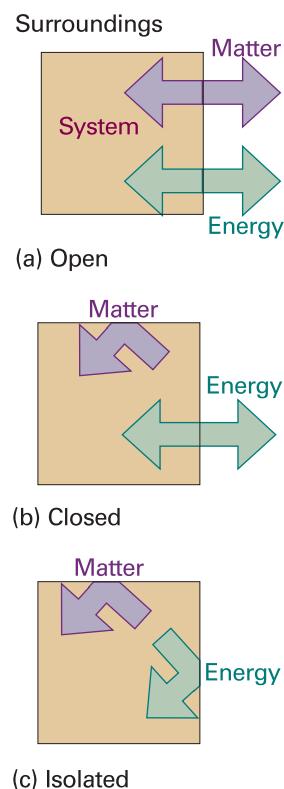


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

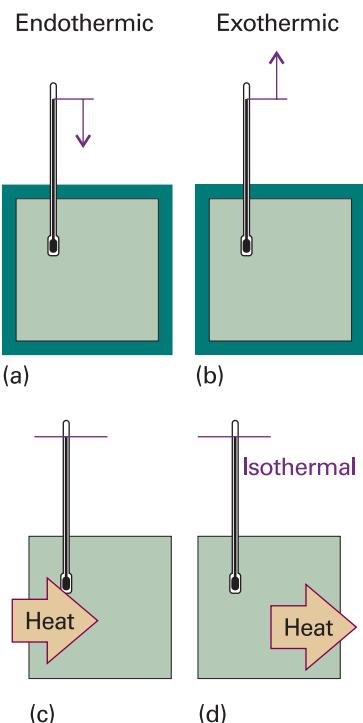


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

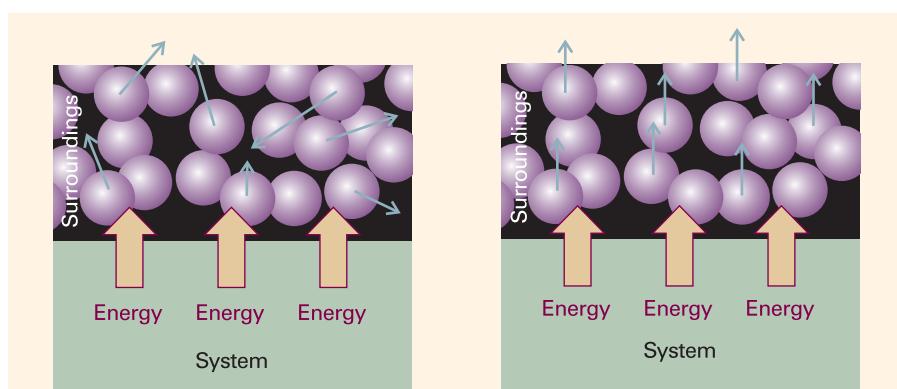


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

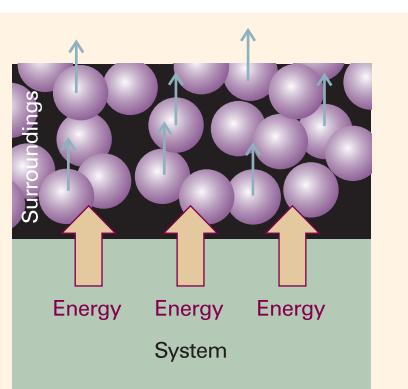


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

electrons in an electric current move in an orderly direction when it flows. When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in a weight are lowered or a current of electrons is passed.

The distinction between work and heat is made in the surroundings. The fact that a falling weight may stimulate thermal motion in the system is irrelevant to the distinction between heat and work: work is identified as energy transfer making use of the organized motion of atoms in the surroundings, and heat is identified as energy transfer making use of thermal motion in the surroundings. In the compression of a gas, for instance, work is done as the atoms of the compressing weight descend in an orderly way, but the effect of the incoming piston is to accelerate the gas molecules to higher average speeds. Because collisions between molecules quickly randomize their directions, the orderly motion of the atoms of the weight is in effect stimulating thermal motion in the gas. We observe the falling weight, the orderly descent of its atoms, and report that work is being done even though it is stimulating thermal motion.

2.2 The internal energy

In thermodynamics, the total energy of a system is called its **internal energy**, U . The internal energy is the total kinetic and potential energy of the molecules in the system (see *Comment 1.3* for the definitions of kinetic and potential energy).¹ We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f :

$$\Delta U = U_f - U_i \quad [2.1]$$

¹ The internal energy does not include the kinetic energy arising from the motion of the system as a whole, such as its kinetic energy as it accompanies the Earth on its orbit round the Sun.

The internal energy is a **state function** in the sense that its value depends only on the current state of the system and is independent of how that state has been prepared. In other words, it is a function of the properties that determine the current state of the system. Changing any one of the state variables, such as the pressure, results in a change in internal energy. The internal energy is an extensive property. That the internal energy is a state function has consequences of the greatest importance, as we start to unfold in Section 2.10.

Internal energy, heat, and work are all measured in the same units, the joule (J). The joule, which is named after the nineteenth-century scientist J.P. Joule, is defined as

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

A joule is quite a small unit of energy: for instance, each beat of the human heart consumes about 1 J. Changes in molar internal energy, ΔU_m , are typically expressed in kilojoules per mole (kJ mol^{-1}). Certain other energy units are also used, but are more common in fields other than thermodynamics. Thus, 1 electronvolt (1 eV) is defined as the kinetic energy acquired when an electron is accelerated from rest through a potential difference of 1 V; the relation between electronvolts and joules is $1 \text{ eV} \approx 0.16 \text{ aJ}$ (where $1 \text{ aJ} = 10^{-18} \text{ J}$). Many processes in chemistry have an energy of several electronvolts. Thus, the energy to remove an electron from a sodium atom is close to 5 eV. Calories (cal) and kilocalories (kcal) are still encountered. The current definition of the calorie in terms of joules is

$$1 \text{ cal} = 4.184 \text{ J exactly}$$

An energy of 1 cal is enough to raise the temperature of 1 g of water by 1°C .

Comment 2.1

An extensive property is a property that depends on the amount of substance in the sample. An intensive property is a property that is independent of the amount of substance in the sample. Two examples of extensive properties are mass and volume. Examples of intensive properties are temperature, mass density (mass divided by volume), and pressure.

Molecular interpretation 2.2 *The internal energy of a gas*

A molecule has a certain number of degrees of freedom, such as the ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For example, a chemical bond might break if a lot of energy becomes concentrated in it.

The *equipartition theorem* of classical mechanics is a useful guide to the average energy associated with each degree of freedom when the sample is at a temperature T . First, we need to know that a ‘quadratic contribution’ to the energy means a contribution that can be expressed as the square of a variable, such as the position or the velocity. For example, the kinetic energy of an atom of mass m as it moves through space is

$$E_K = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

and there are three quadratic contributions to its energy. The equipartition theorem then states that, for a collection of particles at thermal equilibrium at a temperature T , the average value of each quadratic contribution to the energy is the same and equal to $\frac{1}{2}kT$, where k is Boltzmann’s constant ($k = 1.381 \times 10^{-23} \text{ J K}^{-1}$).

The equipartition theorem is a conclusion from classical mechanics and is applicable only when the effects of quantization can be ignored (see Chapters 16 and 17). In practice, it can be used for molecular translation and rotation but not vibration. At 25°C , $\frac{1}{2}kT = 2 \text{ zJ}$ (where $1 \text{ zJ} = 10^{-21} \text{ J}$), or about 13 meV.

According to the equipartition theorem, the average energy of each term in the expression above is $\frac{1}{2}kT$. Therefore, the mean energy of the atoms is $\frac{3}{2}kT$ and the

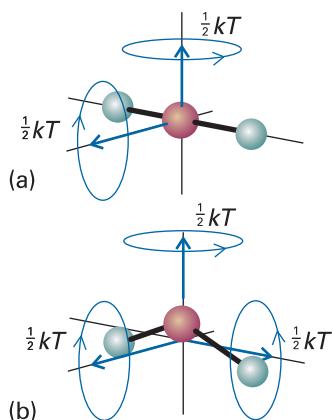


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature T . (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

total energy of the gas (there being no potential energy contribution) is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$ (because $N = nN_A$ and $R = N_A k$). We can therefore write

$$U_m = U_m(0) + \frac{3}{2}RT$$

where $U_m(0)$ is the molar internal energy at $T = 0$, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the internal energy of a perfect gas increases linearly with temperature. At 25°C , $\frac{3}{2}RT = 3.7 \text{ kJ mol}^{-1}$, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules (the remaining contribution arises from the internal structure of the atoms and molecules).

When the gas consists of polyatomic molecules, we need to take into account the effect of rotation and vibration. A linear molecule, such as N_2 and CO_2 , can rotate around two axes perpendicular to the line of the atoms (Fig. 2.5), so it has two rotational modes of motion, each contributing a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT . By adding the translational and rotational contributions, we obtain

$$U_m = U_m(0) + \frac{5}{2}RT \quad (\text{linear molecule, translation and rotation only})$$

A nonlinear molecule, such as CH_4 or water, can rotate around three axes and, again, each mode of motion contributes a term $\frac{1}{2}kT$ to the internal energy. Therefore, the mean rotational energy is $\frac{3}{2}kT$ and there is a rotational contribution of $\frac{3}{2}RT$ to the molar internal energy of the molecule. That is,

$$U_m = U_m(0) + 3RT \quad (\text{nonlinear molecule, translation and rotation only})$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas.

The internal energy of interacting molecules in condensed phases also has a contribution from the potential energy of their interaction. However, no simple expressions can be written down in general. Nevertheless, the crucial molecular point is that, as the temperature of a system is raised, the internal energy increases as the various modes of motion become more highly excited.

It has been found experimentally that the internal energy of a system may be changed either by doing work on the system or by heating it. Whereas we may know how the energy transfer has occurred (because we can see if a weight has been raised or lowered in the surroundings, indicating transfer of energy by doing work, or if ice has melted in the surroundings, indicating transfer of energy as heat), the system is blind to the mode employed. *Heat and work are equivalent ways of changing a system's internal energy.* A system is like a bank: it accepts deposits in either currency, but stores its reserves as internal energy. It is also found experimentally that, if a system is isolated from its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** and expressed as follows:

The internal energy of an isolated system is constant.

We cannot use a system to do work, leave it isolated for a month, and then come back expecting to find it restored to its original state and ready to do the same work again. The evidence for this property is that no 'perpetual motion machine' (a machine that

does work without consuming fuel or some other source of energy) has ever been built.

These remarks may be summarized as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \quad (2.2)$$

Equation 2.2 is the mathematical statement of the First Law, for it summarizes the equivalence of heat and work and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). The equation states that the change in internal energy of a closed system is equal to the energy that passes through its boundary as heat or work. It employs the ‘acquisitive convention’, in which $w > 0$ or $q > 0$ if energy is transferred to the system as work or heat and $w < 0$ or $q < 0$ if energy is lost from the system as work or heat. In other words, we view the flow of energy as work or heat from the system’s perspective.

Illustration 2.1 The sign convention in thermodynamics

If an electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2 \text{ kJ} - 15 \text{ kJ} = -17 \text{ kJ}$$

Suppose that, when a spring was wound, 100 J of work was done on it but 15 J escaped to the surroundings as heat. The change in internal energy of the spring is

$$\Delta U = +100 \text{ kJ} - 15 \text{ kJ} = +85 \text{ kJ}$$

2.3 Expansion work

The way can now be opened to powerful methods of calculation by switching attention to infinitesimal changes of state (such as infinitesimal change in temperature) and infinitesimal changes in the internal energy dU . Then, if the work done on a system is dw and the energy supplied to it as heat is dq , in place of eqn 2.2 we have

$$dU = dq + dw \quad (2.3)$$

To use this expression we must be able to relate dq and dw to events taking place in the surroundings.

We begin by discussing **expansion work**, the work arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation or consumption of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), and the thermodynamic characteristics of a reaction depend on the work it can do. The term ‘expansion work’ also includes work associated with negative changes of volume, that is, compression.

(a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance dz against an opposing force of magnitude F is

$$dw = -Fdz \quad [2.4]$$

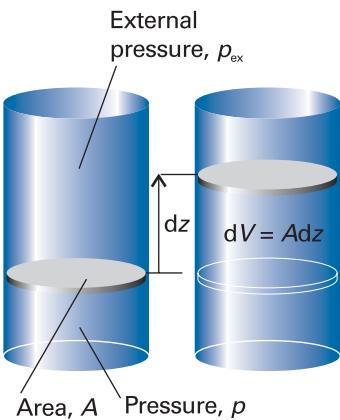


Fig. 2.6 When a piston of area \$A\$ moves out through a distance \$dz\$, it sweeps out a volume \$dV = Adz\$. The external pressure \$p_{\text{ex}}\$ is equivalent to a weight pressing on the piston, and the force opposing expansion is \$F = p_{\text{ex}}A\$.

The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease. Now consider the arrangement shown in Fig. 2.6, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area \$A\$. If the external pressure is \$p_{\text{ex}}\$, the magnitude of the force acting on the outer face of the piston is \$F = p_{\text{ex}}A\$. When the system expands through a distance \$dz\$ against an external pressure \$p_{\text{ex}}\$, it follows that the work done is \$dw = -p_{\text{ex}}Adz\$. But \$Adz\$ is the change in volume, \$dV\$, in the course of the expansion. Therefore, the work done when the system expands by \$dV\$ against a pressure \$p_{\text{ex}}\$ is

$$dw = -p_{\text{ex}}dV \quad (2.5)$$

To obtain the total work done when the volume changes from \$V_i\$ to \$V_f\$ we integrate this expression between the initial and final volumes:

$$w = - \int_{V_i}^{V_f} p_{\text{ex}}dV \quad (2.6)$$

The force acting on the piston, \$p_{\text{ex}}A\$, is equivalent to a weight that is raised as the system expands.

If the system is compressed instead, then the same weight is lowered in the surroundings and eqn 2.6 can still be used, but now \$V_f < V_i\$. It is important to note that it is still the external pressure that determines the magnitude of the work. This somewhat perplexing conclusion seems to be inconsistent with the fact that the gas *inside* the container is opposing the compression. However, when a gas is compressed, the ability of the *surroundings* to do work is diminished by an amount determined by the weight that is lowered, and it is this energy that is transferred into the system.

Other types of work (for example, electrical work), which we shall call either **non-expansion work** or **additional work**, have analogous expressions, with each one the product of an intensive factor (the pressure, for instance) and an extensive factor (the change in volume). Some are collected in Table 2.1. For the present we continue with the work associated with changing the volume, the expansion work, and see what we can extract from eqns 2.5 and 2.6.

(b) Free expansion

By **free expansion** we mean expansion against zero opposing force. It occurs when \$p_{\text{ex}} = 0\$. According to eqn 2.5, \$dw = 0\$ for each stage of the expansion. Hence, overall:

$$\text{Free expansion: } w = 0 \quad (2.7)$$

Table 2.1 Varieties of work*

Type of work	\$dw\$	Comments	Units†
Expansion	\$-p_{\text{ex}}dV\$	\$p_{\text{ex}}\$ is the external pressure \$dV\$ is the change in volume	\$\text{Pa m}^3\$
Surface expansion	\$\gamma d\sigma\$	\$\gamma\$ is the surface tension \$d\sigma\$ is the change in area	\$\text{N m}^{-1} \text{m}^2\$
Extension	\$fdl\$	\$f\$ is the tension \$dl\$ is the change in length	N m
Electrical	\$\phi dQ\$	\$\phi\$ is the electric potential \$dQ\$ is the change in charge	V C

* In general, the work done on a system can be expressed in the form \$dw = -Fdz\$, where \$F\$ is a ‘generalized force’ and \$dz\$ is a ‘generalized displacement’.

† For work in joules (J). Note that \$1 \text{ N m} = 1 \text{ J}\$ and \$1 \text{ V C} = 1 \text{ J}\$.

That is, no work is done when a system expands freely. Expansion of this kind occurs when a system expands into a vacuum.

(c) Expansion against constant pressure

Now suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion. A chemical example of this condition is the expansion of a gas formed in a chemical reaction. We can evaluate eqn 2.6 by taking the constant p_{ex} outside the integral:

$$w = -p_{\text{ex}} \int_{V_i}^{V_f} dV = -p_{\text{ex}}(V_f - V_i)$$

Therefore, if we write the change in volume as $\Delta V = V_f - V_i$,

$$w = -p_{\text{ex}} \Delta V \quad (2.8)$$

This result is illustrated graphically in Fig. 2.7, which makes use of the fact that an integral can be interpreted as an area. The magnitude of w , denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{\text{ex}}$ lying between the initial and final volumes. A p,V -graph used to compute expansion work is called an **indicator diagram**; James Watt first used one to indicate aspects of the operation of his steam engine.

(d) Reversible expansion

A **reversible change** in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word ‘infinitesimal’ sharpens the everyday meaning of the word ‘reversible’ as something that can change direction. We say that a system is in **equilibrium** with its surroundings if an infinitesimal change in the conditions in opposite directions results in opposite changes in its state. One example of reversibility that we have encountered already is the thermal equilibrium of two systems with the same temperature. The transfer of energy as heat between the two is reversible because, if the temperature of either system is lowered infinitesimally, then energy flows into the system with the lower temperature. If the temperature of either system at thermal equilibrium is raised infinitesimally, then energy flows out of the hotter system.

Suppose a gas is confined by a piston and that the external pressure, p_{ex} , is set equal to the pressure, p , of the confined gas. Such a system is in mechanical equilibrium with its surroundings (as illustrated in Section 1.1) because an infinitesimal change in the external pressure in either direction causes changes in volume in opposite directions. If the external pressure is reduced infinitesimally, then the gas expands slightly. If the external pressure is increased infinitesimally, then the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure differs measurably from the internal pressure, then changing p_{ex} infinitesimally will not decrease it below the pressure of the gas, so will not change the direction of the process. Such a system is not in mechanical equilibrium with its surroundings and the expansion is thermodynamically irreversible.

To achieve reversible expansion we set p_{ex} equal to p at each stage of the expansion. In practice, this equalization could be achieved by gradually removing weights from the piston so that the downward force due to the weights always matched the changing upward force due to the pressure of the gas. When we set $p_{\text{ex}} = p$, eqn 2.5 becomes

$$dw = -p_{\text{ex}} dV = -pdV \quad (2.9)_{\text{rev}}$$

(Equations valid only for reversible processes are labelled with a subscript rev.) Although the pressure inside the system appears in this expression for the work, it

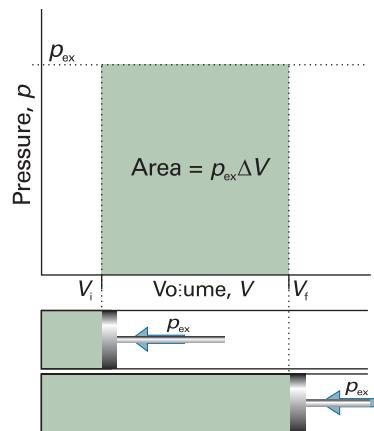
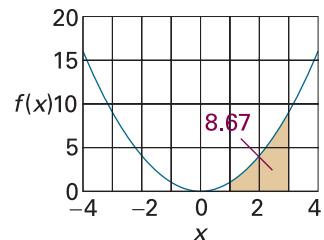


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex} , is equal to the shaded area in this example of an indicator diagram.

Comment 2.2

The value of the integral $\int_a^b f(x)dx$ is equal to the area under the graph of $f(x)$ between $x = a$ and $x = b$. For instance, the area under the curve $f(x) = x^2$ shown in the illustration that lies between $x = 1$ and 3 is

$$\begin{aligned} \int_1^3 x^2 dx &= (\frac{1}{3}x^3 + \text{constant}) \Big|_1^3 \\ &= \frac{1}{3}(3^3 - 1^3) = \frac{26}{3} \approx 8.67 \end{aligned}$$



does so only because p_{ex} has been set equal to p to ensure reversibility. The total work of reversible expansion is therefore

$$w = - \int_{V_i}^{V_f} p dV \quad (2.10)_{\text{rev}}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 2.10 is the link with the material covered in Chapter 1 for, if we know the equation of state of the gas, then we can express p in terms of V and evaluate the integral.

(e) Isothermal reversible expansion

Consider the isothermal, reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its surroundings (which may be a constant-temperature bath). Because the equation of state is $pV = nRT$, we know that at each stage $p = nRT/V$, with V the volume at that stage of the expansion. The temperature T is constant in an isothermal expansion, so (together with n and R) it may be taken outside the integral. It follows that the work of reversible isothermal expansion of a perfect gas from V_i to V_f at a temperature T is

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad (2.11)_{\text{rev}}^{\circ}$$

Comment 2.3

An integral that occurs throughout thermodynamics is

$$\int_a^b \frac{1}{x} dx = (\ln x + \text{constant}) \Big|_a^b = \ln \frac{b}{a}$$

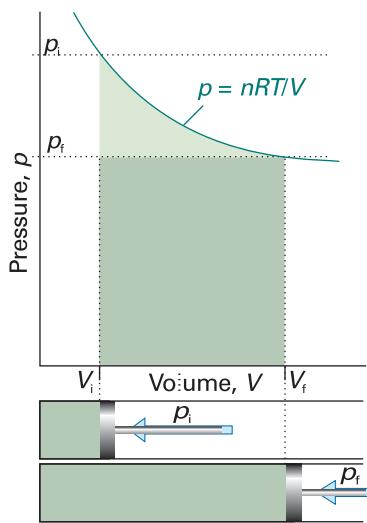


Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work is greater than the irreversible work.

 **Exploration** Calculate the work of isothermal reversible expansion of 1.0 mol CO₂(g) at 298 K from 1.0 m³ to 3.0 m³ on the basis that it obeys the van der Waals equation of state.

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 2.11 is positive and hence $w < 0$. In this case, the system has done work on the surroundings and the internal energy of the system has decreased as a result.² The equations also show that more work is done for a given change of volume when the temperature is increased. The greater pressure of the confined gas then needs a higher opposing pressure to ensure reversibility.

We can express the result of the calculation as an indicator diagram, for the magnitude of the work done is equal to the area under the isotherm $p = nRT/V$ (Fig. 2.8). Superimposed on the diagram is the rectangular area obtained for irreversible expansion against constant external pressure fixed at the same final value as that reached in the reversible expansion. More work is obtained when the expansion is reversible (the area is greater) because matching the external pressure to the internal pressure at each stage of the process ensures that none of the system's pushing power is wasted. We cannot obtain more work than for the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. We may infer from this discussion that, because some pushing power is wasted when $p > p_{\text{ex}}$, the maximum work available from a system operating between specified initial and final states and passing along a specified path is obtained when the change takes place reversibly.

We have introduced the connection between reversibility and maximum work for the special case of a perfect gas undergoing expansion. Later (in Section 3.5) we shall see that it applies to all substances and to all kinds of work.

Example 2.1 Calculating the work of gas production

Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

² We shall see later that there is a compensating influx of energy as heat, so overall the internal energy is constant for the isothermal expansion of a perfect gas.

Method We need to judge the magnitude of the volume change and then to decide how the process occurs. If there is no change in volume, there is no expansion work however the process takes place. If the system expands against a constant external pressure, the work can be calculated from eqn 2.8. A general feature of processes in which a condensed phase changes into a gas is that the volume of the former may usually be neglected relative to that of the gas it forms.

Answer In (a) the volume cannot change, so no expansion work is done and $w=0$. In (b) the gas drives back the atmosphere and therefore $w=-p_{\text{ex}}\Delta V$. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V=V_f-V_i\approx V_f=nRT/p_{\text{ex}}$, where n is the amount of H_2 produced. Therefore,

$$w=-p_{\text{ex}}\Delta V\approx-p_{\text{ex}}\times\frac{nRT}{p_{\text{ex}}}=-nRT$$

Because the reaction is $\text{Fe}(\text{s})+2\text{HCl}(\text{aq})\rightarrow\text{FeCl}_2(\text{aq})+\text{H}_2(\text{g})$, we know that 1 mol H_2 is generated when 1 mol Fe is consumed, and n can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol⁻¹, it follows that

$$\begin{aligned} w &\approx -\frac{50 \text{ g}}{55.85 \text{ g mol}^{-1}} \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &\approx -2.2 \text{ kJ} \end{aligned}$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere. Note that (for this perfect gas system) the magnitude of the external pressure does not affect the final result: the lower the pressure, the larger the volume occupied by the gas, so the effects cancel.

Self-test 2.1 Calculate the expansion work done when 50 g of water is electrolysed under constant pressure at 25°C. [−10 kJ]

2.4 Heat transactions

In general, the change in internal energy of a system is

$$dU=dq+dw_{\text{exp}}+dw_e \quad (2.12)$$

where dw_e is work in addition (e for ‘extra’) to the expansion work, dw_{exp} . For instance, dw_e might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $dw_{\text{exp}}=0$. If the system is also incapable of doing any other kind of work (if it is not, for instance, an electrochemical cell connected to an electric motor), then $dw_e=0$ too. Under these circumstances:

$$dU=dq \quad (\text{at constant volume, no additional work}) \quad (2.13a)$$

We express this relation by writing $dU=dq_V$, where the subscript implies a change at constant volume. For a measurable change,

$$\Delta U=q_V \quad (2.13b)$$

It follows that, by measuring the energy supplied to a constant-volume system as heat ($q>0$) or obtained from it as heat ($q<0$) when it undergoes a change of state, we are in fact measuring the change in its internal energy.

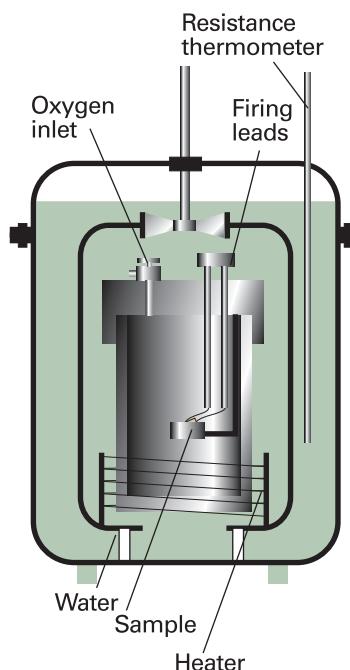


Fig. 2.9 A constant-volume bomb calorimeter. The ‘bomb’ is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

Comment 2.4

Electrical charge is measured in **coulombs**, C. The motion of charge gives rise to an electric current, I, measured in coulombs per second, or **amperes**, A, where $1\text{ A} = 1\text{ C s}^{-1}$. If a constant current I flows through a potential difference \mathcal{V} (measured in volts, V), the total energy supplied in an interval t is

$$\text{Energy supplied} = IVt$$

Because $1\text{ A V s} = 1(\text{C s}^{-1})\text{ V s} = 1\text{ C V} = 1\text{ J}$, the energy is obtained in joules with the current in amperes, the potential difference in volts, and the time in seconds. We write the electrical power, P, as

$$P = (\text{energy supplied}) / (\text{time interval}) \\ = IVt/t = I\mathcal{V}$$

(a) Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring ΔU is an **adiabatic bomb calorimeter** (Fig. 2.9). The process we wish to study—which may be a chemical reaction—is initiated inside a constant-volume container, the ‘bomb’. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic.

The change in temperature, ΔT , of the calorimeter is proportional to the heat that the reaction releases or absorbs. Therefore, by measuring ΔT we can determine q_V and hence find ΔU . The conversion of ΔT to q_V is best achieved by calibrating the calorimeter using a process of known energy output and determining the **calorimeter constant**, the constant C in the relation

$$q = C\Delta T \quad (2.14a)$$

The calorimeter constant may be measured electrically by passing a constant current, I, from a source of known potential difference, \mathcal{V} , through a heater for a known period of time, t, for then

$$q = I\mathcal{V}t \quad (2.14b)$$

Alternatively, C may be determined by burning a known mass of substance (benzoic acid is often used) that has a known heat output. With C known, it is simple to interpret an observed temperature rise as a release of heat.

Illustration 2.2 The calibration of a calorimeter

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 2.14b the energy supplied as heat is

$$q = (10.0\text{ A}) \times (12\text{ V}) \times (300\text{ s}) = 3.6 \times 10^4\text{ A V s} = 36\text{ kJ}$$

because $1\text{ A V s} = 1\text{ J}$. If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36\text{ kJ})/(5.5\text{ K}) = 6.5\text{ kJ K}^{-1}$.

(b) Heat capacity

The internal energy of a substance increases when its temperature is raised. The increase depends on the conditions under which the heating takes place and for the present we suppose that the sample is confined to a constant volume. For example, the sample may be a gas in a container of fixed volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2.10 may be obtained. The slope of the tangent to the curve at any temperature is called the **heat capacity** of the system at that temperature. The **heat capacity at constant volume** is denoted C_V and is defined formally as³

³ If the system can change its composition, it is necessary to distinguish between equilibrium and fixed-composition values of C_V . All applications in this chapter refer to a single substance, so this complication can be ignored.

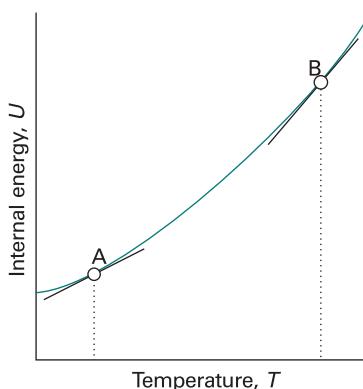


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad [2.15]$$

In this case, the internal energy varies with the temperature and the volume of the sample, but we are interested only in its variation with the temperature, the volume being held constant (Fig. 2.11).

Illustration 2.3 Estimating a constant-volume heat capacity

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived in *Molecular interpretation 2.2*. There we saw that $U_m = U_m(0) + \frac{3}{2}RT$, so from eqn 2.15

$$C_{V,m} = \frac{\partial}{\partial T} (U_m(0) + \frac{3}{2}RT) = \frac{3}{2}R$$

The numerical value is $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$.

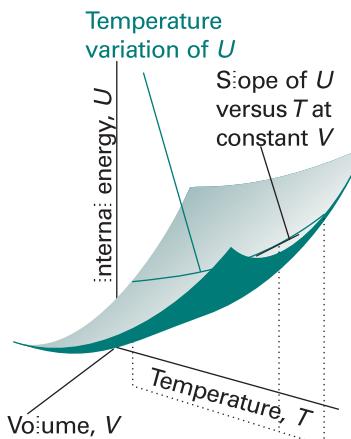


Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial derivative $(\partial U / \partial T)_V$.

Comment 2.5

The partial-differential operation $(\partial z / \partial x)_y$ consists of taking the first derivative of $z(x,y)$ with respect to x , treating y as a constant. For example, if $z(x,y) = x^2y$, then

$$\left(\frac{\partial z}{\partial x} \right)_y = \left(\frac{\partial [x^2y]}{\partial x} \right)_y = y \frac{dx^2}{dx} = 2yx$$

Partial derivatives are reviewed in *Appendix 2*.

Heat capacities are extensive properties: 100 g of water, for instance, has 100 times the heat capacity of 1 g of water (and therefore requires 100 times the energy as heat to bring about the same rise in temperature). The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of material, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to $25 \text{ J K}^{-1} \text{ mol}^{-1}$. For certain applications it is useful to know the **specific heat capacity** (more informally, the ‘specific heat’) of a substance, which is the heat capacity of the sample divided by the mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to $4 \text{ J K}^{-1} \text{ g}^{-1}$. In general,

heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 2.15 that

$$dU = C_V dT \quad (\text{at constant volume}) \quad (2.16a)$$

That is, at constant volume, an infinitesimal change in temperature brings about an infinitesimal change in internal energy, and the constant of proportionality is C_V . If the heat capacity is independent of temperature over the range of temperatures of interest, a measurable change of temperature, ΔT , brings about a measurable increase in internal energy, ΔU , where

$$\Delta U = C_V \Delta T \quad (\text{at constant volume}) \quad (2.16b)$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.13b), the last equation can be written

$$q_V = C_V \Delta T \quad (2.17)$$

This relation provides a simple way of measuring the heat capacity of a sample: a measured quantity of energy is transferred as heat to the sample (electrically, for example), and the resulting increase in temperature is monitored. The ratio of the energy transferred as heat to the temperature rise it causes ($q_V/\Delta T$) is the constant-volume heat capacity of the sample.

A large heat capacity implies that, for a given quantity of energy transferred as heat, there will be only a small increase in temperature (the sample has a large capacity for heat). An infinite heat capacity implies that there will be no increase in temperature however much energy is supplied as heat. At a phase transition, such as at the boiling point of water, the temperature of a substance does not rise as energy is supplied as heat: the energy is used to drive the endothermic transition, in this case to vaporize the water, rather than to increase its temperature. Therefore, at the temperature of a phase transition, the heat capacity of a sample is infinite. The properties of heat capacities close to phase transitions are treated more fully in Section 4.7.

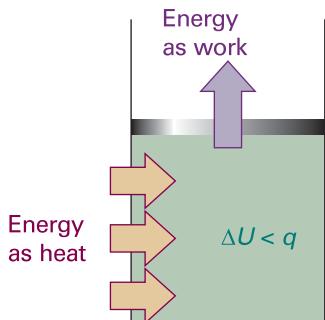


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

2.5 Enthalpy

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 2.12), so dU is less than dq . However, we shall now show that in this case the energy supplied as heat at constant pressure is equal to the change in another thermodynamic property of the system, the enthalpy.

(a) The definition of enthalpy

The **enthalpy**, H , is defined as

$$H = U + pV \quad [2.18]$$

where p is the pressure of the system and V is its volume. Because U , p , and V are all state functions, the enthalpy is a state function too. As is true of any state function, the change in enthalpy, ΔH , between any pair of initial and final states is independent of the path between them.

Although the definition of enthalpy may appear arbitrary, it has important implications for thermochemistry. For instance, we show in the following *Justification* that eqn 2.18 implies that *the change in enthalpy is equal to the energy supplied as heat at constant pressure* (provided the system does no additional work):

$$dH = dq \quad (\text{at constant pressure, no additional work}) \quad (2.19a)$$

For a measurable change,

$$\Delta H = q_p \quad (2.19b)$$

Justification 2.1 *The relation $\Delta H = q_p$*

For a general infinitesimal change in the state of the system, U changes to $U + dU$, p changes to $p + dp$, and V changes to $V + dV$, so from the definition in eqn 2.18, H changes from $U + pV$ to

$$\begin{aligned} H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + pdV + Vdp + pdV \end{aligned}$$

The last term is the product of two infinitesimally small quantities and can therefore be neglected. As a result, after recognizing $U + pV = H$ on the right, we find that H changes to

$$H + dH = H + dU + pdV + Vdp$$

and hence that

$$dH = dU + pdV + Vdp$$

If we now substitute $dU = dq + dw$ into this expression, we get

$$dH = dq + dw + pdV + Vdp$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, we can write $dw = -pdV$ and obtain

$$dH = dq + Vdp$$

Now we impose the condition that the heating occurs at constant pressure by writing $dp = 0$. Then

$$dH = dq \quad (\text{at constant pressure, no additional work})$$

as in eqn 2.19a.

The result expressed in eqn 2.19 states that, when a system is subjected to a constant pressure, and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat. For example, if we supply 36 kJ of energy through an electric heater immersed in an open beaker of water, then the enthalpy of the water increases by 36 kJ and we write $\Delta H = +36$ kJ.

(b) The measurement of an enthalpy change

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change occurring at constant pressure. A calorimeter for studying processes at constant pressure is called an **isobaric calorimeter**. A simple example is a thermally insulated vessel open to the atmosphere: the heat released in the reaction is monitored by measuring the change in temperature

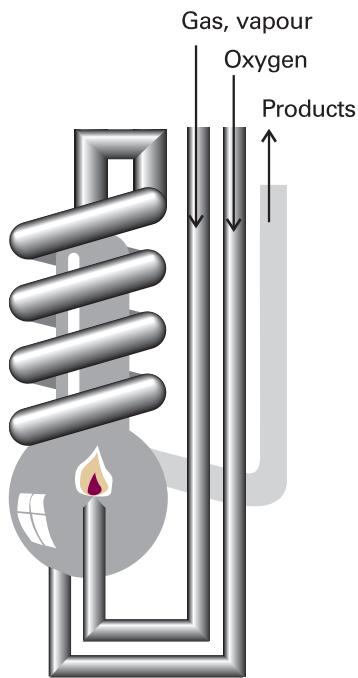


Fig. 2.13 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

of the contents. For a combustion reaction an **adiabatic flame calorimeter** may be used to measure ΔT when a given amount of substance burns in a supply of oxygen (Fig. 2.13). Another route to ΔH is to measure the internal energy change by using a bomb calorimeter, and then to convert ΔU to ΔH . Because solids and liquids have small molar volumes, for them pV_m is so small that the molar enthalpy and molar internal energy are almost identical ($H_m = U_m + pV_m \approx U_m$). Consequently, if a process involves only solids or liquids, the values of ΔH and ΔU are almost identical. Physically, such processes are accompanied by a very small change in volume, the system does negligible work on the surroundings when the process occurs, so the energy supplied as heat stays entirely within the system. The most sophisticated way to measure enthalpy changes, however, is to use a **differential scanning calorimeter** (DSC). Changes in enthalpy and internal energy may also be measured by noncalorimetric methods (see Chapter 7).

Example 2.2 Relating ΔH and ΔU

The internal energy change when 1.0 mol CaCO_3 in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 g cm^{-3} and 2.93 g cm^{-3} , respectively.

Method The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2.18). The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses, M , and their mass densities, ρ , by using $\rho = M/V_m$.

Answer The change in enthalpy when the transition occurs is

$$\begin{aligned}\Delta H &= H(\text{aronite}) - H(\text{calcite}) \\ &= \{U(a) + pV(a)\} - \{U(c) + pV(c)\} \\ &= \Delta U + p\{V(a) - V(c)\} = \Delta U + p\Delta V\end{aligned}$$

The volume of 1.0 mol CaCO_3 (100 g) as aragonite is 34 cm^3 , and that of 1.0 mol CaCO_3 as calcite is 37 cm^3 . Therefore,

$$p\Delta V = (1.0 \times 10^5 \text{ Pa}) \times (34 - 37) \times 10^{-6} \text{ m}^3 = -0.3 \text{ J}$$

(because $1 \text{ Pa m}^3 = 1 \text{ J}$). Hence,

$$\Delta H - \Delta U = -0.3 \text{ J}$$

which is only 0.1 per cent of the value of ΔU . We see that it is usually justifiable to ignore the difference between the enthalpy and internal energy of condensed phases, except at very high pressures, when pV is no longer negligible.

Self-test 2.2 Calculate the difference between ΔH and ΔU when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = +2.1 \text{ kJ}$. $[\Delta H - \Delta U = -4.4 \text{ J}]$

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H :

$$H = U + pV = U + nRT \quad (2.20)^{\circ}$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_g RT \quad (2.21)^\circ$$

where Δn_g is the change in the amount of gas molecules in the reaction.

Illustration 2.4 The relation between ΔH and ΔU for gas-phase reactions

In the reaction $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$, 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so $\Delta n_g = -3 \text{ mol}$. Therefore, at 298 K, when $RT = 2.5 \text{ kJ mol}^{-1}$, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H - \Delta U = (-3 \text{ mol}) \times RT \approx -7.4 \text{ kJ}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2.2. The enthalpy change is smaller (in this case, less negative) than the change in internal energy because, although heat escapes from the system when the reaction occurs, the system contracts when the liquid is formed, so energy is restored to it from the surroundings.

Example 2.3 Calculating a change in enthalpy

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).

Method Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, the strategy is to calculate the energy supplied as heat (from $q = IVt$), express that as an enthalpy change, and then convert the result to a molar enthalpy change by division by the amount of H_2O molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas and use eqn 2.21.

Answer The enthalpy change is

$$\Delta H = q_p = (0.50 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = +(0.50 \times 12 \times 300) \text{ J}$$

Here we have used $1 \text{ A V s} = 1 \text{ J}$ (see *Comment 2.4*). Because 0.798 g of water is $(0.798 \text{ g})/(18.02 \text{ g mol}^{-1}) = (0.798/18.02) \text{ mol H}_2\text{O}$, the enthalpy of vaporization per mole of H_2O is

$$\Delta H_m = +\frac{0.50 \times 12 \times 300 \text{ J}}{(0.798/18.02) \text{ mol}} = +41 \text{ kJ mol}^{-1}$$

In the process $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ the change in the amount of gas molecules is $\Delta n_g = +1 \text{ mol}$, so

$$\Delta U_m = \Delta H_m - RT = +38 \text{ kJ mol}^{-1}$$

The plus sign is added to positive quantities to emphasize that they represent an increase in internal energy or enthalpy. Notice that the internal energy change is smaller than the enthalpy change because energy has been used to drive back the surrounding atmosphere to make room for the vapour.

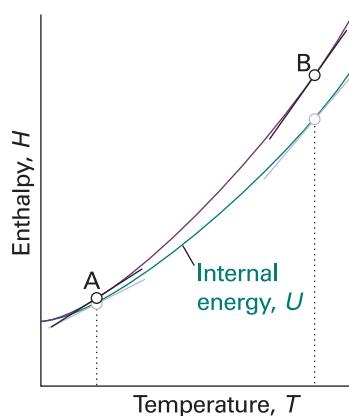


Fig. 2.14 The slope of the tangent to a curve of the enthalpy of a system subjected to a constant pressure plotted against temperature is the constant-pressure heat capacity. The slope may change with temperature, in which case the heat capacity varies with temperature. Thus, the heat capacities at A and B are different. For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{V,m}$.

Self-test 2.3 The molar enthalpy of vaporization of benzene at its boiling point (353.25 K) is 30.8 kJ mol⁻¹. What is the molar internal energy change? For how long would the same 12 V source need to supply a 0.50 A current in order to vaporize a 10 g sample? [+27.9 kJ mol⁻¹, 660 s]

(c) The variation of enthalpy with temperature

The enthalpy of a substance increases as its temperature is raised. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The most important condition is constant pressure, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p , at a given temperature (Fig. 2.14). More formally:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad [2.22]$$

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume, and is an extensive property.⁴ The **molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of material; it is an intensive property.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature,

$$dH = C_p dT \quad (\text{at constant pressure}) \quad (2.23a)$$

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p \Delta T \quad (\text{at constant pressure}) \quad (2.23b)$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p \Delta T \quad (2.24)$$

This expression shows us how to measure the heat capacity of a sample: a measured quantity of energy is supplied as heat under conditions of constant pressure (as in a sample exposed to the atmosphere and free to expand), and the temperature rise is monitored.

The variation of heat capacity with temperature can sometimes be ignored if the temperature range is small; this approximation is highly accurate for a monatomic perfect gas (for instance, one of the noble gases at low pressure). However, when it is necessary to take the variation into account, a convenient approximate empirical expression is

$$C_{p,m} = a + bT + \frac{c}{T^2} \quad (2.25)$$

The empirical parameters a , b , and c are independent of temperature (Table 2.2).

⁴ As in the case of C_V , if the system can change its composition it is necessary to distinguish between equilibrium and fixed-composition values. All applications in this chapter refer to pure substances, so this complication can be ignored.

Synoptic Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + c/T^2$

	a	$b/(10^{-3} \text{ K})$	$c/(10^5 \text{ K}^2)$
C(s, graphite)	16.86	4.77	-8.54
CO ₂ (g)	44.22	8.79	-8.62
H ₂ O(l)	75.29	0	0
N ₂ (g)	28.58	3.77	-0.50

* More values are given in the *Data section*.

Example 2.4 Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N₂ when it is heated from 25°C to 100°C? Use the heat capacity information in Table 2.2.

Method The heat capacity of N₂ changes with temperature, so we cannot use eqn 2.23b (which assumes that the heat capacity of the substance is constant). Therefore, we must use eqn 2.23a, substitute eqn 2.25 for the temperature dependence of the heat capacity, and integrate the resulting expression from 25°C to 100°C.

Answer For convenience, we denote the two temperatures T_1 (298 K) and T_2 (373 K). The integrals we require are

$$\int_{H(T_1)}^{H(T_2)} dH = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT$$

Notice how the limits of integration correspond on each side of the equation: the integration over H on the left ranges from $H(T_1)$, the value of H at T_1 , up to $H(T_2)$, the value of H at T_2 , while on the right the integration over the temperature ranges from T_1 to T_2 . Now we use the integrals

$$\int dx = x + \text{constant} \quad \int x dx = \frac{1}{2}x^2 + \text{constant} \quad \int \frac{dx}{x^2} = -\frac{1}{x} + \text{constant}$$

to obtain

$$H(T_2) - H(T_1) = a(T_2 - T_1) + \frac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Substitution of the numerical data results in

$$H(373 \text{ K}) = H(298 \text{ K}) + 2.20 \text{ kJ mol}^{-1}$$

If we had assumed a constant heat capacity of 29.14 J K⁻¹ mol⁻¹ (the value given by eqn 2.25 at 25°C), we would have found that the two enthalpies differed by 2.19 kJ mol⁻¹.

Self-test 2.4 At very low temperatures the heat capacity of a solid is proportional to T^3 , and we can write $C_p = aT^3$. What is the change in enthalpy of such a substance when it is heated from 0 to a temperature T (with T close to 0)? [$\Delta H = \frac{1}{4}aT^4$]

Comment 2.6

Integrals commonly encountered in physical chemistry are listed inside the front cover.

Most systems expand when heated at constant pressure. Such systems do work on the surroundings and therefore some of the energy supplied to them as heat escapes

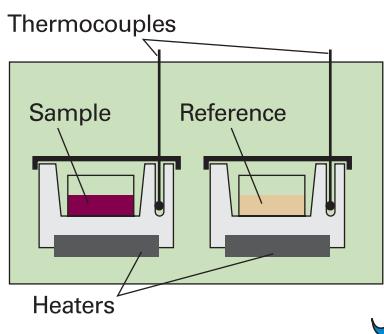


Fig. 2.15 A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

back to the surroundings. As a result, the temperature of the system rises less than when the heating occurs at constant volume. A smaller increase in temperature implies a larger heat capacity, so we conclude that in most cases the heat capacity at constant pressure of a system is larger than its heat capacity at constant volume. We show later (Section 2.11) that there is a simple relation between the two heat capacities of a perfect gas:

$$C_p - C_V = nR \quad (2.26)^{\circ}$$

It follows that the molar heat capacity of a perfect gas is about $8 \text{ J K}^{-1} \text{ mol}^{-1}$ larger at constant pressure than at constant volume. Because the heat capacity at constant volume of a monatomic gas is about $12 \text{ J K}^{-1} \text{ mol}^{-1}$, the difference is highly significant and must be taken into account.

IMPACT ON BIOCHEMISTRY AND MATERIALS SCIENCE

12.1 Differential scanning calorimetry

A *differential scanning calorimeter* (DSC) measures the energy transferred as heat to or from a sample at constant pressure during a physical or chemical change. The term ‘differential’ refers to the fact that the behaviour of the sample is compared to that of a reference material which does not undergo a physical or chemical change during the analysis. The term ‘scanning’ refers to the fact that the temperatures of the sample and reference material are increased, or scanned, during the analysis.

A DSC consists of two small compartments that are heated electrically at a constant rate. The temperature, T , at time t during a linear scan is $T = T_0 + \alpha t$, where T_0 is the initial temperature and α is the temperature scan rate (in kelvin per second, K s^{-1}). A computer controls the electrical power output in order to maintain the same temperature in the sample and reference compartments throughout the analysis (see Fig. 2.15).

The temperature of the sample changes significantly relative to that of the reference material if a chemical or physical process involving the transfer of energy as heat occurs in the sample during the scan. To maintain the same temperature in both compartments, excess energy is transferred as heat to or from the sample during the process. For example, an endothermic process lowers the temperature of the sample relative to that of the reference and, as a result, the sample must be heated more strongly than the reference in order to maintain equal temperatures.

If no physical or chemical change occurs in the sample at temperature T , we write the heat transferred to the sample as $q_p = C_p \Delta T$, where $\Delta T = T - T_0$ and we have assumed that C_p is independent of temperature. The chemical or physical process requires the transfer of $q_p + q_{p,\text{ex}}$, where $q_{p,\text{ex}}$ is excess energy transferred as heat, to attain the same change in temperature of the sample. We interpret $q_{p,\text{ex}}$ in terms of an apparent change in the heat capacity at constant pressure of the sample, C_p , during the temperature scan. Then we write the heat capacity of the sample as $C_p + C_{p,\text{ex}}$, and

$$q_p + q_{p,\text{ex}} = (C_p + C_{p,\text{ex}})\Delta T$$

It follows that

$$C_{p,\text{ex}} = \frac{q_{p,\text{ex}}}{\Delta T} = \frac{q_{p,\text{ex}}}{\alpha t} = \frac{P_{\text{ex}}}{\alpha}$$

where $P_{\text{ex}} = q_{p,\text{ex}}/t$ is the excess electrical power necessary to equalize the temperature of the sample and reference compartments.

A DSC trace, also called a *thermogram*, consists of a plot of P_{ex} or $C_{p,\text{ex}}$ against T (see Fig. 2.16). Broad peaks in the thermogram indicate processes requiring transfer of energy as heat. From eqn 2.23a, the enthalpy change associated with the process is

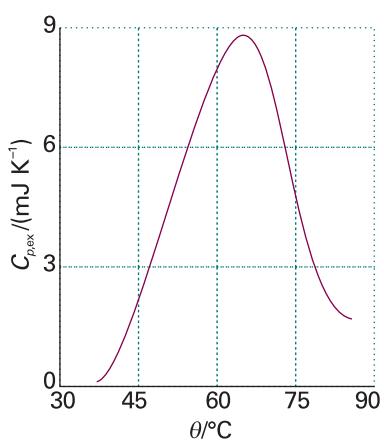


Fig. 2.16 A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* 74, 236 (1997).)

$$\Delta H = \int_{T_1}^{T_2} C_{p,\text{ex}} dT$$

where T_1 and T_2 are, respectively, the temperatures at which the process begins and ends. This relation shows that the enthalpy change is then the area under the curve of $C_{p,\text{ex}}$ against T . With a DSC, enthalpy changes may be determined in samples of masses as low as 0.5 mg, which is a significant advantage over bomb or flame calorimeters, which require several grams of material.

Differential scanning calorimetry is used in the chemical industry to characterize polymers and in the biochemistry laboratory to assess the stability of proteins, nucleic acids, and membranes. Large molecules, such as synthetic or biological polymers, attain complex three-dimensional structures due to intra- and intermolecular interactions, such as hydrogen bonding and hydrophobic interactions (Chapter 18). Disruption of these interactions is an endothermic process that can be studied with a DSC. For example, the thermogram shown in the illustration indicated that the protein ubiquitin retains its native structure up to about 45°C. At higher temperatures, the protein undergoes an endothermic conformational change that results in the loss of its three-dimensional structure. The same principles also apply to the study of structural integrity and stability of synthetic polymers, such as plastics.

2.6 Adiabatic changes

We are now equipped to deal with the changes that occur when a perfect gas expands adiabatically. A decrease in temperature should be expected: because work is done but no heat enters the system, the internal energy falls, and therefore the temperature of the working gas also falls. In molecular terms, the kinetic energy of the molecules falls as work is done, so their average speed decreases, and hence the temperature falls.

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as the sum of two steps (Fig. 2.17). In the first step, only the volume changes and the temperature is held constant at its initial value. However, because the internal energy of a perfect gas is independent of the volume the molecules occupy, the overall change in internal energy arises solely from the second step, the change in temperature at constant volume. Provided the heat capacity is independent of temperature, this change is

$$\Delta U = C_V(T_f - T_i) = C_V\Delta T$$

Because the expansion is adiabatic, we know that $q = 0$; because $\Delta U = q + w$, it then follows that $\Delta U = w_{\text{ad}}$. The subscript ‘ad’ denotes an adiabatic process. Therefore, by equating the two values we have obtained for ΔU , we obtain

$$w_{\text{ad}} = C_V\Delta T \quad (2.27)$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states. That is exactly what we expect on molecular grounds, because the mean kinetic energy is proportional to T , so a change in internal energy arising from temperature alone is also expected to be proportional to ΔT . In *Further information 2.1* we show that the initial and final temperatures of a perfect gas that undergoes reversible adiabatic expansion (reversible expansion in a thermally insulated container) can be calculated from

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad (2.28a)^\circ_{\text{rev}}$$

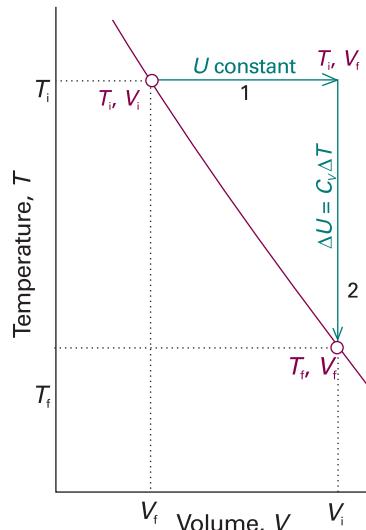


Fig. 2.17 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.

where $c = C_{V,m}/R$, or equivalently

$$V_i T_i^c = V_f T_f^c \quad (2.28b)_{\text{rev}}^{\circ}$$

This result is often summarized in the form $VT^c = \text{constant}$.

Illustration 2.5 Work of adiabatic expansion

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm³ to 1.00 dm³. The molar heat capacity of argon at constant volume is 12.48 J K⁻¹ mol⁻¹, so $c = 1.501$. Therefore, from eqn 2.28a,

$$T_f = (298 \text{ K}) \times \left(\frac{0.50 \text{ dm}^3}{1.00 \text{ dm}^3} \right)^{1/1.501} = 188 \text{ K}$$

It follows that $\Delta T = -110 \text{ K}$, and therefore, from eqn 2.27, that

$$w = \{(0.020 \text{ mol}) \times (12.48 \text{ J K}^{-1} \text{ mol}^{-1})\} \times (-110 \text{ K}) = -27 \text{ J}$$

Note that temperature change is independent of the amount of gas but the work is not.

Self-test 2.5 Calculate the final temperature, the work done, and the change of internal energy when ammonia is used in a reversible adiabatic expansion from 0.50 dm³ to 2.00 dm³, the other initial conditions being the same.

[195 K, -56 J, -56 J]

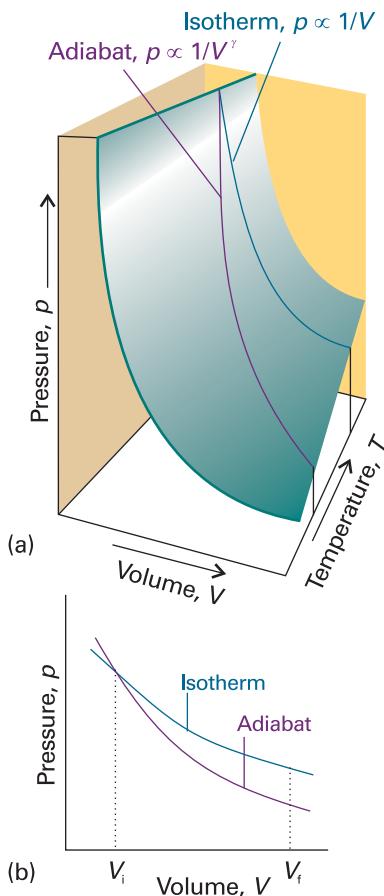


Fig. 2.18 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically. (a) An adiabat for a perfect gas undergoing reversible expansion. (b) Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

Exploration Explore how the parameter γ affects the dependence of the pressure on the volume. Does the pressure–volume dependence become stronger or weaker with increasing volume?

We also show in *Further information 2.1* that the pressure of a perfect gas that undergoes reversible adiabatic expansion from a volume V_i to a volume V_f is related to its initial pressure by

$$p_f V_f^\gamma = p_i V_i^\gamma \quad (2.29)_{\text{rev}}^{\circ}$$

where $\gamma = C_{p,m}/C_{V,m}$. This result is summarized in the form $pV^\gamma = \text{constant}$. For a monatomic perfect gas, $C_{V,m} = \frac{3}{2}R$ (see *Illustration 2.3*), and from eqn 2.26 $C_{p,m} = \frac{5}{2}R$; so $\gamma = \frac{5}{3}$. For a gas of nonlinear polyatomic molecules (which can rotate as well as translate), $C_{V,m} = 3R$, so $\gamma = \frac{4}{3}$. The curves of pressure versus volume for adiabatic change are known as **adiabats**, and one for a reversible path is illustrated in Fig. 2.18. Because $\gamma > 1$, an adiabat falls more steeply ($p \propto 1/V^\gamma$) than the corresponding isotherm ($p \propto 1/V$). The physical reason for the difference is that, in an isothermal expansion, energy flows into the system as heat and maintains the temperature; as a result, the pressure does not fall as much as in an adiabatic expansion.

Illustration 2.6 The pressure change accompanying adiabatic expansion

When a sample of argon (for which $\gamma = \frac{5}{3}$) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_f = \left(\frac{V_i}{V_f} \right)^\gamma p_i = \left(\frac{1}{2} \right)^{5/3} \times (100 \text{ kPa}) = 32 \text{ kPa}$$

For an isothermal doubling of volume, the final pressure would be 50 kPa.

Thermochemistry

The study of the energy transferred as heat during the course of chemical reactions is called **thermochemistry**. Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system, and chemical reactions result in the exchange of energy between the system and the surroundings. Thus we can use calorimetry to measure the energy supplied or discarded as heat by a reaction, and can identify q with a change in internal energy (if the reaction occurs at constant volume) or a change in enthalpy (if the reaction occurs at constant pressure). Conversely, if we know ΔU or ΔH for a reaction, we can predict the energy (transferred as heat) the reaction can produce.

We have already remarked that a process that releases energy by heating the surroundings is classified as exothermic and one that absorbs energy by cooling the surroundings is classified as endothermic. Because the release of energy by heating the surroundings signifies a decrease in the enthalpy of a system (at constant pressure), we can now see that an exothermic process at constant pressure is one for which $\Delta H < 0$. Conversely, because the absorption of energy by cooling the surroundings results in an increase in enthalpy, an endothermic process at constant pressure has $\Delta H > 0$.

2.7 Standard enthalpy changes

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, ΔH° , the change in enthalpy for a process in which the initial and final substances are in their standard states:

The **standard state** of a substance at a specified temperature is its pure form at 1 bar.⁵

For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 298 K and 1 bar; the standard state of solid iron at 500 K is pure iron at 500 K and 1 bar. The standard enthalpy change for a reaction or a physical process is the difference between the products in their standard states and the reactants in their standard states, all at the same specified temperature.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*, $\Delta_{\text{vap}}H^\circ$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in



As implied by the examples, standard enthalpies may be reported for any temperature. However, the conventional temperature for reporting thermodynamic data is 298.15 K (corresponding to 25.00°C). Unless otherwise mentioned, all thermodynamic data in this text will refer to this conventional temperature.

A note on good practice The attachment of the name of the transition to the symbol Δ , as in $\Delta_{\text{vap}}H$, is the modern convention. However, the older convention, ΔH_{vap} , is still widely used. The new convention is more logical because the subscript identifies the type of change, not the physical observable related to the change.

⁵ The definition of standard state is more sophisticated for a real gas (*Further information 3.2*) and for solutions (Sections 5.6 and 5.7).

Synoptic Table 2.3* Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{\text{trs}}H^\ominus/(\text{kJ mol}^{-1})$

	T_f/K	Fusion	T_b/K	Vaporization
Ar	83.81	1.188	87.29	6.506
C ₆ H ₆	278.61	10.59	353.2	30.8
H ₂ O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

* More values are given in the *Data section*.

(a) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{\text{trs}}H^\ominus$ (Table 2.3). The **standard enthalpy of vaporization**, $\Delta_{\text{vap}}H^\ominus$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_{\text{fus}}H^\ominus$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

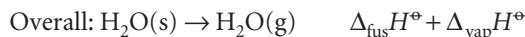


As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature.

Because enthalpy is a state function, a change in enthalpy is independent of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of ΔH^\ominus will be obtained however the change is brought about between the same initial and final states. For example, we can picture the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour),



or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:



Because the overall result of the indirect path is the same as that of the direct path, the overall enthalpy change is the same in each case (1), and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus \quad (2.30)$$

An immediate conclusion is that, because all enthalpies of fusion are positive, the enthalpy of sublimation of a substance is greater than its enthalpy of vaporization (at a given temperature).

Another consequence of H being a state function is that the standard enthalpy changes of a forward process and its reverse differ in sign (2):

$$\Delta H^\ominus(A \rightarrow B) = -\Delta H^\ominus(B \rightarrow A) \quad (2.31)$$

For instance, because the enthalpy of vaporization of water is $+44 \text{ kJ mol}^{-1}$ at 298 K, its enthalpy of condensation at that temperature is -44 kJ mol^{-1} .

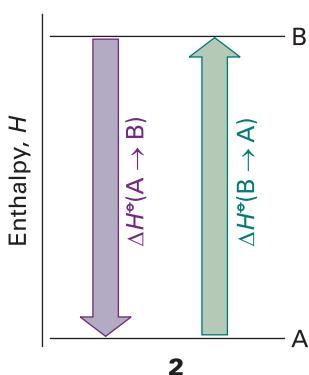
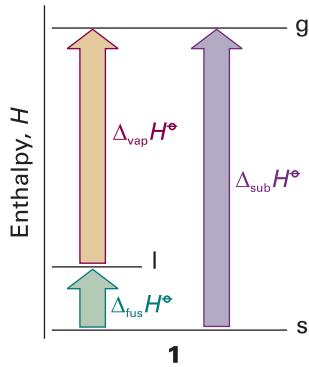


Table 2.4 Enthalpies of transition

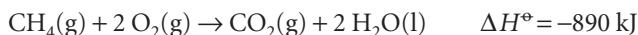
Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{trs}H$
Fusion	s \rightarrow l	$\Delta_{fus}H$
Vaporization	l \rightarrow g	$\Delta_{vap}H$
Sublimation	s \rightarrow g	$\Delta_{sub}H$
Mixing	Pure \rightarrow mixture	$\Delta_{mix}H$
Solution	Solute \rightarrow solution	$\Delta_{sol}H$
Hydration	$X^\pm(g) \rightarrow X^\pm(aq)$	$\Delta_{hyd}H$
Atomization	Species(s, l, g) \rightarrow atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{eg}H$
Reaction	Reactants \rightarrow products	Δ_rH
Combustion	Compounds(s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	Δ_cH
Formation	Elements \rightarrow compound	Δ_fH
Activation	Reactants \rightarrow activated complex	$\Delta^\ddagger H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH , as in ΔH_{trs} .

The different types of enthalpies encountered in thermochemistry are summarized in Table 2.4. We shall meet them again in various locations throughout the text.

(b) Enthalpies of chemical change

Now we consider enthalpy changes that accompany chemical reactions. There are two ways of reporting the change in enthalpy that accompanies a chemical reaction. One is to write the **thermochemical equation**, a combination of a chemical equation and the corresponding change in standard enthalpy:



ΔH° is the change in enthalpy when reactants in their standard states change to products in their standard states:

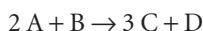
Pure, separate reactants in their standard states
 \rightarrow pure, separate products in their standard states

Except in the case of ionic reactions in solution, the enthalpy changes accompanying mixing and separation are insignificant in comparison with the contribution from the reaction itself. For the combustion of methane, the standard value refers to the reaction in which 1 mol CH_4 in the form of pure methane gas at 1 bar reacts completely with 2 mol O_2 in the form of pure oxygen gas to produce 1 mol CO_2 as pure carbon dioxide at 1 bar and 2 mol H_2O as pure liquid water at 1 bar; the numerical value is for the reaction at 298 K.

Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**, Δ_rH° . Thus, for the combustion of reaction, we write



For the reaction



Synoptic Table 2.5* Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^\ominus/(kJ\ mol^{-1})$	$\Delta_c H^\ominus/(kJ\ mol^{-1})$
Benzene, C ₆ H ₆ (l)	+49.0	-3268
Ethane, C ₂ H ₆ (g)	-84.7	-1560
Glucose, C ₆ H ₁₂ O ₆ (s)	-1274	-2808
Methane, CH ₄ (g)	-74.8	-890
Methanol, CH ₃ OH(l)	-238.7	-721

* More values are given in the *Data section*.

the standard reaction enthalpy is

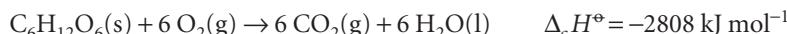
$$\Delta_r H^\ominus = \{3H_m^\ominus(C) + H_m^\ominus(D)\} - \{2H_m^\ominus(A) + H_m^\ominus(B)\}$$

where $H_m^\ominus(J)$ is the standard molar enthalpy of species J at the temperature of interest. Note how the ‘per mole’ of $\Delta_r H^\ominus$ comes directly from the fact that molar enthalpies appear in this expression. We interpret the ‘per mole’ by noting the stoichiometric coefficients in the chemical equation. In this case ‘per mole’ in $\Delta_r H^\ominus$ means ‘per 2 mol A’, ‘per mole B’, ‘per 3 mol C’, or ‘per mol D’. In general,

$$\Delta_r H^\ominus = \sum_{\text{Products}} vH_m^\ominus - \sum_{\text{Reactants}} vH_m^\ominus \quad (2.32)$$

where in each case the molar enthalpies of the species are multiplied by their stoichiometric coefficients, v .⁶

Some standard reaction enthalpies have special names and a particular significance. For instance, the **standard enthalpy of combustion**, $\Delta_c H^\ominus$, is the standard reaction enthalpy for the complete oxidation of an organic compound to CO₂ gas and liquid H₂O if the compound contains C, H, and O, and to N₂ gas if N is also present. An example is the combustion of glucose:



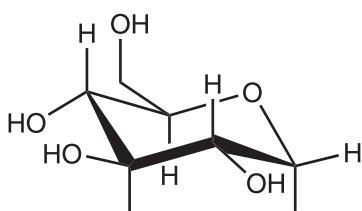
The value quoted shows that 2808 kJ of heat is released when 1 mol C₆H₁₂O₆ burns under standard conditions (at 298 K). Some further values are listed in Table 2.5.



IMPACT ON BIOLOGY 12.2 Food and energy reserves

The thermochemical properties of fuels Table 2.6 and foods are commonly discussed in terms of their *specific enthalpy*, the enthalpy of combustion per gram of material. Thus, if the standard enthalpy of combustion is $\Delta_c H^\ominus$ and the molar mass of the compound is M , then the specific enthalpy is $\Delta_c H^\ominus/M$. Table 2.6 lists the specific enthalpies of several fuels.

A typical 18–20 year old man requires a daily input of about 12 MJ; a woman of the same age needs about 9 MJ. If the entire consumption were in the form of glucose (3; which has a specific enthalpy of 16 kJ g⁻¹), that would require the consumption of 750 g of glucose for a man and 560 g for a woman. In fact, digestible carbohydrates have a slightly higher specific enthalpy (17 kJ g⁻¹) than glucose itself, so a carbohydrate



⁶ In this and similar expressions, all stoichiometric coefficients are positive. For a more sophisticated way of writing eqn 2.32, see Section 7.2.

Table 2.6 Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\ominus$ / (kJ mol ⁻¹)	Specific enthalpy/ (kJ g ⁻¹)	Enthalpy density/ (kJ dm ⁻³)
Hydrogen	$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$	-286	142	13
Methane	$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$	-890	55	40
Octane	$C_8H_{18}(l) + \frac{25}{2} O_2(g) \rightarrow 8 CO_2(g) + 9 H_2O(l)$	-5471	48	3.8×10^4
Methanol	$CH_3OH(l) + \frac{3}{2} O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$	-726	23	1.8×10^4

diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fibre, the indigestible cellulose that helps move digestion products through the intestine.

The specific enthalpy of fats, which are long-chain esters like tristearin (beef fat), is much greater than that of carbohydrates, at around 38 kJ g⁻¹, slightly less than the value for the hydrocarbon oils used as fuel (48 kJ g⁻¹). Fats are commonly used as an energy store, to be used only when the more readily accessible carbohydrates have fallen into short supply. In Arctic species, the stored fat also acts as a layer of insulation; in desert species (such as the camel), the fat is also a source of water, one of its oxidation products.

Proteins are also used as a source of energy, but their components, the amino acids, are often too valuable to squander in this way, and are used to construct other proteins instead. When proteins are oxidized (to urea, $CO(NH_2)_2$), the equivalent enthalpy density is comparable to that of carbohydrates.

The heat released by the oxidation of foods needs to be discarded in order to maintain body temperature within its typical range of 35.6–37.8°C. A variety of mechanisms contribute to this aspect of homeostasis, the ability of an organism to counteract environmental changes with physiological responses. The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When heat needs to be dissipated rapidly, warm blood is allowed to flow through the capillaries of the skin, so producing flushing. Radiation is one means of discarding heat; another is evaporation and the energy demands of the enthalpy of vaporization of water. Evaporation removes about 2.4 kJ per gram of water perspired. When vigorous exercise promotes sweating (through the influence of heat selectors on the hypothalamus), 1–2 dm³ of perspired water can be produced per hour, corresponding to a heat loss of 2.4–5.0 MJ h⁻¹.

(c) Hess's law

Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction. This application of the First Law is called **Hess's law**:

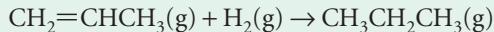
The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.

The individual steps need not be realizable in practice: they may be hypothetical reactions, the only requirement being that their chemical equations should balance. The thermodynamic basis of the law is the path-independence of the value of $\Delta_r H^\ominus$ and the implication that we may take the specified reactants, pass through any (possibly hypothetical) set of reactions to the specified products, and overall obtain the same change of enthalpy. The importance of Hess's law is that information about a

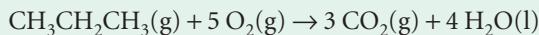
reaction of interest, which may be difficult to determine directly, can be assembled from information on other reactions.

Example 2.5 *Using Hess's law*

The standard reaction enthalpy for the hydrogenation of propene,



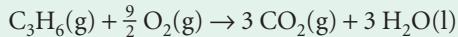
is -124 kJ mol^{-1} . The standard reaction enthalpy for the combustion of propane,



is $-2220 \text{ kJ mol}^{-1}$. Calculate the standard enthalpy of combustion of propene.

Method The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way. Additional data are in Table 2.5.

Answer The combustion reaction we require is



This reaction can be recreated from the following sum:

	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$
$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$	-124
$\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$	-2220
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{ O}_2(\text{g})$	$+286$
$\text{C}_3\text{H}_6(\text{g}) + \frac{9}{2} \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l})$	-2058

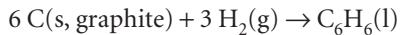
Synoptic Table 2.7* Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$
$\text{H}_2\text{O}(\text{l})$	-285.83
$\text{H}_2\text{O}(\text{g})$	-187.78
$\text{NH}_3(\text{g})$	-46.11
$\text{N}_2\text{H}_4(\text{l})$	$+50.63$
$\text{NO}_2(\text{g})$	33.18
$\text{N}_2\text{O}_4(\text{g})$	$+9.16$
$\text{NaCl}(\text{s})$	-411.15
$\text{KCl}(\text{s})$	-436.75

* More values are given in the *Data section*.

2.8 Standard enthalpies of formation

The **standard enthalpy of formation**, $\Delta_f H^\circ$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The **reference state** of an element is its most stable state at the specified temperature and 1 bar. For example, at 298 K the reference state of nitrogen is a gas of N_2 molecules, that of mercury is liquid mercury, that of carbon is graphite, and that of tin is the white (metallic) form. There is one exception to this general prescription of reference states: the reference state of phosphorus is taken to be white phosphorus despite this allotrope not being the most stable form but simply the more reproducible form of the element. Standard enthalpies of formation are expressed as enthalpies per mole of molecules or (for ionic substances) formula units of the compound. The standard enthalpy of formation of liquid benzene at 298 K, for example, refers to the reaction



and is $+49.0 \text{ kJ mol}^{-1}$. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $\text{N}_2(\text{g}) \rightarrow \text{N}_2(\text{g})$. Some enthalpies of formation are listed in Tables 2.5 and 2.7.

Comment 2.7

The NIST WebBook listed in the web site for this book links to online databases of thermochemical data.

The standard enthalpy of formation of ions in solution poses a special problem because it is impossible to prepare a solution of cations alone or of anions alone. This problem is solved by defining one ion, conventionally the hydrogen ion, to have zero standard enthalpy of formation at all temperatures:

$$\Delta_f H^\circ(H^+, \text{aq}) = 0 \quad [2.33]$$

Thus, if the enthalpy of formation of HBr(aq) is found to be -122 kJ mol^{-1} , then the whole of that value is ascribed to the formation of Br⁻(aq), and we write $\Delta_f H^\circ(\text{Br}^-, \text{aq}) = -122 \text{ kJ mol}^{-1}$. That value may then be combined with, for instance, the enthalpy formation of AgBr(aq) to determine the value of $\Delta_f H^\circ(\text{Ag}^+, \text{aq})$, and so on. In essence, this definition adjusts the actual values of the enthalpies of formation of ions by a fixed amount, which is chosen so that the standard value for one of them, H⁺(aq), has the value zero.

(a) The reaction enthalpy in terms of enthalpies of formation

Conceptually, we can regard a reaction as proceeding by decomposing the reactants into their elements and then forming those elements into the products. The value of $\Delta_r H^\circ$ for the overall reaction is the sum of these ‘unforming’ and forming enthalpies. Because ‘unforming’ is the reverse of forming, the enthalpy of an unforming step is the negative of the enthalpy of formation (4). Hence, in the enthalpies of formation of substances, we have enough information to calculate the enthalpy of any reaction by using

$$\Delta_r H^\circ = \sum_{\text{Products}} v \Delta_f H^\circ - \sum_{\text{Reactants}} v \Delta_f H^\circ \quad (2.34)$$

where in each case the enthalpies of formation of the species that occur are multiplied by their stoichiometric coefficients.

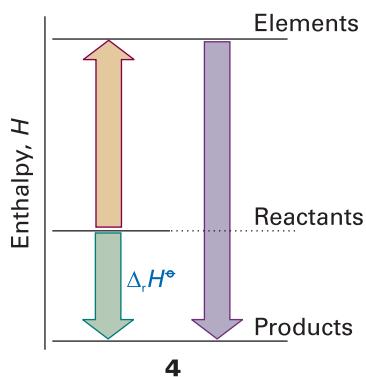


Illustration 2.7 Using standard enthalpies of formation

The standard reaction enthalpy of $2 \text{HN}_3(\text{l}) + 2 \text{NO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 4 \text{N}_2(\text{g})$ is calculated as follows:

$$\begin{aligned} \Delta_r H^\circ &= \{\Delta_f H^\circ(\text{H}_2\text{O}_2, \text{l}) + 4\Delta_f H^\circ(\text{N}_2, \text{g})\} - \{2\Delta_f H^\circ(\text{HN}_3, \text{l}) + 2\Delta_f H^\circ(\text{NO}, \text{g})\} \\ &= \{-187.78 + 4(0)\} \text{ kJ mol}^{-1} - \{2(264.0) + 2(90.25)\} \text{ kJ mol}^{-1} \\ &= -896.3 \text{ kJ mol}^{-1} \end{aligned}$$

(b) Enthalpies of formation and molecular modelling

We have seen how to construct standard reaction enthalpies by combining standard enthalpies of formation. The question that now arises is whether we can construct standard enthalpies of formation from a knowledge of the chemical constitution of the species. The short answer is that there is no thermodynamically exact way of expressing enthalpies of formation in terms of contributions from individual atoms and bonds. In the past, approximate procedures based on **mean bond enthalpies**, $\Delta H(A-B)$, the average enthalpy change associated with the breaking of a specific A–B bond,



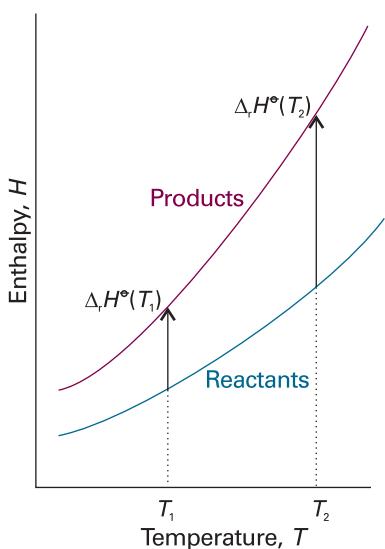


Fig. 2.19 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

have been used. However, this procedure is notoriously unreliable, in part because the $\Delta H(A-B)$ are average values for a series of related compounds. Nor does the approach distinguish between geometrical isomers, where the same atoms and bonds may be present but experimentally the enthalpies of formation might be significantly different.

Computer-aided molecular modelling has largely displaced this more primitive approach. Commercial software packages use the principles developed in Chapter 11 to calculate the standard enthalpy of formation of a molecule drawn on the computer screen. These techniques can be applied to different conformations of the same molecule. In the case of methylcyclohexane, for instance, the calculated conformational energy difference ranges from 5.9 to 7.9 kJ mol⁻¹, with the equatorial conformer having the lower standard enthalpy of formation. These estimates compare favourably with the experimental value of 7.5 kJ mol⁻¹. However, good agreement between calculated and experimental values is relatively rare. Computational methods almost always predict correctly which conformer is more stable but do not always predict the correct magnitude of the conformational energy difference.

2.9 The temperature-dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 2.19). In many cases heat capacity data are more accurate than reaction enthalpies so, providing the information is available, the procedure we are about to describe is more accurate than a direct measurement of a reaction enthalpy at an elevated temperature.

It follows from eqn 2.23a that, when a substance is heated from T_1 to T_2 , its enthalpy changes from $H(T_1)$ to

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT \quad (2.35)$$

(We have assumed that no phase transition takes place in the temperature range of interest.) Because this equation applies to each substance in the reaction, the standard reaction enthalpy changes from $\Delta_r H^\circ(T_1)$ to

$$\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\circ dT \quad (2.36)$$

where $\Delta_r C_p^\circ$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^\circ = \sum_{\text{Products}} v C_{p,m}^\circ - \sum_{\text{Reactants}} v C_{p,m}^\circ \quad [2.37]$$

Equation 2.36 is known as **Kirchhoff's law**. It is normally a good approximation to assume that $\Delta_r C_p$ is independent of the temperature, at least over reasonably limited ranges, as illustrated in the following example. Although the individual heat capacities may vary, their difference varies less significantly. In some cases the temperature dependence of heat capacities is taken into account by using eqn 2.25.

Example 2.6 Using Kirchhoff's law

The standard enthalpy of formation of gaseous H₂O at 298 K is $-241.82 \text{ kJ mol}^{-1}$. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: H₂O(g): $33.58 \text{ J K}^{-1} \text{ mol}^{-1}$; H₂(g): $28.84 \text{ J K}^{-1} \text{ mol}^{-1}$; O₂(g): $29.37 \text{ J K}^{-1} \text{ mol}^{-1}$. Assume that the heat capacities are independent of temperature.

Method When ΔC_p° is independent of temperature in the range T_1 to T_2 , the integral in eqn 2.36 evaluates to $(T_2 - T_1)\Delta_r C_p^\circ$. Therefore,

$$\Delta_f H^\circ(T_2) = \Delta_f H^\circ(T_1) + (T_2 - T_1)\Delta_r C_p^\circ$$

To proceed, write the chemical equation, identify the stoichiometric coefficients, and calculate $\Delta_r C_p^\circ$ from the data.

Answer The reaction is $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$, so

$$\Delta_r C_p^\circ = C_{p,m}^\circ(\text{H}_2\text{O}, \text{g}) - \{C_{p,m}^\circ(\text{H}_2, \text{g}) + \frac{1}{2}C_{p,m}^\circ(\text{O}_2, \text{g})\} = -9.94 \text{ J K}^{-1} \text{ mol}^{-1}$$

It then follows that

$$\Delta_f H^\circ(373 \text{ K}) = -241.82 \text{ kJ mol}^{-1} + (75 \text{ K}) \times (-9.94 \text{ J K}^{-1} \text{ mol}^{-1}) = -242.6 \text{ kJ mol}^{-1}$$

Self-test 2.7 Estimate the standard enthalpy of formation of cyclohexene at 400 K from the data in Table 2.5. [−163 kJ mol^{−1}]

State functions and exact differentials

We saw in Section 2.2 that a ‘state function’ is a property that is independent of how a sample is prepared. In general, such properties are functions of variables that define the current state of the system, such as pressure and temperature. The internal energy and enthalpy are examples of state functions, for they depend on the current state of the system and are independent of its previous history. Processes that describe the preparation of the state are called **path functions**. Examples of path functions are the work and heating that are done when preparing a state. We do not speak of a system in a particular state as possessing work or heat. In each case, the energy transferred as work or heat relates to the path being taken between states, not the current state itself.

We can use the mathematical properties of state functions to draw far-reaching conclusions about the relations between physical properties and establish connections that may be completely unexpected. The practical importance of these results is that we can combine measurements of different properties to obtain the value of a property we require.

2.10 Exact and inexact differentials

Consider a system undergoing the changes depicted in Fig. 2.20. The initial state of the system is i and in this state the internal energy is U_i . Work is done by the system as it expands adiabatically to a state f. In this state the system has an internal energy U_f and the work done on the system as it changes along Path 1 from i to f is w . Notice our use of language: U is a property of the state; w is a property of the path. Now consider another process, Path 2, in which the initial and final states are the same as those in Path 1 but in which the expansion is not adiabatic. The internal energy of both the

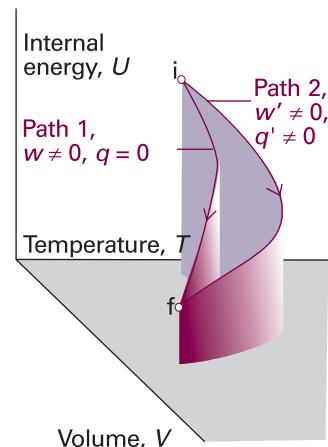


Fig. 2.20 As the volume and temperature of a system are changed, the internal energy changes. An adiabatic and a non-adiabatic path are shown as Path 1 and Path 2, respectively: they correspond to different values of q and w but to the same value of ΔU .

initial and the final states are the same as before (because U is a state function). However, in the second path an energy q' enters the system as heat and the work w' is not the same as w . The work and the heat are path functions. In terms of the mountaineering analogy in Section 2.2, the change in altitude (a state function) is independent of the path, but the distance travelled (a path function) does depend on the path taken between the fixed endpoints.

If a system is taken along a path (for example, by heating it), U changes from U_i to U_f and the overall change is the sum (integral) of all the infinitesimal changes along the path:

$$\Delta U = \int_i^f dU \quad (2.38)$$

The value of ΔU depends on the initial and final states of the system but is independent of the path between them. This path-independence of the integral is expressed by saying that dU is an ‘exact differential’. In general, an **exact differential** is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

When a system is heated, the total energy transferred as heat is the sum of all individual contributions at each point of the path:

$$q = \int_{i, \text{path}}^f dq \quad (2.39)$$

Notice the difference between this equation and eqn 2.38. First, we do not write Δq , because q is not a state function and the energy supplied as heat cannot be expressed as $q_f - q_i$. Secondly, we must specify the path of integration because q depends on the path selected (for example, an adiabatic path has $q = 0$, whereas a nonadiabatic path between the same two states would have $q \neq 0$). This path-dependence is expressed by saying that dq is an ‘inexact differential’. In general, an **inexact differential** is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states. Often dq is written dq to emphasize that it is inexact and requires the specification of a path.

The work done on a system to change it from one state to another depends on the path taken between the two specified states; for example, in general the work is different if the change takes place adiabatically and non-adiabatically. It follows that dw is an inexact differential. It is often written dw .

Example 2.7 Calculating work, heat, and internal energy

Consider a perfect gas inside a cylinder fitted with a piston. Let the initial state be T, V_i and the final state be T, V_f . The change of state can be brought about in many ways, of which the two simplest are the following: Path 1, in which there is free expansion against zero external pressure; Path 2, in which there is reversible, isothermal expansion. Calculate w , q , and ΔU for each process.

Method To find a starting point for a calculation in thermodynamics, it is often a good idea to go back to first principles, and to look for a way of expressing the quantity we are asked to calculate in terms of other quantities that are easier to calculate. We saw in *Molecular interpretation 2.2* that the internal energy of a perfect gas depends only on the temperature and is independent of the volume those molecules occupy, so for any isothermal change, $\Delta U = 0$. We also know that in general $\Delta U = q + w$. The question depends on being able to combine the two

expressions. In this chapter, we derived a number of expressions for the work done in a variety of processes, and here we need to select the appropriate ones.

Answer Because $\Delta U = 0$ for both paths and $\Delta U = q + w$, in each case $q = -w$. The work of free expansion is zero (Section 2.3b); so in Path 1, $w = 0$ and $q = 0$. For Path 2, the work is given by eqn 2.11, so $w = -nRT \ln(V_f/V_i)$ and consequently $q = nRT \ln(V_f/V_i)$. These results are consequences of the path independence of U , a state function, and the path dependence of q and w , which are path functions.

Self-test 2.8 Calculate the values of q , w , and ΔU for an irreversible isothermal expansion of a perfect gas against a constant nonzero external pressure.

$$[q = p_{\text{ex}} \Delta V, w = -p_{\text{ex}} \Delta V, \Delta U = 0]$$

2.11 Changes in internal energy

We begin to unfold the consequences of dU being an exact differential by exploring a closed system of constant composition (the only type of system considered in the rest of this chapter). The internal energy U can be regarded as a function of V , T , and p , but, because there is an equation of state, stating the values of two of the variables fixes the value of the third. Therefore, it is possible to write U in terms of just two independent variables: V and T , p and T , or p and V . Expressing U as a function of volume and temperature fits the purpose of our discussion.

(a) General considerations

When V changes to $V + dV$ at constant temperature, U changes to

$$U' = U + \left(\frac{\partial U}{\partial V} \right)_T dV$$

The coefficient $(\partial U / \partial V)_T$, the slope of a plot of U against V at constant temperature, is the partial derivative of U with respect to V (Fig. 2.21). If, instead, T changes to $T + dT$ at constant volume (Fig. 2.22), then the internal energy changes to

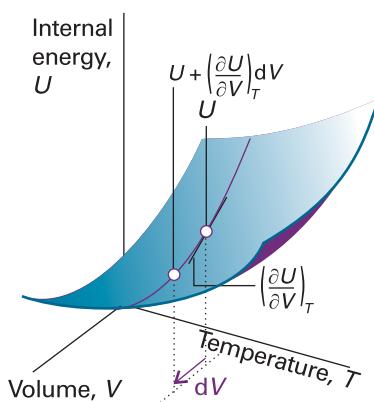


Fig. 2.21 The partial derivative $(\partial U / \partial V)_T$ is the slope of U with respect to V with the temperature T held constant.

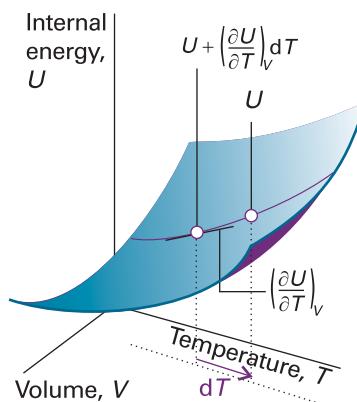


Fig. 2.22 The partial derivative $(\partial U / \partial T)_V$ is the slope of U with respect to T with the volume V held constant.

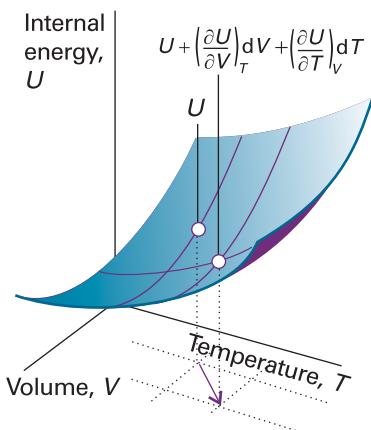


Fig. 2.23 An overall change in U , which is denoted dU , arises when both V and T are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

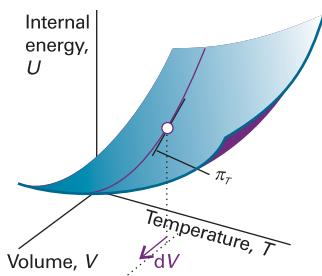


Fig. 2.24 The internal pressure, π_T , is the slope of U with respect to V with the temperature T held constant.

$$U' = U + \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

Now suppose that V and T both change infinitesimally (Fig. 2.23). The new internal energy, neglecting second-order infinitesimals (those proportional to $dVdT$), is the sum of the changes arising from each increment:

$$U' = U + \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT$$

As a result of the infinitesimal changes in conditions, the internal energy U' differs from U by the infinitesimal amount dU , so we can write $U' = U + dU$. Therefore, from the last equation we obtain the very important result that

$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT \quad (2.40)$$

The interpretation of this equation is that, in a closed system of constant composition, any infinitesimal change in the internal energy is proportional to the infinitesimal changes of volume and temperature, the coefficients of proportionality being the two partial derivatives.

In many cases partial derivatives have a straightforward physical interpretation, and thermodynamics gets shapeless and difficult only when that interpretation is not kept in sight. In the present case, we have already met $(\partial U / \partial T)_V$ in eqn 2.15, where we saw that it is the constant-volume heat capacity, C_V . The other coefficient, $(\partial U / \partial V)_T$, plays a major role in thermodynamics because it is a measure of the variation of the internal energy of a substance as its volume is changed at constant temperature (Fig. 2.24). We shall denote it π_T and, because it has the same dimensions as pressure, call it the **internal pressure**:

$$\pi_T = \left(\frac{\partial U}{\partial V} \right)_T \quad [2.41]$$

In terms of the notation C_V and π_T , eqn 2.40 can now be written

$$dU = \pi_T dV + C_V dT \quad (2.42)$$

(b) The Joule experiment

When there are no interactions between the molecules, the internal energy is independent of their separation and hence independent of the volume of the sample (see *Molecular interpretation 2.2*). Therefore, for a perfect gas we can write $\pi_T = 0$. The statement $\pi_T = 0$ (that is, the internal energy is independent of the volume occupied by the sample) can be taken to be the definition of a perfect gas, for later we shall see that it implies the equation of state $pV = nRT$. If the internal energy increases ($dU > 0$) as the volume of the sample expands isothermally ($dV > 0$), which is the case when there are attractive forces between the particles, then a plot of internal energy against volume slopes upwards and $\pi_T > 0$ (Fig. 2.25).

James Joule thought that he could measure π_T by observing the change in temperature of a gas when it is allowed to expand into a vacuum. He used two metal vessels immersed in a water bath (Fig. 2.26). One was filled with air at about 22 atm and the other was evacuated. He then tried to measure the change in temperature of the water of the bath when a stopcock was opened and the air expanded into a vacuum. He observed no change in temperature.

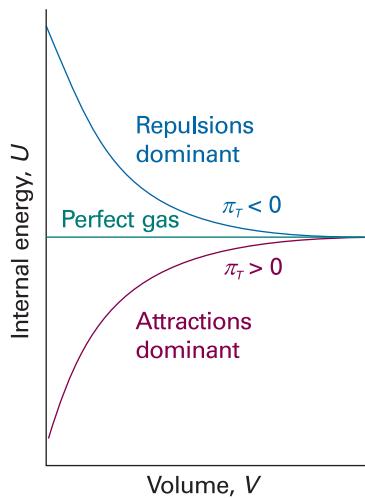


Fig. 2.25 For a perfect gas, the internal energy is independent of the volume (at constant temperature). If attractions are dominant in a real gas, the internal energy increases with volume because the molecules become farther apart on average. If repulsions are dominant, the internal energy decreases as the gas expands.

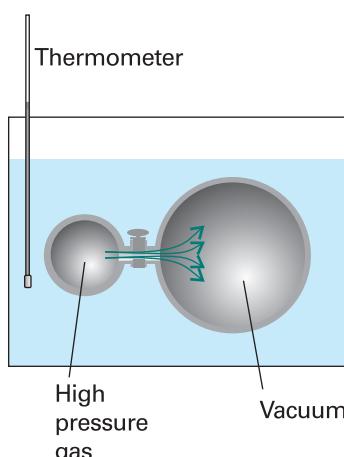


Fig. 2.26 A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally. The heat absorbed by the gas is proportional to the change in temperature of the bath.

The thermodynamic implications of the experiment are as follows. No work was done in the expansion into a vacuum, so $w = 0$. No energy entered or left the system (the gas) as heat because the temperature of the bath did not change, so $q = 0$. Consequently, within the accuracy of the experiment, $\Delta U = 0$. It follows that U does not change much when a gas expands isothermally and therefore that $\pi_T = 0$.

Joule's experiment was crude. In particular, the heat capacity of the apparatus was so large that the temperature change that gases do in fact cause was too small to measure. From his experiment Joule extracted an essential limiting property of a gas, a property of a perfect gas, without detecting the small deviations characteristic of real gases.

(c) Changes in internal energy at constant pressure

Partial derivatives have many useful properties and some that we shall draw on frequently are reviewed in Appendix 2. Skilful use of them can often turn some unfamiliar quantity into a quantity that can be recognized, interpreted, or measured.

As an example, suppose we want to find out how the internal energy varies with temperature when the pressure of the system is kept constant. If we divide both sides of eqn 2.42 by dT and impose the condition of constant pressure on the resulting differentials, so that dU/dT on the left becomes $(\partial U/\partial T)_p$, we obtain

$$\left(\frac{\partial U}{\partial T} \right)_p = \pi_T \left(\frac{\partial V}{\partial T} \right)_p + C_V$$

It is usually sensible in thermodynamics to inspect the output of a manipulation like this to see if it contains any recognizable physical quantity. The partial derivative on the right in this expression is the slope of the plot of volume against temperature (at

Synoptic Table 2.8* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Data section*.

constant pressure). This property is normally tabulated as the **expansion coefficient**, α , of a substance,⁷ which is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad [2.43]$$

and physically is the fractional change in volume that accompanies a rise in temperature. A large value of α means that the volume of the sample responds strongly to changes in temperature. Table 2.8 lists some experimental values of α and of the **isothermal compressibility**, κ_T (kappa), which is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad [2.44]$$

The isothermal compressibility is a measure of the fractional change in volume when the pressure is increased by a small amount; the negative sign in the definition ensures that the compressibility is a positive quantity, because an increase of pressure, implying a positive dp , brings about a reduction of volume, a negative dV .

Example 2.8 Calculating the expansion coefficient of a gas

Derive an expression for the expansion coefficient of a perfect gas.

Method The expansion coefficient is defined in eqn 2.43. To use this expression, substitute the expression for V in terms of T obtained from the equation of state for the gas. As implied by the subscript in eqn 2.43, the pressure, p , is treated as a constant.

Answer Because $pV = nRT$, we can write

$$\alpha = \frac{1}{V} \left(\frac{\partial(nRT/p)}{\partial T} \right)_p = \frac{1}{V} \times \frac{nR}{p} \frac{dT}{dT} = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

Self-test 2.9 Derive an expression for the isothermal compressibility of a perfect gas. $[\kappa_T = 1/p]$

When we introduce the definition of α into the equation for $(\partial U/\partial T)_p$, we obtain

$$\left(\frac{\partial U}{\partial T} \right)_p = \alpha \pi_T V + C_V \quad (2.45)$$

This equation is entirely general (provided the system is closed and its composition is constant). It expresses the dependence of the internal energy on the temperature at constant pressure in terms of C_V , which can be measured in one experiment, in terms of α , which can be measured in another, and in terms of the quantity π_T . For a perfect gas, $\pi_T = 0$, so then

$$\left(\frac{\partial U}{\partial T} \right)_p = C_V \quad (2.46)^o$$

⁷ As for heat capacities, the expansion coefficients of a mixture depends on whether or not the composition is allowed to change. Throughout this chapter, we deal only with pure substances, so this complication can be disregarded.

That is, although the constant-volume heat capacity of a perfect gas is defined as the slope of a plot of internal energy against temperature at constant volume, for a perfect gas C_V is also the slope at constant pressure.

Equation 2.46 provides an easy way to derive the relation between C_p and C_V for a perfect gas expressed in eqn 2.26. Thus, we can use it to express both heat capacities in terms of derivatives at constant pressure:

$$C_p - C_V = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_p \quad (2.47)^\circ$$

Then we introduce $H = U + pV = U + nRT$ into the first term, which results in

$$C_p - C_V = \left(\frac{\partial U}{\partial T} \right)_p + nR - \left(\frac{\partial U}{\partial T} \right)_p = nR \quad (2.48)^\circ$$

which is eqn 2.26. We show in *Further information 2.2* that in general

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T} \quad (2.49)$$

Equation 2.49 applies to any substance (that is, it is ‘universally true’). It reduces to eqn 2.48 for a perfect gas when we set $\alpha = 1/T$ and $\kappa_T = 1/p$. Because expansion coefficients α of liquids and solids are small, it is tempting to deduce from eqn 2.49 that for them $C_p \approx C_V$. But this is not always so, because the compressibility κ_T might also be small, so α^2/κ_T might be large. That is, although only a little work need be done to push back the atmosphere, a great deal of work may have to be done to pull atoms apart from one another as the solid expands. As an illustration, for water at 25°C, eqn 2.49 gives $C_{p,m} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ compared with $C_{V,m} = 74.8 \text{ J K}^{-1} \text{ mol}^{-1}$. In some cases, the two heat capacities differ by as much as 30 per cent.

2.12 The Joule–Thomson effect

We can carry out a similar set of operations on the enthalpy, $H = U + pV$. The quantities U , p , and V are all state functions; therefore H is also a state function and dH is an exact differential. It turns out that H is a useful thermodynamic function when the pressure is under our control: we saw a sign of that in the relation $\Delta H = q_p$ (eqn 2.19). We shall therefore regard H as a function of p and T , and adapt the argument in Section 2.10 to find an expression for the variation of H with temperature at constant volume. As set out in *Justification 2.2*, we find that for a closed system of constant composition,

$$dH = -\mu C_p dp + C_p dT \quad (2.50)$$

where the **Joule–Thomson coefficient**, μ (mu), is defined as

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \quad [2.51]$$

This relation will prove useful for relating the heat capacities at constant pressure and volume and for a discussion of the liquefaction of gases.

Justification 2.2 The variation of enthalpy with pressure and temperature

By the same argument that led to eqn 2.40 but with H regarded as a function of p and T we can write

$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT \quad (2.52)$$

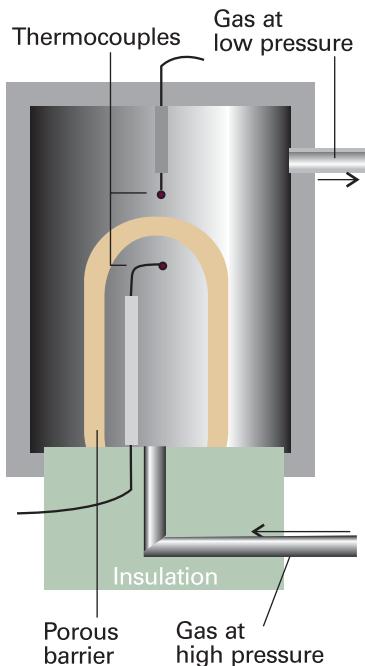


Fig. 2.27 The apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.

The second partial derivative is C_p ; our task here is to express $(\partial H/\partial p)_T$ in terms of recognizable quantities. The chain relation (see *Further information 2.2*) lets us write

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{(\partial p/\partial T)_H (\partial T/\partial H)_p}$$

and both partial derivatives can be brought into the numerator by using the reciprocal identity (see *Further information 2.2*) twice:

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{(\partial T/\partial p)_H}{(\partial T/\partial H)_p} = \left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p \quad (2.53)$$

We have used the definitions of the constant-pressure heat capacity, C_p , and the Joule–Thomson coefficient, μ (eqn 2.51). Equation 2.50 now follows directly.

The analysis of the Joule–Thomson coefficient is central to the technological problems associated with the liquefaction of gases. We need to be able to interpret it physically and to measure it. As shown in the *Justification* below, the cunning required to impose the constraint of constant enthalpy, so that the process is **isenthalpic**, was supplied by Joule and William Thomson (later Lord Kelvin). They let a gas expand through a porous barrier from one constant pressure to another, and monitored the difference of temperature that arose from the expansion (Fig. 2.27). The whole apparatus was insulated so that the process was adiabatic. They observed a lower temperature on the low pressure side, the difference in temperature being proportional to the pressure difference they maintained. This cooling by isenthalpic expansion is now called the **Joule–Thomson effect**.

Justification 2.3 The Joule–Thomson effect

Here we show that the experimental arrangement results in expansion at constant enthalpy. Because all changes to the gas occur adiabatically,

$$q = 0, \text{ which implies } \Delta U = w$$

Consider the work done as the gas passes through the barrier. We focus on the passage of a fixed amount of gas from the high pressure side, where the pressure is p_i , the temperature T_i , and the gas occupies a volume V_i (Fig. 2.28). The gas emerges on the low pressure side, where the same amount of gas has a pressure p_f , a temperature T_f , and occupies a volume V_f . The gas on the left is compressed isothermally by the upstream gas acting as a piston. The relevant pressure is p_i and the volume changes from V_i to 0; therefore, the work done on the gas is

$$w_1 = -p_i(0 - V_i) = p_i V_i$$

The gas expands isothermally on the right of the barrier (but possibly at a different constant temperature) against the pressure p_f provided by the downstream gas acting as a piston to be driven out. The volume changes from 0 to V_f , so the work done on the gas in this stage is

$$w_2 = -p_f(V_f - 0) = -p_f V_f$$

The total work done on the gas is the sum of these two quantities, or

$$w = w_1 + w_2 = p_i V_i - p_f V_f$$

It follows that the change of internal energy of the gas as it moves adiabatically from one side of the barrier to the other is

$$U_f - U_i = w = p_i V_i - p_f V_f$$

Reorganization of this expression gives

$$U_f + p_f V_f = U_i + p_i V_i, \text{ or } H_f = H_i$$

Therefore, the expansion occurs without change of enthalpy.

The property measured in the experiment is the ratio of the temperature change to the change of pressure, $\Delta T/\Delta p$. Adding the constraint of constant enthalpy and taking the limit of small Δp implies that the thermodynamic quantity measured is $(\partial T/\partial p)_H$, which is the Joule–Thomson coefficient, μ . In other words, the physical interpretation of μ is that it is the ratio of the change in temperature to the change in pressure when a gas expands under conditions that ensure there is no change in enthalpy.

The modern method of measuring μ is indirect, and involves measuring the **isothermal Joule–Thomson coefficient**, the quantity

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T \quad [2.54]$$

which is the slope of a plot of enthalpy against pressure at constant temperature (Fig. 2.29). Comparing eqns 2.53 and 2.54, we see that the two coefficients are related by:

$$\mu_T = -C_p \mu \quad [2.55]$$

To measure μ_T , the gas is pumped continuously at a steady pressure through a heat exchanger (which brings it to the required temperature), and then through a porous plug inside a thermally insulated container. The steep pressure drop is measured, and the cooling effect is exactly offset by an electric heater placed immediately after the plug (Fig. 2.30). The energy provided by the heater is monitored. Because the energy transferred as heat can be identified with the value of ΔH for the gas (because

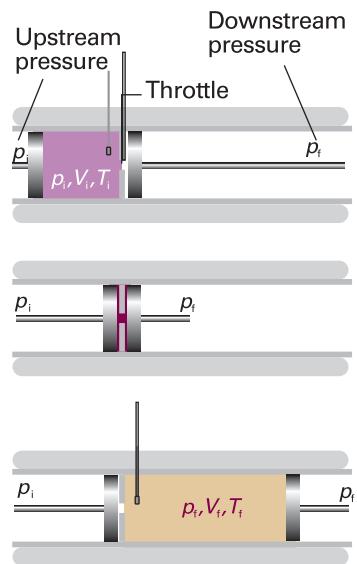


Fig. 2.28 The thermodynamic basis of Joule–Thomson expansion. The pistons represent the upstream and downstream gases, which maintain constant pressures either side of the throttle. The transition from the top diagram to the bottom diagram, which represents the passage of a given amount of gas through the throttle, occurs without change of enthalpy.

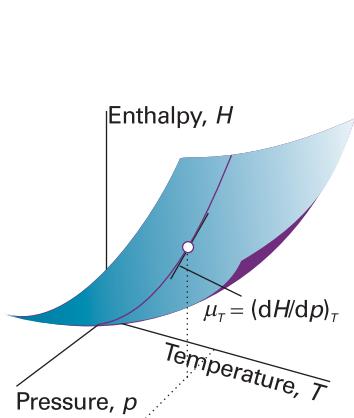


Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

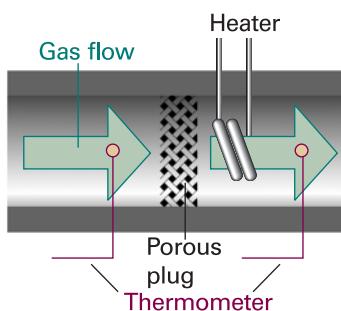


Fig. 2.30 A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as ΔH and used to calculate $(\partial H/\partial p)_T$, which is then converted to μ as explained in the text.

Synoptic Table 2.9* Inversion temperatures (T_I), normal freezing (T_f) and boiling (T_b) points, and Joule–Thomson coefficient (μ) at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	$\mu/(K \text{ bar}^{-1})$
Ar	723	83.8	87.3	
CO_2	1500		194.7	+1.10
He	40		4.2	-0.060
N_2	621	63.3	77.4	+0.25

* More values are given in the Data section.

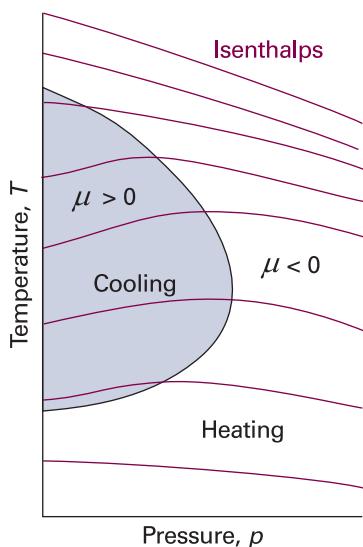


Fig. 2.31 The sign of the Joule–Thomson coefficient, μ , depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the ‘inversion temperature’ of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required but, if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.

$\Delta H = q_p$), and the pressure change Δp is known, we can find μ_T from the limiting value of $\Delta H/\Delta p$ as $\Delta p \rightarrow 0$, and then convert it to μ . Table 2.9 lists some values obtained in this way.

Real gases have nonzero Joule–Thomson coefficients. Depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces (see *Molecular interpretation 2.1*), and the temperature, the sign of the coefficient may be either positive or negative (Fig. 2.31). A positive sign implies that dT is negative when dp is negative, in which case the gas cools on expansion. Gases that show a heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when the temperature is below their upper **inversion temperature**, T_I (Table 2.9, Fig. 2.32). As indicated in Fig. 2.32, a gas typically has two inversion temperatures, one at high temperature and the other at low.

The ‘Linde refrigerator’ makes use of Joule–Thomson expansion to liquefy gases (Fig. 2.33). The gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas. That gas is cooled, and its subsequent expansion cools it still further. There comes a stage when the circulating gas becomes so cold that it condenses to a liquid.

For a perfect gas, $\mu = 0$; hence, the temperature of a perfect gas is unchanged by Joule–Thomson expansion.⁸ This characteristic points clearly to the involvement of intermolecular forces in determining the size of the effect. However, the Joule–Thomson coefficient of a real gas does not necessarily approach zero as the pressure is reduced even though the equation of state of the gas approaches that of a perfect gas. The coefficient behaves like the properties discussed in Section 1.3b in the sense that it depends on derivatives and not on p , V , and T themselves.

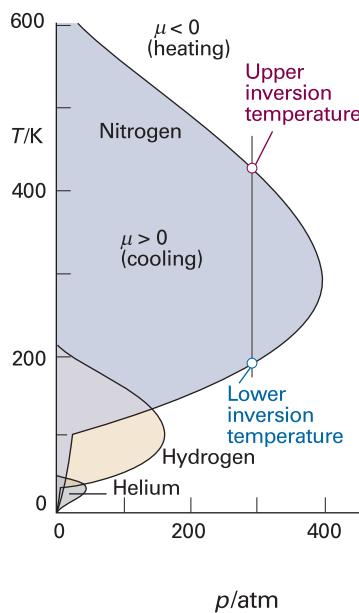


Fig. 2.32 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.

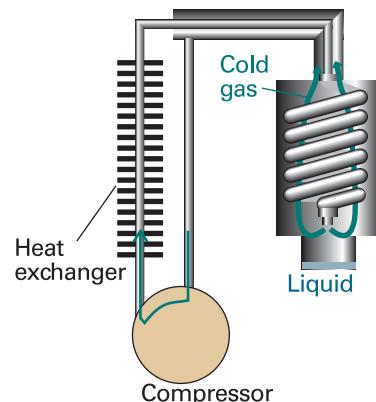


Fig. 2.33 The principle of the Linde refrigerator is shown in this diagram. The gas is recirculated, and so long as it is beneath its inversion temperature it cools on expansion through the throttle. The cooled gas cools the high-pressure gas, which cools still further as it expands. Eventually liquefied gas drips from the throttle.

⁸ Simple adiabatic expansion does cool a perfect gas, because the gas does work; recall Section 2.6.

Molecular interpretation 2.3 Molecular interactions and the Joule–Thomson effect

The kinetic model of gases (*Molecular interpretation 1.1*) and the equipartition theorem (*Molecular interpretation 2.2*) imply that the mean kinetic energy of molecules in a gas is proportional to the temperature. It follows that reducing the average speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can be reduced to the point that neighbours can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid.

To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. We saw in Section 1.3 that molecules in a real gas attract each other (the attraction is not gravitational, but the effect is the same). It follows that, if we can cause the molecules to move apart from each other, like a ball rising from a planet, then they should slow. It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any energy to enter from outside as heat. As the gas expands, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbours. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to $\mu > 0$, is observed under conditions when attractive interactions are dominant ($Z < 1$, eqn 1.17), because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant ($Z > 1$), the Joule–Thomson effect results in the gas becoming warmer, or $\mu < 0$.

Checklist of key ideas

- 1. Thermodynamics is the study of the transformations of energy.
- 2. The system is the part of the world in which we have a special interest. The surroundings is the region outside the system where we make our measurements.
- 3. An open system has a boundary through which matter can be transferred. A closed system has a boundary through which matter cannot be transferred. An isolated system has a boundary through which neither matter nor energy can be transferred.
- 4. Energy is the capacity to do work. The internal energy is the total energy of a system.
- 5. Work is the transfer of energy by motion against an opposing force, $dw = -Fdz$. Heat is the transfer of energy as a result of a temperature difference between the system and the surroundings.
- 6. An exothermic process releases energy as heat to the surroundings. An endothermic process absorbs energy as heat from the surroundings.
- 7. A state function is a property that depends only on the current state of the system and is independent of how that state has been prepared.
- 8. The First Law of thermodynamics states that the internal energy of an isolated system is constant, $\Delta U = q + w$.
- 9. Expansion work is the work of expansion (or compression) of a system, $dw = -p_{\text{ex}} dV$. The work of free expansion is $w = 0$. The work of expansion against a constant external pressure is $w = -p_{\text{ex}} \Delta V$. The work of isothermal reversible expansion of a perfect gas is $w = -nRT \ln(V_f/V_i)$.
- 10. A reversible change is a change that can be reversed by an infinitesimal modification of a variable.
- 11. Maximum work is achieved in a reversible change.

- 12. Calorimetry is the study of heat transfers during physical and chemical processes.
- 13. The heat capacity at constant volume is defined as $C_V = (\partial U / \partial T)_V$. The heat capacity at constant pressure is $C_p = (\partial H / \partial T)_p$. For a perfect gas, the heat capacities are related by $C_p - C_V = nR$.
- 14. The enthalpy is defined as $H = U + pV$. The enthalpy change is the energy transferred as heat at constant pressure, $\Delta H = q_p$.
- 15. During a reversible adiabatic change, the temperature of a perfect gas varies according to $T_f = T_i(V_i/V_f)^{1/c}$, $c = C_{V,m}/R$. The pressure and volume are related by $pV^\gamma = \text{constant}$, with $\gamma = C_{p,m}/C_{V,m}$.
- 16. The standard enthalpy change is the change in enthalpy for a process in which the initial and final substances are in their standard states. The standard state is the pure substance at 1 bar.
- 17. Enthalpy changes are additive, as in $\Delta_{\text{sub}}H^\circ = \Delta_{\text{fus}}H^\circ + \Delta_{\text{vap}}H^\circ$.
- 18. The enthalpy change for a process and its reverse are related by $\Delta_{\text{forward}}H^\circ = -\Delta_{\text{reverse}}H^\circ$.
- 19. The standard enthalpy of combustion is the standard reaction enthalpy for the complete oxidation of an organic compound to CO₂ gas and liquid H₂O if the compound contains C, H, and O, and to N₂ gas if N is also present.
- 20. Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.
- 21. The standard enthalpy of formation (Δ_fH°) is the standard reaction enthalpy for the formation of the compound from its elements in their reference states. The reference state is the most stable state of an element at the specified temperature and 1 bar.
- 22. The standard reaction enthalpy may be estimated by combining enthalpies of formation, $\Delta_rH^\circ = \sum_{\text{Products}} v\Delta_fH^\circ - \sum_{\text{Reactants}} v\Delta_fH^\circ$.
- 23. The temperature dependence of the reaction enthalpy is given by Kirchhoff's law, $\Delta_rH^\circ(T_2) = \Delta_rH^\circ(T_1) + \int_{T_1}^{T_2} \Delta_rC_p^\circ dT$.
- 24. An exact differential is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states. An inexact differential is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states.
- 25. The internal pressure is defined as $\pi_T = (\partial U / \partial V)_T$. For a perfect gas, $\pi_T = 0$.
- 26. The Joule–Thomson effect is the cooling of a gas by isenthalpic expansion.
- 27. The Joule–Thomson coefficient is defined as $\mu = (\partial T / \partial p)_H$. The isothermal Joule–Thomson coefficient is defined as $\mu_T = (\partial H / \partial p)_T = -C_p\mu$.
- 28. The inversion temperature is the temperature at which the Joule–Thomson coefficient changes sign.

Further reading

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Further information

Further information 2.1 Adiabatic processes

Consider a stage in a reversible adiabatic expansion when the pressure inside and out is p . The work done when the gas expands by dV is $dw = -pdV$; however, for a perfect gas, $dU = C_V dT$.

Therefore, because for an adiabatic change ($dq = 0$) $dU = dw + dq = dw$, we can equate these two expressions for dU and write

$$C_V dT = -pdV$$

We are dealing with a perfect gas, so we can replace p by nRT/V and obtain

$$\frac{C_V dT}{T} = -\frac{nR dV}{V}$$

To integrate this expression we note that T is equal to T_i when V is equal to V_i , and is equal to T_f when V is equal to V_f at the end of the expansion. Therefore,

$$C_V \int_{T_i}^{T_f} \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V}$$

(We are taking C_V to be independent of temperature.) Then, because $\int dx/x = \ln x + \text{constant}$, we obtain

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

Because $\ln(x/y) = -\ln(y/x)$, this expression rearranges to

$$\frac{C_V}{nR} \ln \frac{T_f}{T_i} = \ln \frac{V_i}{V_f}$$

With $c = C_V/nR$ we obtain (because $\ln x^a = a \ln x$)

$$\ln \left(\frac{T_f}{T_i} \right)^c = \ln \left(\frac{V_i}{V_f} \right)$$

which implies that $(T_f/T_i)^c = (V_i/V_f)$ and, upon rearrangement, eqn 2.28.

The initial and final states of a perfect gas satisfy the perfect gas law regardless of how the change of state takes place, so we can use $pV = nRT$ to write

$$\frac{p_i V_i}{p_f V_f} = \frac{T_i}{T_f}$$

However, we have just shown that

$$\frac{T_i}{T_f} = \left(\frac{V_f}{V_i} \right)^{1/c} = \left(\frac{V_f}{V_i} \right)^{\gamma-1}$$

where we use the definition of the heat capacity ratio where

$\gamma = C_{p,m}/C_{V,m}$ and the fact that, for a perfect gas, $C_{p,m} - C_{V,m} = R$ (the molar version of eqn 2.26). Then we combine the two expressions, to obtain

$$\frac{p_i}{p_f} = \frac{V_f}{V_i} \times \left(\frac{V_f}{V_i} \right)^{\gamma-1} = \left(\frac{V_f}{V_i} \right)^\gamma$$

which rearranges to $p_i V_i^\gamma = p_f V_f^\gamma$, which is eqn 2.29.

Further information 2.2 The relation between heat capacities

A useful rule when doing a problem in thermodynamics is to go back to first principles. In the present problem we do this twice, first by expressing C_p and C_V in terms of their definitions and then by inserting the definition $H = U + pV$:

$$\begin{aligned} C_p - C_V &= \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V \\ &= \left(\frac{\partial U}{\partial T} \right)_p + \left(\frac{\partial(pV)}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_V \end{aligned}$$

We have already calculated the difference of the first and third terms on the right, and eqn 2.45 lets us write this difference as $\alpha \pi_T V$. The factor αV gives the change in volume when the temperature is raised, and $\pi_T = (\partial U/\partial V)_T$ converts this change in volume into a change in internal energy. We can simplify the remaining term by noting that, because p is constant,

$$\left(\frac{\partial(pV)}{\partial T} \right)_p = p \left(\frac{\partial V}{\partial T} \right)_p = \alpha p V$$

The middle term of this expression identifies it as the contribution to the work of pushing back the atmosphere: $(\partial V/\partial T)_p$ is the change of volume caused by a change of temperature, and multiplication by p converts this expansion into work.

Collecting the two contributions gives

$$C_p - C_V = \alpha(p + \pi_T)V \quad (2.56)$$

As just remarked, the first term on the right, $\alpha p V$, is a measure of the work needed to push back the atmosphere; the second term on the right, $\alpha \pi_T V$, is the work required to separate the molecules composing the system.

At this point we can go further by using the result we prove in Section 3.8 that

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$$

When this expression is inserted in the last equation we obtain

$$C_p - C_V = \alpha TV \left(\frac{\partial p}{\partial T} \right)_V \quad (2.57)$$

We now transform the remaining partial derivative. It follows from Euler's chain relation that

$$\left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_p \left(\frac{\partial V}{\partial p} \right)_T = -1$$

Comment 2.8

The Euler chain relation states that, for a differentiable function $z = z(x, y)$,

$$\left(\frac{\partial y}{\partial x} \right)_z \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x = -1$$

For instance, if $z(x, y) = x^2 y$,

$$\begin{aligned}\left(\frac{\partial y}{\partial x}\right)_z &= \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z \frac{d(1/x^2)}{dx} = -\frac{2z}{x^3} \\ \left(\frac{\partial x}{\partial z}\right)_y &= \left(\frac{\partial(z/y)^{1/2}}{\partial z}\right)_y = \frac{1}{y^{1/2}} \frac{dz^{1/2}}{dz} = \frac{1}{2(yz)^{1/2}} \\ \left(\frac{\partial z}{\partial y}\right)_x &= \left(\frac{\partial(x^2)y}{\partial y}\right)_x = x^2 \frac{dy}{dy} = x^2\end{aligned}$$

Multiplication of the three terms together gives the result -1 .

and therefore that

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_p (\partial V/\partial p)_T}$$

Unfortunately, $(\partial T/\partial V)_p$ occurs instead of $(\partial V/\partial T)_p$. However, the ‘reciprocal identity’ allows us to invert partial derivatives and to write

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

Comment 2.9

The reciprocal identity states that

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{(\partial x/\partial y)_z}$$

For example, for the function $z(x,y) = x^2y$,

$$\left(\frac{\partial y}{\partial x}\right)_z = \left(\frac{\partial(z/x^2)}{\partial x}\right)_z = z \frac{d(1/x^2)}{dx} = -\frac{2z}{x^3}$$

We can also write $x = (z/y)^{1/2}$, in which case

$$\begin{aligned}\left(\frac{\partial x}{\partial y}\right)_z &= \left(\frac{\partial(z/y)^{1/2}}{\partial y}\right)_z = z^{1/2} \frac{d(1/y^{1/2})}{dy} \\ &= -\frac{z^{1/2}}{2y^{3/2}} = -\frac{z^{1/2}}{2(z/x^2)^{3/2}} = -\frac{x^3}{2z}\end{aligned}$$

which is the reciprocal of the coefficient derived above.

Insertion of this relation into eqn 2.57 produces eqn 2.49.

Discussion questions

- 2.1** Provide mechanical and molecular definitions of work and heat.
- 2.2** Consider the reversible expansion of a perfect gas. Provide a physical interpretation for the fact that $pV^\gamma = \text{constant}$ for an adiabatic change, whereas $pV = \text{constant}$ for an isothermal change.
- 2.3** Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.
- 2.4** Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.

- 2.5** Explain the significance of the Joule and Joule–Thomson experiments. What would Joule observe in a more sensitive apparatus?
- 2.6** Suggest (with explanation) how the internal energy of a van der Waals gas should vary with volume at constant temperature.
- 2.7** In many experimental thermograms, such as that shown in Fig. 2.16, the baseline below T_1 is at a different level from that above T_2 . Explain this observation.

Exercises

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298.15 K.

- 2.1(a)** Calculate the work needed for a 65 kg person to climb through 4.0 m on the surface of (a) the Earth and (b) the Moon ($g = 1.60 \text{ m s}^{-2}$).
- 2.1(b)** Calculate the work needed for a bird of mass 120 g to fly to a height of 50 m from the surface of the Earth.
- 2.2(a)** A chemical reaction takes place in a container of cross-sectional area 100 cm². As a result of the reaction, a piston is pushed out through 10 cm against an external pressure of 1.0 atm. Calculate the work done by the system.
- 2.2(b)** A chemical reaction takes place in a container of cross-sectional area 50.0 cm². As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.
- 2.3(a)** A sample consisting of 1.00 mol Ar is expanded isothermally at 0°C from 22.4 dm³ to 44.8 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

- 2.3(b)** A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm³ to 31.7 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q , w , ΔU , and ΔH .

- 2.4(a)** A sample consisting of 1.00 mol of perfect gas atoms, for which $C_{V,m} = \frac{3}{2}R$, initially at $p_1 = 1.00 \text{ atm}$ and $T_1 = 300 \text{ K}$, is heated reversibly to 400 K at constant volume. Calculate the final pressure, ΔU , q , and w .

- 2.4(b)** A sample consisting of 2.00 mol of perfect gas molecules, for which $C_{V,m} = \frac{5}{2}R$, initially at $p_1 = 111 \text{ kPa}$ and $T_1 = 277 \text{ K}$, is heated reversibly to 356 K at constant volume. Calculate the final pressure, ΔU , q , and w .

- 2.5(a)** A sample of 4.50 g of methane occupies 12.7 dm³ at 310 K.
(a) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 dm³. (b) Calculate the work that would be done if the same expansion occurred reversibly.

- 2.5(b)** A sample of argon of mass 6.56 g occupies 18.5 dm³ at 305 K.
(a) Calculate the work done when the gas expands isothermally against a

constant external pressure of 7.7 kPa until its volume has increased by 2.5 dm³.
 (b) Calculate the work that would be done if the same expansion occurred reversibly.

2.6(a) A sample of 1.00 mol H₂O(g) is condensed isothermally and reversibly to liquid water at 100°C. The standard enthalpy of vaporization of water at 100°C is 40.656 kJ mol⁻¹. Find *w*, *q*, ΔU , and ΔH for this process.

2.6(b) A sample of 2.00 mol CH₃OH(g) is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ mol⁻¹. Find *w*, *q*, ΔU , and ΔH for this process.

2.7(a) A strip of magnesium of mass 15 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.0 atm and the temperature 25°C.

2.7(b) A piece of zinc of mass 5.0 g is dropped into a beaker of dilute hydrochloric acid. Calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1.1 atm and the temperature 23°C.

2.8(a) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(J\ K^{-1}) = 20.17 + 0.3665(T/K)$. Calculate *q*, *w*, ΔU , and ΔH when the temperature is raised from 25°C to 200°C (a) at constant pressure, (b) at constant volume.

2.8(b) The constant-pressure heat capacity of a sample of a perfect gas was found to vary with temperature according to the expression $C_p/(J\ K^{-1}) = 20.17 + 0.4001(T/K)$. Calculate *q*, *w*, ΔU , and ΔH when the temperature is raised from 0°C to 100°C (a) at constant pressure, (b) at constant volume.

2.9(a) Calculate the final temperature of a sample of argon of mass 12.0 g that is expanded reversibly and adiabatically from 1.0 dm³ at 273.15 K to 3.0 dm³.

2.9(b) Calculate the final temperature of a sample of carbon dioxide of mass 16.0 g that is expanded reversibly and adiabatically from 500 cm³ at 298.15 K to 2.00 dm³.

2.10(a) A sample of carbon dioxide of mass 2.45 g at 27.0°C is allowed to expand reversibly and adiabatically from 500 cm³ to 3.00 dm³. What is the work done by the gas?

2.10(b) A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm³ to 2.00 dm³. What is the work done by the gas?

2.11(a) Calculate the final pressure of a sample of carbon dioxide that expands reversibly and adiabatically from 57.4 kPa and 1.0 dm³ to a final volume of 2.0 dm³. Take $\gamma = 1.4$.

2.11(b) Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 87.3 Torr and 500 cm³ to a final volume of 3.0 dm³. Take $\gamma = 1.3$.

2.12(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g), the temperature of the sample increases by 2.55 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2.12(b) When 178 J of energy is supplied as heat to 1.9 mol of gas molecules, the temperature of the sample increases by 1.78 K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

2.13(a) When 3.0 mol O₂ is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O₂ at constant pressure is 29.4 J K⁻¹ mol⁻¹, calculate *q*, ΔH , and ΔU .

2.13(b) When 2.0 mol CO₂ is heated at a constant pressure of 1.25 atm, its temperature increases from 250 K to 277 K. Given that the molar heat capacity of CO₂ at constant pressure is 37.11 J K⁻¹ mol⁻¹, calculate *q*, ΔH , and ΔU .

2.14(a) A sample of 4.0 mol O₂ is originally confined in 20 dm³ at 270 K and then undergoes adiabatic expansion against a constant pressure of 600 Torr until the volume has increased by a factor of 3.0. Calculate *q*, *w*, ΔT , ΔU , and ΔH . (The final pressure of the gas is not necessarily 600 Torr.)

2.14(b) A sample of 5.0 mol CO₂ is originally confined in 15 dm³ at 280 K and then undergoes adiabatic expansion against a constant pressure of 78.5 kPa until the volume has increased by a factor of 4.0. Calculate *q*, *w*, ΔT , ΔU , and ΔH . (The final pressure of the gas is not necessarily 78.5 kPa.)

2.15(a) A sample consisting of 1.0 mol of perfect gas molecules with $C_V = 20.8 \text{ J K}^{-1}$ is initially at 3.25 atm and 310 K. It undergoes reversible adiabatic expansion until its pressure reaches 2.50 atm. Calculate the final volume and temperature and the work done.

2.15(b) A sample consisting of 1.5 mol of perfect gas molecules with $C_{p,m} = 20.8 \text{ J K}^{-1} \text{ mol}^{-1}$ is initially at 230 kPa and 315 K. It undergoes reversible adiabatic expansion until its pressure reaches 170 kPa. Calculate the final volume and temperature and the work done.

2.16(a) A certain liquid has $\Delta_{\text{vap}}H^\circ = 26.0 \text{ kJ mol}^{-1}$. Calculate *q*, *w*, ΔH , and ΔU when 0.50 mol is vaporized at 250 K and 750 Torr.

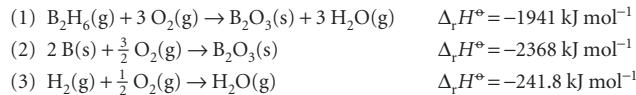
2.16(b) A certain liquid has $\Delta_{\text{vap}}H^\circ = 32.0 \text{ kJ mol}^{-1}$. Calculate *q*, *w*, ΔH , and ΔU when 0.75 mol is vaporized at 260 K and 765 Torr.

2.17(a) The standard enthalpy of formation of ethylbenzene is $-12.5 \text{ kJ mol}^{-1}$. Calculate its standard enthalpy of combustion.

2.17(b) The standard enthalpy of formation of phenol is $-165.0 \text{ kJ mol}^{-1}$. Calculate its standard enthalpy of combustion.

2.18(a) The standard enthalpy of combustion of cyclopropane is $-2091 \text{ kJ mol}^{-1}$ at 25°C. From this information and enthalpy of formation data for CO₂(g) and H₂O(g), calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is $+20.42 \text{ kJ mol}^{-1}$. Calculate the enthalpy of isomerization of cyclopropane to propene.

2.18(b) From the following data, determine Δ_fH° for diborane, B₂H₆(g), at 298 K:



2.19(a) When 120 mg of naphthalene, C₁₀H₈(s), was burned in a bomb calorimeter the temperature rose by 3.05 K. Calculate the calorimeter constant. By how much will the temperature rise when 10 mg of phenol, C₆H₅OH(s), is burned in the calorimeter under the same conditions?

2.19(b) When 2.25 mg of anthracene, C₁₄H₁₀(s), was burned in a bomb calorimeter the temperature rose by 1.35 K. Calculate the calorimeter constant. By how much will the temperature rise when 135 mg of phenol, C₆H₅OH(s), is burned in the calorimeter under the same conditions? ($\Delta_fH^\circ(C_{14}\text{H}_{10}, \text{s}) = -7061 \text{ kJ mol}^{-1}$)

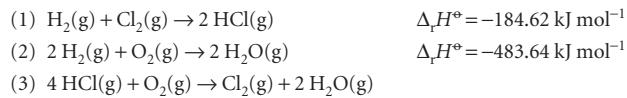
2.20(a) Calculate the standard enthalpy of solution of AgCl(s) in water from the enthalpies of formation of the solid and the aqueous ions.

2.20(b) Calculate the standard enthalpy of solution of AgBr(s) in water from the enthalpies of formation of the solid and the aqueous ions.

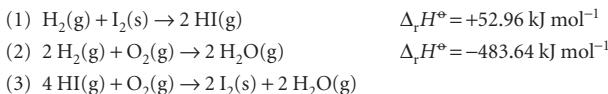
2.21(a) The standard enthalpy of decomposition of the yellow complex H₃NSO₂ into NH₃ and SO₂ is $+40 \text{ kJ mol}^{-1}$. Calculate the standard enthalpy of formation of H₃NSO₂.

2.21(b) Given that the standard enthalpy of combustion of graphite is $-393.51 \text{ kJ mol}^{-1}$ and that of diamond is $-395.41 \text{ kJ mol}^{-1}$, calculate the enthalpy of the graphite-to-diamond transition.

2.22(a) Given the reactions (1) and (2) below, determine (a) Δ_rH° and Δ_rU° for reaction (3), (b) Δ_fH° for both HCl(g) and H₂O(g) all at 298 K.



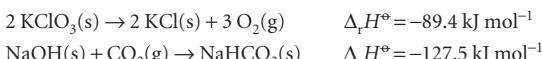
2.22(b) Given the reactions (1) and (2) below, determine (a) $\Delta_f H^\circ$ and $\Delta_r U^\circ$ for reaction (3), (b) $\Delta_f H^\circ$ for both HCl(g) and $\text{H}_2\text{O(g)}$ all at 298 K.



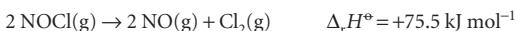
2.23(a) For the reaction $\text{C}_2\text{H}_5\text{OH(l)} + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O(g)}$, $\Delta_r U^\circ = -1373 \text{ kJ mol}^{-1}$ at 298 K. Calculate $\Delta_f H^\circ$.

2.23(b) For the reaction $2 \text{C}_6\text{H}_5\text{COOH(s)} + 13 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O(g)}$, $\Delta_r U^\circ = -772.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate $\Delta_f H^\circ$.

2.24(a) Calculate the standard enthalpies of formation of (a) $\text{KClO}_3(\text{s})$ from the enthalpy of formation of KCl , (b) $\text{NaHCO}_3(\text{s})$ from the enthalpies of formation of CO_2 and NaOH together with the following information:



2.24(b) Calculate the standard enthalpy of formation of NOCl(g) from the enthalpy of formation of NO given in Table 2.5, together with the following information:



2.25(a) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ at 100°C from its value at 25°C.

2.25(b) Use the information in Table 2.5 to predict the standard reaction enthalpy of $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O(l)}$ at 100°C from its value at 25°C.

2.26(a) From the data in Table 2.5, calculate $\Delta_f H^\circ$ and $\Delta_r U^\circ$ at (a) 298 K, (b) 378 K for the reaction $\text{C(graphite)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(\text{g})$. Assume all heat capacities to be constant over the temperature range of interest.

2.26(b) Calculate $\Delta_f H^\circ$ and $\Delta_r U^\circ$ at 298 K and $\Delta_f H^\circ$ at 348 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2.5 and 2.7. Assume the heat capacities to be constant over the temperature range involved.

2.27(a) Calculate $\Delta_f H^\circ$ for the reaction $\text{Zn(s)} + \text{CuSO}_4(\text{aq}) \rightarrow \text{ZnSO}_4(\text{aq}) + \text{Cu(s)}$ from the information in Table 2.7 in the *Data section*.

2.27(b) Calculate $\Delta_f H^\circ$ for the reaction $\text{NaCl(aq)} + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl(s)} + \text{NaNO}_3(\text{aq})$ from the information in Table 2.7 in the *Data section*.

2.28(a) Set up a thermodynamic cycle for determining the enthalpy of hydration of Mg^{2+} ions using the following data: enthalpy of sublimation of Mg(s) , +167.2 kJ mol⁻¹; first and second ionization enthalpies of Mg(g) , 7.646 eV and 15.035 eV; dissociation enthalpy of $\text{Cl}_2(\text{g})$, +241.6 kJ mol⁻¹; electron gain enthalpy of Cl(g) , -3.78 eV; enthalpy of solution of $\text{MgCl}_2(\text{s})$, -150.5 kJ mol⁻¹; enthalpy of hydration of $\text{Cl}^-(\text{g})$, -383.7 kJ mol⁻¹.

2.28(b) Set up a thermodynamic cycle for determining the enthalpy of hydration of Ca^{2+} ions using the following data: enthalpy of sublimation of Ca(s) , +178.2 kJ mol⁻¹; first and second ionization enthalpies of Ca(g) , 589.7 kJ mol⁻¹ and 1145 kJ mol⁻¹; enthalpy of vaporization of bromine, +30.91 kJ mol⁻¹; dissociation enthalpy of $\text{Br}_2(\text{g})$, +192.9 kJ mol⁻¹; electron gain enthalpy of Br(g) , -331.0 kJ mol⁻¹; enthalpy of solution of $\text{CaBr}_2(\text{s})$, -103.1 kJ mol⁻¹; enthalpy of hydration of $\text{Br}^-(\text{g})$, -337 kJ mol⁻¹.

2.29(a) When a certain freon used in refrigeration was expanded adiabatically from an initial pressure of 32 atm and 0°C to a final pressure of 1.00 atm, the temperature fell by 22 K. Calculate the Joule–Thomson coefficient, μ , at 0°C, assuming it remains constant over this temperature range.

2.29(b) A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient, μ , at 5°C, assuming it remains constant over this temperature range.

2.30(a) For a van der Waals gas, $\pi_T = a/V_m^2$. Calculate ΔU_m for the isothermal expansion of nitrogen gas from an initial volume of 1.00 dm³ to 24.8 dm³ at 298 K. What are the values of q and w ?

2.30(b) Repeat Exercise 2.30(a) for argon, from an initial volume of 1.00 dm³ to 22.1 dm³ at 298 K.

2.31(a) The volume of a certain liquid varies with temperature as

$$V = V' \{0.75 + 3.9 \times 10^{-4}(T/\text{K}) + 1.48 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 300 K. Calculate its expansion coefficient, α , at 320 K.

2.31(b) The volume of a certain liquid varies with temperature as

$$V = V' \{0.77 + 3.7 \times 10^{-4}(T/\text{K}) + 1.52 \times 10^{-6}(T/\text{K})^2\}$$

where V' is its volume at 298 K. Calculate its expansion coefficient, α , at 310 K.

2.32(a) The isothermal compressibility of copper at 293 K is $7.35 \times 10^{-7} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.32(b) The isothermal compressibility of lead at 293 K is $2.21 \times 10^{-6} \text{ atm}^{-1}$. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.

2.33(a) Given that $\mu = 0.25 \text{ K atm}^{-1}$ for nitrogen, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 15.0 mol N_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 75 atm.

2.33(b) Given that $\mu = 1.11 \text{ K atm}^{-1}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 12.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

Problems*

Assume all gases are perfect unless stated otherwise. Note that 1 atm = 1.013 25 bar. Unless otherwise stated, thermochemical data are for 298.15 K.

Numerical problems

- 2.1** A sample consisting of 1 mol of perfect gas atoms (for which $C_{V,m} = \frac{3}{2}R$) is taken through the cycle shown in Fig. 2.34. (a) Determine the temperature at the points 1, 2, and 3. (b) Calculate q , w , ΔU , and ΔH for each step and for the overall cycle. If a numerical answer cannot be obtained from the information given, then write in +, -, 0, or ? as appropriate.

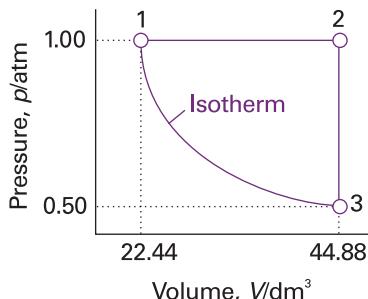


Fig. 2.34

- 2.2** A sample consisting of 1.0 mol $\text{CaCO}_3(\text{s})$ was heated to 800°C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

- 2.3** A sample consisting of 2.0 mol CO_2 occupies a fixed volume of 15.0 dm³ at 300 K. When it is supplied with 2.35 kJ of energy as heat its temperature increases to 341 K. Assume that CO_2 is described by the van der Waals equation of state, and calculate w , ΔU , and ΔH .

- 2.4** A sample of 70 mmol $\text{Kr}(\text{g})$ expands reversibly and isothermally at 373 K from 5.25 cm³ to 6.29 cm³, and the internal energy of the sample is known to increase by 83.5 J. Use the virial equation of state up to the second coefficient $B = -28.7 \text{ cm}^3 \text{ mol}^{-1}$ to calculate w , q , and ΔH for this change of state.

- 2.5** A sample of 1.00 mol perfect gas molecules with $C_{p,m} = \frac{7}{2}R$ is put through the following cycle: (a) constant-volume heating to twice its initial volume, (b) reversible, adiabatic expansion back to its initial temperature, (c) reversible isothermal compression back to 1.00 atm. Calculate q , w , ΔU , and ΔH for each step and overall.

- 2.6** Calculate the work done during the isothermal reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients a and b appear in the final expression. Plot on the same graph the indicator diagrams for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which $a = 0$ and $b = 5.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$, and (c) $a = 4.2 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0$. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take $V_i = 1.0 \text{ dm}^3$, $n = 1.0 \text{ mol}$, and $T = 298 \text{ K}$.

- 2.7** The molar heat capacity of ethane is represented in the temperature range 298 K to 400 K by the empirical expression $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = 14.73 + 0.1272(T/\text{K})$. The corresponding expressions for $\text{C}(\text{s})$ and $\text{H}_2(\text{g})$ are given in

Table 2.2. Calculate the standard enthalpy of formation of ethane at 350 K from its value at 298 K.

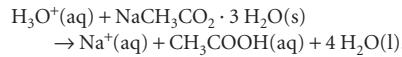
- 2.8** A sample of the sugar $\text{D}-\text{ribose}$ ($\text{C}_5\text{H}_{10}\text{O}_5$) of mass 0.727 g was placed in a calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is $-3251 \text{ kJ mol}^{-1}$, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of $\text{D}-\text{ribose}$ and its enthalpy of formation.

- 2.9** The standard enthalpy of formation of the metallocene bis(benzene)chromium was measured in a calorimeter. It was found for the reaction $\text{Cr}(\text{C}_6\text{H}_6)_2(\text{s}) \rightarrow \text{Cr}(\text{s}) + 2 \text{C}_6\text{H}_6(\text{g})$ that $\Delta_fU^\circ(583 \text{ K}) = +8.0 \text{ kJ mol}^{-1}$. Find the corresponding reaction enthalpy and estimate the standard enthalpy of formation of the compound at 583 K. The constant-pressure molar heat capacity of benzene is $136.1 \text{ J K}^{-1} \text{ mol}^{-1}$ in its liquid range and $81.67 \text{ J K}^{-1} \text{ mol}^{-1}$ as a gas.

- 2.10‡** From the enthalpy of combustion data in Table 2.5 for the alkanes methane through octane, test the extent to which the relation $\Delta_cH^\circ = k\{(M/(g \text{ mol}^{-1}))^n\}$ holds and find the numerical values for k and n . Predict Δ_cH° for decane and compare to the known value.

- 2.11** It is possible to investigate the thermochemical properties of hydrocarbons with molecular modelling methods. (a) Use electronic structure software to predict Δ_cH° values for the alkanes methane through pentane. To calculate Δ_cH° values, estimate the standard enthalpy of formation of $\text{C}_n\text{H}_{2(n+1)}(\text{g})$ by performing semi-empirical calculations (for example, AM1 or PM3 methods) and use experimental standard enthalpy of formation values for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. (b) Compare your estimated values with the experimental values of Δ_cH° (Table 2.5) and comment on the reliability of the molecular modelling method. (c) Test the extent to which the relation $\Delta_cH^\circ = k\{(M/(g \text{ mol}^{-1}))^n\}$ holds and find the numerical values for k and n .

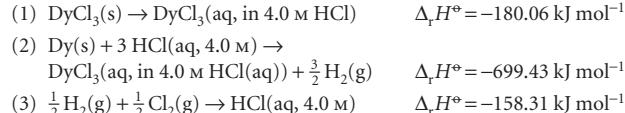
- 2.12‡** When 1.3584 g of sodium acetate trihydrate was mixed into 100.0 cm³ of 0.2000 M $\text{HCl}(\text{aq})$ at 25°C in a solution calorimeter, its temperature fell by 0.397°C on account of the reaction:



The heat capacity of the calorimeter is 91.0 J K^{-1} and the heat capacity density of the acid solution is $4.144 \text{ J K}^{-1} \text{ cm}^{-3}$. Determine the standard enthalpy of formation of the aqueous sodium cation. The standard enthalpy of formation of sodium acetate trihydrate is $-1064 \text{ kJ mol}^{-1}$.

- 2.13‡** Since their discovery in 1985, fullerenes have received the attention of many chemical researchers. Kolesov *et al.* reported the standard enthalpy of combustion and of formation of crystalline C_{60} based on calorimetric measurements (V.P. Kolesov, S.M. Pimenova, V.K. Pavlovich, N.B. Tamm, and A.A. Kurskaya, *J. Chem. Thermodynamics* **28**, 1121 (1996)). In one of their runs, they found the standard specific internal energy of combustion to be $-36.0334 \text{ kJ g}^{-1}$ at 298.15 K. Compute Δ_cH° and Δ_fH° of C_{60} .

- 2.14‡** A thermodynamic study of DyCl_3 (E.H.P. Cordfunke, A.S. Boorji, and M. Yu. Furkaliouk, *J. Chem. Thermodynamics* **28**, 1387 (1996)) determined its standard enthalpy of formation from the following information



Determine $\Delta_fH^\circ(\text{DyCl}_3, \text{s})$ from these data.

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

2.15‡ Silylene (SiH_2) is a key intermediate in the thermal decomposition of silicon hydrides such as silane (SiH_4) and disilane (Si_2H_6). Moffat *et al.* (H.K. Moffat, K.F. Jensen, and R.W. Carr, *J. Phys. Chem.* **95**, 145 (1991)) report $\Delta_f H^\circ(\text{SiH}_2) = +274 \text{ kJ mol}^{-1}$. If $\Delta_f H^\circ(\text{SiH}_4) = +34.3 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{Si}_2\text{H}_6) = +80.3 \text{ kJ mol}^{-1}$ (*CRC Handbook* (2004)), compute the standard enthalpies of the following reactions:

- $\text{SiH}_4(\text{g}) \rightarrow \text{SiH}_2(\text{g}) + \text{H}_2(\text{g})$
- $\text{Si}_2\text{H}_6(\text{g}) \rightarrow \text{SiH}_2(\text{g}) + \text{SiH}_4(\text{g})$

2.16‡ Silanone (SiH_3O) and silanol (SiH_3OH) are species believed to be important in the oxidation of silane (SiH_4). These species are much more elusive than their carbon counterparts. C.L. Darling and H.B. Schlegel (*J. Phys. Chem.* **97**, 8207 (1993)) report the following values (converted from calories) from a computational study: $\Delta_f H^\circ(\text{SiH}_3\text{O}) = -98.3 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{SiH}_3\text{OH}) = -282 \text{ kJ mol}^{-1}$. Compute the standard enthalpies of the following reactions:

- $\text{SiH}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SiH}_3\text{OH}(\text{g})$
- $\text{SiH}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{SiH}_3\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l})$
- $\text{SiH}_3\text{OH}(\text{g}) \rightarrow \text{SiH}_3\text{O}(\text{g}) + \text{H}_2(\text{g})$

Note that $\Delta_f H^\circ(\text{SiH}_4, \text{g}) = +34.3 \text{ kJ mol}^{-1}$ (*CRC Handbook* (2004)).

2.17 The constant-volume heat capacity of a gas can be measured by observing the decrease in temperature when it expands adiabatically and reversibly. If the decrease in pressure is also measured, we can use it to infer the value of $\gamma = C_p/C_V$ and hence, by combining the two values, deduce the constant-pressure heat capacity. A fluorocarbon gas was allowed to expand reversibly and adiabatically to twice its volume; as a result, the temperature fell from 298.15 K to 248.44 K and its pressure fell from 202.94 kPa to 81.840 kPa. Evaluate C_p .

2.18 A sample consisting of 1.00 mol of a van der Waals gas is compressed from 20.0 dm^3 to 10.0 dm^3 at 300 K. In the process, 20.2 kJ of work is done on the gas. Given that $\mu = \{(2a/RT) - b\}/C_{p,m}$, with $C_{p,m} = 38.4 \text{ J K}^{-1} \text{ mol}^{-1}$, $a = 3.60 \text{ dm}^6 \text{ atm mol}^{-2}$, and $b = 0.44 \text{ dm}^3 \text{ mol}^{-1}$, calculate ΔH for the process.

2.19 Take nitrogen to be a van der Waals gas with $a = 1.352 \text{ dm}^6 \text{ atm mol}^{-2}$ and $b = 0.0387 \text{ dm}^3 \text{ mol}^{-1}$, and calculate ΔH_m when the pressure on the gas is decreased from 500 atm to 1.00 atm at 300 K. For a van der Waals gas, $\mu = \{(2a/RT) - b\}/C_{p,m}$. Assume $C_{p,m} = \frac{7}{2}R$.

Theoretical problems

2.20 Show that the following functions have exact differentials: (a) $x^2y + 3y^2$, (b) $x \cos xy$, (c) x^3y^2 , (d) $t(t + e^t) + s$.

2.21 (a) What is the total differential of $z = x^2 + 2y^2 - 2xy + 2x - 4y - 8$? (b) Show that $\partial^2 z / \partial y \partial x = \partial^2 z / \partial x \partial y$ for this function. (c) Let $z = xy - y + \ln x + 2$. Find dz and show that it is exact.

2.22 (a) Express $(\partial C_V / \partial V)_T$ as a second derivative of U and find its relation to $(\partial U / \partial V)_T$ and $(\partial C_p / \partial p)_T$ as a second derivative of H and find its relation to $(\partial H / \partial p)_T$. (b) From these relations show that $(\partial C_V / \partial V)_T = 0$ and $(\partial C_p / \partial p)_T = 0$ for a perfect gas.

2.23 (a) Derive the relation $C_V = -(\partial U / \partial V)_T (\partial V / \partial T)_U$ from the expression for the total differential of $U(T, V)$ and (b) starting from the expression for the total differential of $H(T, p)$, express $(\partial H / \partial p)_T$ in terms of C_p and the Joule–Thomson coefficient, μ .

2.24 Starting from the expression $C_p - C_V = T(\partial p / \partial T)_V (\partial V / \partial T)_p$, use the appropriate relations between partial derivatives to show that

$$C_p - C_V = \frac{T(\partial V / \partial T)_p^2}{(\partial V / \partial T)_T}$$

Evaluate $C_p - C_V$ for a perfect gas.

2.25 (a) By direct differentiation of $H = U + pV$, obtain a relation between $(\partial H / \partial U)_p$ and $(\partial U / \partial V)_p$. (b) Confirm that $(\partial H / \partial U)_p = 1 + p(\partial V / \partial U)_p$ by

expressing $(\partial H / \partial U)_p$ as the ratio of two derivatives with respect to volume and then using the definition of enthalpy.

2.26 (a) Write expressions for dV and dp given that V is a function of p and T and p is a function of V and T . (b) Deduce expressions for $d \ln V$ and $d \ln p$ in terms of the expansion coefficient and the isothermal compressibility.

2.27 Calculate the work done during the isothermal reversible expansion of a gas that satisfies the virial equation of state, eqn 1.19. Evaluate (a) the work for 1.0 mol Ar at 273 K (for data, see Table 1.3) and (b) the same amount of a perfect gas. Let the expansion be from 500 cm^3 to 1000 cm^3 in each case.

2.28 Express the work of isothermal reversible expansion of a van der Waals gas in reduced variables and find a definition of reduced work that makes the overall expression independent of the identity of the gas. Calculate the work of isothermal reversible expansion along the critical isotherm from V_c to xV_c .

2.29‡ A gas obeying the equation of state $p(V - nb) = nRT$ is subjected to a Joule–Thomson expansion. Will the temperature increase, decrease, or remain the same?

2.30 Use the fact that $(\partial U / \partial V)_T = a/V_m^2$ for a van der Waals gas to show that $\mu C_{p,m} \approx (2a/RT) - b$ by using the definition of μ and appropriate relations between partial derivatives. (*Hint*. Use the approximation $pV_m \approx RT$ when it is justifiable to do so.)

2.31 Rearrange the van der Waals equation of state to give an expression for T as a function of p and V (with n constant). Calculate $(\partial T / \partial p)_V$ and confirm that $(\partial T / \partial p)_V = 1 / (\partial p / \partial T)_V$. Go on to confirm Euler's chain relation.

2.32 Calculate the isothermal compressibility and the expansion coefficient of a van der Waals gas. Show, using Euler's chain relation, that $\kappa_T R = \alpha(V_m - b)$.

2.33 Given that $\mu C_p = T(\partial V / \partial T)_p - V$, derive an expression for μ in terms of the van der Waals parameters a and b , and express it in terms of reduced variables. Evaluate μ at 25°C and 1.0 atm , when the molar volume of the gas is $24.6 \text{ dm}^3 \text{ mol}^{-1}$. Use the expression obtained to derive a formula for the inversion temperature of a van der Waals gas in terms of reduced variables, and evaluate it for the xenon sample.

2.34 The thermodynamic equation of state $(\partial U / \partial V)_T = T(\partial p / \partial T)_V - p$ was quoted in the chapter. Derive its partner

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V$$

from it and the general relations between partial differentials.

2.35 Show that for a van der Waals gas,

$$C_{p,m} - C_{V,m} = \lambda R \quad \frac{1}{\lambda} = 1 - \frac{(3V_r - 1)^2}{4V_r^3 T_r}$$

and evaluate the difference for xenon at 25°C and 10.0 atm .

2.36 The speed of sound, c_s , in a gas of molar mass M is related to the ratio of heat capacities γ by $c_s = (\gamma RT/M)^{1/2}$. Show that $c_s = (\gamma p / \rho)^{1/2}$, where ρ is the mass density of the gas. Calculate the speed of sound in argon at 25°C .

2.37‡ A gas obeys the equation of state $V_m = RT/p + aT^2$ and its constant-pressure heat capacity is given by $C_{p,m} = A + BT + Cp$, where a , A , B , and C are constants independent of T and p . Obtain expressions for (a) the Joule–Thomson coefficient and (b) its constant-volume heat capacity.

Applications: to biology, materials science, and the environment

2.38 It is possible to see with the aid of a powerful microscope that a long piece of double-stranded DNA is flexible, with the distance between the ends of the chain adopting a wide range of values. This flexibility is important because it allows DNA to adopt very compact conformations as it is packaged in a chromosome (see Chapter 18). It is convenient to visualize a long piece

of DNA as a *freely jointed chain*, a chain of N small, rigid units of length l that are free to make any angle with respect to each other. The length l , the *persistence length*, is approximately 45 nm, corresponding to approximately 130 base pairs. You will now explore the work associated with extending a DNA molecule. (a) Suppose that a DNA molecule resists being extended from an equilibrium, more compact conformation with a *restoring force* $F = -k_F x$, where x is the difference in the end-to-end distance of the chain from an equilibrium value and k_F is the *force constant*. Systems showing this behaviour are said to obey *Hooke's law*. (i) What are the limitations of this model of the DNA molecule? (ii) Using this model, write an expression for the work that must be done to extend a DNA molecule by x . Draw a graph of your conclusion. (b) A better model of a DNA molecule is the *one-dimensional freely jointed chain*, in which a rigid unit of length l can only make an angle of 0° or 180° with an adjacent unit. In this case, the restoring force of a chain extended by $x = nl$ is given by

$$F = \frac{kT}{2l} \ln \left(\frac{1+v}{1-v} \right) \quad v = n/N$$

where $k = 1.381 \times 10^{-23}$ J K $^{-1}$ is *Boltzmann's constant* (not a force constant). (i) What are the limitations of this model? (ii) What is the magnitude of the force that must be applied to extend a DNA molecule with $N = 200$ by 90 nm? (iii) Plot the restoring force against v , noting that v can be either positive or negative. How is the variation of the restoring force with end-to-end distance different from that predicted by Hooke's law? (iv) Keeping in mind that the difference in end-to-end distance from an equilibrium value is $x = nl$ and, consequently, $dx = ldn = Nldv$, write an expression for the work of extending a DNA molecule. (v) Calculate the work of extending a DNA molecule from $v=0$ to $v=1.0$. Hint. You must integrate the expression for w . The task can be accomplished easily with mathematical software. (c) Show that for small extensions of the chain, when $v \ll 1$, the restoring force is given by

$$F \approx \frac{vkT}{l} = \frac{nkT}{Nl}$$

Hint. See Appendix 2 for a review of series expansions of functions. (d) Is the variation of the restoring force with extension of the chain given in part (c) different from that predicted by Hooke's law? Explain your answer.

2.39 There are no dietary recommendations for consumption of carbohydrates. Some nutritionists recommend diets that are largely devoid of carbohydrates, with most of the energy needs being met by fats. However, the most common recommendation is that at least 65 per cent of our food calories should come from carbohydrates. A $\frac{3}{4}$ -cup serving of pasta contains 40 g of carbohydrates. What percentage of the daily calorie requirement for a person on a 2200 Calorie diet (1 Cal = 1 kcal) does this serving represent?

2.40 An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

2.41 Glucose and fructose are simple sugars with the molecular formula C₆H₁₂O₆. Sucrose, or table sugar, is a complex sugar with molecular formula C₁₂H₂₂O₁₁ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is given off as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could you climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

2.42 In biological cells that have a plentiful supply of O₂, glucose is oxidized completely to CO₂ and H₂O by a process called *aerobic oxidation*. Muscle cells may be deprived of O₂ during vigorous exercise and, in that case, one

molecule of glucose is converted to two molecules of lactic acid (CH₃CH(OH)COOH) by a process called *anaerobic glycolysis* (see Impact 17.2). (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K $^{-1}$ the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

2.43 You have at your disposal a sample of pure polymer P and a sample of P that has just been synthesized in a large chemical reactor and that may contain impurities. Describe how you would use differential scanning calorimetry to determine the mole percentage composition of P in the allegedly impure sample.

2.44† Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. Seakins *et al.* (P.W. Seakins, M.J. Pilling, J.T. Niiranen, D. Gutman, and L.N. Krasnoperov, *J. Phys. Chem.* **96**, 9847 (1992)) report $\Delta_f H^\circ$ for a variety of alkyl radicals in the gas phase, information that is applicable to studies of pyrolysis and oxidation reactions of hydrocarbons. This information can be combined with thermodynamic data on alkenes to determine the reaction enthalpy for possible fragmentation of a large alkyl radical into smaller radicals and alkenes. Use the following set of data to compute the standard reaction enthalpies for three possible fates of the *tert*-butyl radical, namely, (a) *tert*-C₄H₉ → *sec*-C₄H₉, (b) *tert*-C₄H₉ → C₃H₆ + CH₃, (c) *tert*-C₄H₉ → C₂H₄ + C₂H₅.

Species:	C ₂ H ₅	<i>sec</i> -C ₄ H ₉	<i>tert</i> -C ₄ H ₉
$\Delta_f H^\circ/(kJ \text{ mol}^{-1})$	+121.0	+67.5	+51.3

2.45† In 1995, the Intergovernmental Panel on Climate Change (IPCC) considered a global average temperature rise of 1.0–3.5°C likely by the year 2100, with 2.0°C its best estimate. Predict the average rise in sea level due to thermal expansion of sea water based on temperature rises of 1.0°C, 2.0°C, and 3.5°C given that the volume of the Earth's oceans is 1.37×10^9 km 3 and their surface area is 361×10^6 km 2 , and state the approximations that go into the estimates.

2.46† Concerns over the harmful effects of chlorofluorocarbons on stratospheric ozone have motivated a search for new refrigerants. One such alternative is 2,2-dichloro-1,1,1-trifluoroethane (refrigerant 123). Younglove and McLinden published a compendium of thermophysical properties of this substance (B.A. Younglove and M. McLinden, *J. Phys. Chem. Ref. Data* **23**, 7 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 1.00 bar and 50°C given that $(\partial H/\partial p)_T = -3.29 \times 10^3$ J MPa $^{-1}$ mol $^{-1}$ and $C_{p,m} = 110.0$ J K $^{-1}$ mol $^{-1}$. (b) Compute the temperature change that would accompany adiabatic expansion of 2.0 mol of this refrigerant from 1.5 bar to 0.5 bar at 50°C.

2.47† Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (R. Tillner-Roth and H.D. Baehr, *J. Phys. Chem. Ref. Data* **23**, 657 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K):

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg $^{-1}$)	426.48	426.12	425.76

(The specific constant-pressure heat capacity is 0.7649 kJ K $^{-1}$ kg $^{-1}$.)

(b) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg $^{-1}$)	461.93	459.12	456.15

(The specific constant-pressure heat capacity is 1.0392 kJ K $^{-1}$ kg $^{-1}$.)