TOPIC 2A Internal energy

➤ **Why do you need to know this material?**

The First Law of thermodynamics is the foundation of the discussion of the role of energy in chemistry. Wherever the generation or use of energy in physical transformations or chemical reactions is of interest, lying in the background are the concepts introduced by the First Law.

➤ **What is the key idea?**

The total energy of an isolated system is constant.

➤ **What do you need to know already?**

This Topic makes use of the discussion of the properties of gases (Topic 1A), particularly the perfect gas law. It builds on the definition of work given in *The chemist's toolkit* 6.

For the purposes of thermodynamics, the universe is divided into two parts, the system and its surroundings. The **system** is the part of the world of 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 measurements are made. The type of system depends on the characteristics of the boundary that divides it from the surroundings (Fig. 2A.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.
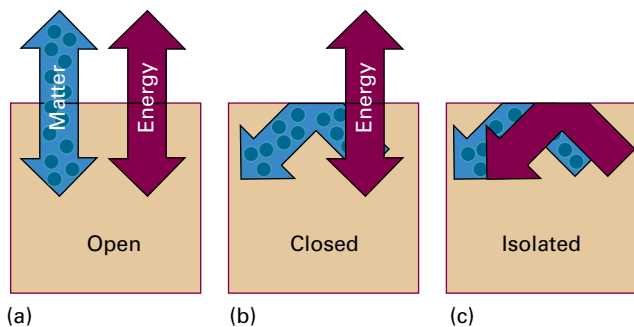

Figure 2A.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

For example, a closed system can expand and thereby raise a weight in the surroundings; a closed system may also transfer energy to the surroundings if they are at a lower temperature. An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

2A.1 Work, heat, and energy

Although thermodynamics deals with observations on bulk systems, it is immeasurably enriched by understanding the molecular origins of these observations.

(a) Operational definitions

The fundamental physical property in thermodynamics is work: **work** is done to achieve motion against an opposing force (*The chemist's toolkit* 6). A simple example is the process of raising a weight against the pull of gravity. A process does work if in principle it can be harnessed to raise a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston: the motion of the piston can in principle be used to raise a weight. Another example is a chemical reaction in a cell, which leads to an electric current that can drive a motor and be used to raise a weight.

The **energy** of a system is its capacity to do work (see *The chemist's toolkit* 6 for more detail). 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 the energy is said to be 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. Boundaries that do permit the transfer of energy as heat are called **diathermic**; those that do not are called **adiabatic**.

The chemist's toolkit 6   Work and energy

Work, w, is done when a body is moved against an opposing force. For an infinitesimal displacement through ds (a vector), the work done *on the body* is

$$\mathrm{d}w_{\mathrm{body}} = -F \cdot \mathrm{d}s$$

Work done on body [definition]

where $F \cdot \mathrm{d}s$ is the 'scalar product' of the vectors F and ds:

$$F \cdot \mathrm{d}s = F_x \mathrm{d}x + F_y \mathrm{d}y + F_z \mathrm{d}z$$

Scalar product [definition]

The energy lost as work by the system, dw, is the negative of the work done on the body, so

$$\mathrm{d}w = F \cdot \mathrm{d}s$$

Work done on system [definition]

For motion in one dimension, $\mathrm{d}w = F_x \mathrm{d}x$, with $F_x < 0$ (so $F_x = -|F_x|$) if it opposed the motion. The total work done along a path is the integral of this expression, allowing for the possibility that F changes in direction and magnitude at each point of the path. With force in newtons (N) and distance in metres, the units of work are joules (J), with

$$1\,\mathrm{J} = 1\,\mathrm{N\,m} = 1\,\mathrm{kg\,m^2\,s^{-2}}$$

Energy is the capacity to do work. The SI unit of energy is the same as that of work, namely the joule. The rate of supply of energy is called the **power** (P), and is expressed in watts (W):

$$1\,\mathrm{W} = 1\,\mathrm{J\,s^{-1}}$$

A particle may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**, E_k, of a body is the energy the body possesses as a result of its motion. For a body of mass m travelling at a speed v,

$$E_k = \tfrac{1}{2}mv^2$$

Kinetic energy [definition]

Because $p = mv$ (*The chemist's toolkit* 3 of Topic 1B), where p is the magnitude of the linear momentum, it follows that

$$E_k = \frac{p^2}{2m}$$

Kinetic energy [definition]

The **potential energy**, E_p, (and commonly V, but do not confuse that with the volume!) of a body is the energy it possesses as a result of its position. In the absence of losses, the potential energy of a stationary particle is equal to the work that had to be done on the body to bring it to its current location. Because $\mathrm{d}w_{\mathrm{body}} = -F_x \mathrm{d}x$, it follows that $\mathrm{d}E_p = -F_x \mathrm{d}x$ and therefore

$$F_x = -\frac{\mathrm{d}E_p}{\mathrm{d}x}$$

Potential energy [relation to force]

If E_p increases as x increases, then F_x is negative (directed towards negative x, Sketch 1). Thus, the steeper the gradient (the more strongly the potential energy depends on position), the greater is the force.
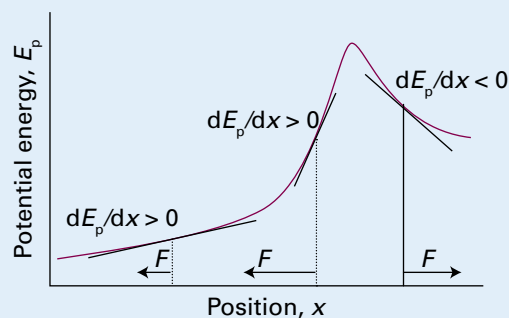
Sketch 1

No universal expression for the potential energy can be given because it depends on the type of force the body experiences. For a particle of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$E_p(h) = E_p(0) + mgh$$

Gravitational potential energy

where g is the **acceleration of free fall** (g depends on location, but its 'standard value' is close to $9.81\,\mathrm{m\,s^{-2}}$). The zero of potential energy is arbitrary. For a particle close to the surface of the Earth, it is common to set $E_p(0) = 0$.

The **Coulomb potential energy** of two electric charges, Q_1 and Q_2, separated by a distance r is

$$E_p = \frac{Q_1 Q_2}{4\pi\varepsilon r}$$

Coulomb potential energy

The quantity ε (epsilon) is the **permittivity**; its value depends upon the nature of the medium between the charges. If the charges are separated by a vacuum, then the constant is known as the **vacuum permittivity**, ε_0 (epsilon zero), or the **electric constant**, which has the value $8.854 \times 10^{-12}\,\mathrm{J^{-1}\,C^2\,m^{-1}}$. The permittivity is greater for other media, such as air, water, or oil. It is commonly expressed as a multiple of the vacuum permittivity:

$$\varepsilon = \varepsilon_r \varepsilon_0$$

Permittivity [definition]

with ε_r the dimensionless **relative permittivity** (formerly, the *dielectric constant*).

The **total energy** of a particle is the sum of its kinetic and potential energies:

$$E = E_k + E_p$$

Total energy [definition]

Provided no external forces are acting on the body, its total energy is constant. This central statement of physics is known as the **law of the conservation of energy**. Potential and kinetic energy may be freely interchanged, but their sum remains constant in the absence of external influences.

An **exothermic process** is a process that releases energy as heat. For example, combustions are chemical reactions in which substances react with oxygen, normally with a flame. The combustion of methane gas, $CH_4(g)$, is written as:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$$
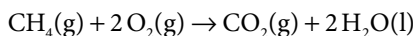
All combustions are exothermic. Although the temperature rises in the course of the combustion, given enough time, a system in a diathermic vessel returns to the temperature of its surroundings, so it is possible to speak of a combustion 'at 25 °C', for instance. If the combustion takes place in an adiabatic container, the energy released as heat remains inside the container and results in a permanent rise in temperature.

An **endothermic process** is a process in which energy is acquired as heat. An example of an endothermic process is the vaporization of water. To avoid a lot of awkward language, it is common to 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 to restore the temperature to that of the surroundings. 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. 2A.2.
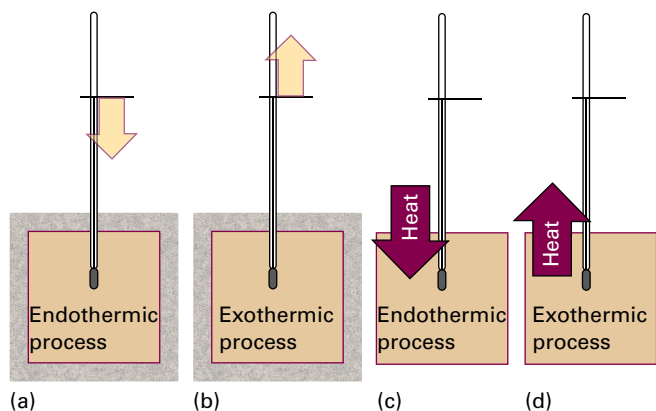

Figure 2A.2　(a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, then the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings (which remain at the same temperature), and the system remains at the same temperature. (d) If the process is exothermic, then energy leaves as heat, and the process is isothermal.

(b)　The molecular interpretation of heat and work

In molecular terms, heating is the transfer of energy that makes use of disorderly, apparently random, molecular motion in the surroundings. 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 cooler system is increased. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings (Fig. 2A.3).

In contrast, work is the transfer of energy that makes use of organized motion in the surroundings (Fig. 2A.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 electrons in an electric current
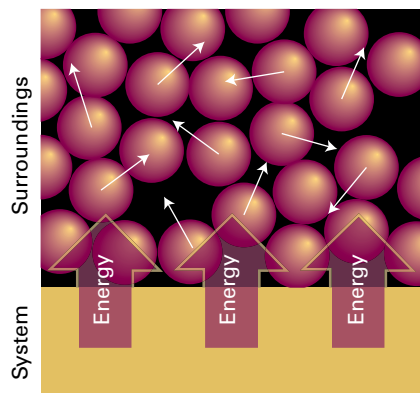

Figure 2A.3　When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.
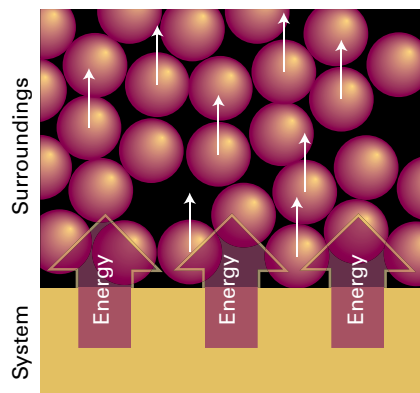

Figure 2A.4　When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

move in the same direction. 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 in an adiabatic enclosure, for instance, work is done on the system 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. The weight is observed to fall, leading to the orderly descent of its atoms, and work is done even though it is stimulating thermal motion.

2A.2 The definition of 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 constituents (the atoms, ions, or molecules) of the system. It 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. That is, the internal energy is the energy 'internal' to the system. The change in internal energy is denoted by ΔU when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f:

$$\Delta U = U_f - U_i \tag{2A.1}$$

A convention used throughout thermodynamics is that $\Delta X = X_f - X_i$, where X is a property (a 'state function') of the system.

The internal energy is a **state function**, a property with a value that depends only on the current state of the system and is independent of how that state has been prepared. In other words, internal energy is a function of the variables that determine the current state of the system. Changing any one of the state variables, such as the pressure, may result in a change in internal energy. That the internal energy is a state function has consequences of the greatest importance (Topic 2D).

The internal energy is an extensive property of a system (a property that depends on the amount of substance present; see *The chemist's toolkit* 2 in Topic 1A) and is measured in joules $(1\,J = 1\,kg\,m^2\,s^{-2})$. The molar internal energy, U_m, is the internal energy divided by the amount of substance in a system, $U_m = U/n$; it is an intensive property (a property independent of the amount of substance) and is commonly reported in kilojoules per mole $(kJ\,mol^{-1})$.

(a) Molecular interpretation of internal energy

A molecule has a certain number of motional degrees of freedom, such as the ability to move through space (this motion is called 'translation'), rotate, or vibrate. 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, for instance as vigorous vibration. The internal energy of a sample increases as the temperature is raised and states of higher energy become more highly populated.

The 'equipartition theorem' of classical mechanics, introduced in *The chemist's toolkit* 7, can be used to predict the contributions of each mode of motion of a molecule to the total energy of a collection of non-interacting molecules (that is, of a perfect gas, and providing quantum effects can be ignored).

The chemist's toolkit 7 The equipartition theorem

The Boltzmann distribution (see the *Prologue*) can be used to calculate the average energy associated with each mode of motion of an atom or molecule in a sample at a given temperature. However, when the temperature is so high that many energy levels are occupied, there is a much simpler way to find the average energy, through the **equipartition theorem**:

For a sample at thermal equilibrium the average value of each quadratic contribution to the energy is $\frac{1}{2}kT$.

A 'quadratic contribution' is a term that is proportional to the square of the momentum (as in the expression for the kinetic ener-

gy, $E_k = p^2/2m$; *The chemist's toolkit* 6) or the displacement from an equilibrium position (as for the potential energy of a harmonic oscillator, $E_p = \frac{1}{2}k_f x^2$). The theorem is a conclusion from classical mechanics and for quantized systems is applicable only when the separation between the energy levels is so small compared to kT that many states are populated. Under normal conditions the equipartition theorem gives good estimates for the average energies associated with translation and rotation. However, the separation between vibrational and electronic states is typically much greater than for rotation or translation, and for these types of motion the equipartition theorem is unlikely to apply.

An atom in a gas can move in three dimensions, so its translational kinetic energy is the sum of three quadratic contributions:

$$E_{\text{trans}} = \tfrac{1}{2}mv_x^2 + \tfrac{1}{2}mv_y^2 + \tfrac{1}{2}mv_z^2$$

The equipartition theorem predicts that the average energy for each of these quadratic contributions is $\tfrac{1}{2}kT$. Thus, the average kinetic energy is $E_{\text{trans}} = 3 \times \tfrac{1}{2}kT = \tfrac{3}{2}kT$. The molar translational energy is therefore $E_{\text{trans,m}} = \tfrac{3}{2}kT \times N_A = \tfrac{3}{2}RT$. At 25 °C, $RT = 2.48\,\text{kJ mol}^{-1}$, so the contribution of translation to the molar internal energy of a perfect gas is 3.72 kJ mol^{-1}.

The contribution to the internal energy of a collection of perfect gas molecules is independent of the volume occupied by the molecules: there are no intermolecular interactions in a perfect gas, so the distance between the molecules has no effect on the energy. That is,

> The internal energy of a perfect gas is independent of the volume it occupies.

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

(b) The formulation of the First Law

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 it might be known how the energy transfer has occurred (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. That is,

> Heat and work are equivalent ways of changing the internal energy of a system.

A system is like a bank: it accepts deposits in either currency (work or heat), but stores its reserves as internal energy. It is also found experimentally that if a system is isolated from its surroundings, meaning that it can exchange neither matter nor energy with its surroundings, then no change in internal energy takes place. This summary of observations is now known as the **First Law of thermodynamics** and is expressed as follows:

> The internal energy of an isolated system is constant.
>
> First Law of thermodynamics

It is not possible to use a system to do work, leave it isolated, and then come back expecting to find it restored to its original state with the same capacity for doing work. The experimental evidence for this observation is that no 'perpetual motion machine', a machine that does work without consuming fuel or using some other source of energy, has ever been built.

These remarks may be expressed symbolically as follows. If w is the work done on a system, q is the energy transferred as heat to a system, and ΔU is the resulting change in internal energy, then

$$\Delta U = q + w \qquad \text{Mathematical statement of the First Law} \qquad (2A.2)$$

Equation 2A.2 summarizes the equivalence of heat and work for bringing about changes in the internal energy and the fact that the internal energy is constant in an isolated system (for which $q = 0$ and $w = 0$). It 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. Equation 2A.2 employs the 'acquisitive convention', in which w and q are positive if energy is transferred to the system as work or heat and are negative if energy is lost from the system.[1] In other words, the flow of energy as work or heat is viewed from the system's perspective.

If an electric motor produces 15 kJ of energy each second as mechanical work and loses 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 is wound, 100 J of work is done on it but 15 J escapes to the surroundings as heat. The change in internal energy of the spring is $\Delta U = 100\,\text{J} - 15\,\text{J} = +85\,\text{J}$.

A note on good practice Always include the sign of ΔU (and of ΔX in general), even if it is positive.

2A.3 Expansion work

The way is opened to powerful methods of calculation by switching attention to infinitesimal changes in the variables that describe the state of the system (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 2A.2, it follows that

$$dU = dq + dw \qquad (2A.3)$$

---

[1] Many engineering texts adopt a different convention for work: $w > 0$ if energy is used to do work in the surroundings.

The ability to use this expression depends on being able to relate dq and dw to events taking place in the surroundings.

A good starting point is a discussion of **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 of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of hydrocarbons), and the thermodynamic characteristics of the reaction depend on the work that must be done to make room for the gas it has produced. 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 in *The chemist's toolkit* 6 with the sign of the opposing force written explicitly:

$$dw = -|F|dz \qquad \text{Work done [definition]} \qquad (2A.4)$$

The negative sign implies that the internal energy of the system doing the work decreases when the system moves an object against an opposing force of magnitude $|F|$, and there are no other changes. That is, if dz is positive (motion to positive z), dw is negative, and the internal energy decreases (dU in eqn 2A.3 is negative provided that $dq = 0$).

Now consider the arrangement shown in Fig. 2A.5, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A. If the external pressure is p_{ex}, the magnitude of the force acting on the outer face of the piston is $|F| = p_{ex}A$. The work done when the system expands through a distance dz against an external pressure p_{ex}, is $dw = -p_{ex}Adz$. The quantity 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_{ex} is

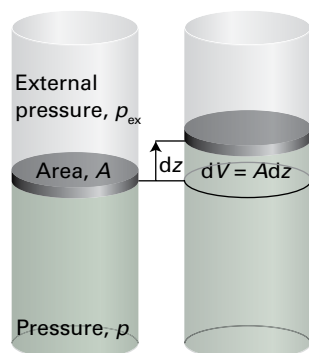$$dw = -p_{ex}dV \qquad \text{Expansion work} \qquad (2A.5a)$$

Figure 2A.5 When a piston of area A moves out through a distance dz, it sweeps out a volume $dV = Adz$. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the magnitude of the force opposing expansion is $p_{ex}A$.

Table 2A.1 Varieties of work*

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

* In general, the work done on a system can be expressed in the form $dw = -|F|dz$, where $|F|$ is the magnitude of a 'generalized force' and dz is a 'generalized displacement'.

[†] For work in joules (J). Note that 1 N m $= 1$ J and 1 V C $= 1$ J.

To obtain the total work done when the volume changes from an initial value V_i to a final value V_f it is necessary to integrate this expression between the initial and final volumes:

$$w = -\int_{V_i}^{V_f} p_{ex} \, dV \qquad (2A.5b)$$

The force acting on the piston, $p_{ex}A$, is equivalent to the force arising from 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 2A.5b 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 to an extent determined by the weight that is lowered, and it is this energy that is transferred into the system.

Other types of work (e.g. electrical work), which are called 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 (such as a change in volume). Some are collected in Table 2A.1. The present discussion focuses on how the work associated with changing the volume, the expansion work, can be extracted from eqn 2A.5b.

(b) Expansion against constant pressure

Suppose that the external pressure is constant throughout the expansion. For example, the piston might 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 in a container
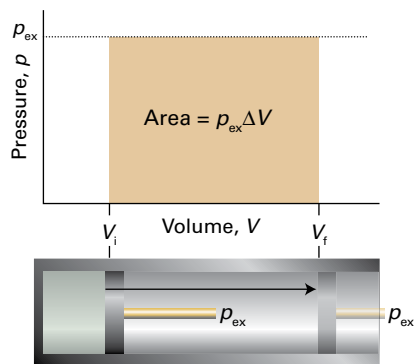
Figure 2A.6 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

that can expand. Equation 2A.5b is then evaluated by taking the constant p_{ex} outside the integral:

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

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

$$w = -p_{ex}\Delta V \qquad \boxed{\text{Expansion work [constant external pressure]}} \qquad (2A.6)$$

This result is illustrated graphically in Fig. 2A.6, which makes use of the fact that the magnitude of an integral can be interpreted as an area. The magnitude of w, denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{ex}$ lying between the initial and final volumes. A p,V-graph used to illustrate expansion work is called an **indicator diagram**; James Watt first used one to indicate aspects of the operation of his steam engine.

Free expansion is expansion against zero opposing force. It occurs when $p_{ex} = 0$. According to eqn 2A.6, in this case

$$w = 0 \qquad \boxed{\text{Work of free expansion}} \qquad (2A.7)$$

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

Example 2A.1 Calculating the work of gas production

Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $FeCl_2(aq)$ and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25 °C.

Collect your thoughts You 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 2A.6. A general feature of processes in which a condensed

phase changes into a gas is that you can usually neglect the volume of a condensed phase relative to the volume of the gas it forms.

The solution 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 $w = -p_{ex}\Delta V$. The initial volume can be neglected because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/p_{ex}$, where n is the amount of H_2 produced. Therefore,

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

Because the reaction is $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$, 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

$$w = -\frac{50\,g}{55.85\,g\,mol^{-1}} \times (8.3145\,JK^{-1}\,mol^{-1}) \times (298\,K)$$

$$\approx -2.2\,kJ$$

The system (the reaction mixture) does 2.2 kJ of work driving back the atmosphere.

Comment. The magnitude of the external pressure does not affect the final result: the lower the pressure, the larger is the volume occupied by the gas, so the effects cancel.

Self-test 2A.1 Calculate the expansion work done when 50 g of water is electrolysed under constant pressure at 25 °C.

Answer: −10 kJ

(c) 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. One example of reversibility 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. There is obviously a very close relationship between reversibility and equilibrium: systems at equilibrium are poised to undergo reversible change.

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 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, the gas expands slightly. If the external pressure is increased infinitesimally, the gas contracts slightly. In either case the change is reversible in the thermodynamic sense. If, on the other hand, the external pressure is measurably greater than the internal pressure, then decreasing 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 compression is thermodynamically irreversible.

To achieve reversible expansion p_{ex} is set 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 matches the changing upward force due to the pressure of the gas or by gradually adjusting the external pressure to match the pressure of the expanding gas. When $p_{ex} = p$, eqn 2A.5a becomes

$$\mathrm{d}w = -p_{ex}\mathrm{d}V = -p\mathrm{d}V \qquad \text{Reversible expansion work} \quad (2A.8a)$$

Although the pressure inside the system appears in this expression for the work, it does so only because p_{ex} has been arranged to be equal to p to ensure reversibility. The total work of reversible expansion from an initial volume V_i to a final volume V_f is therefore

$$w = -\int_{V_i}^{V_f} p\,\mathrm{d}V \qquad\qquad (2A.8b)$$

The integral can be evaluated once it is known how the pressure of the confined gas depends on its volume. Equation 2A.8b is the link with the material covered in Focus 1 because, if the equation of state of the gas is known, p can be expressed in terms of V and the integral can be evaluated.

(d) Isothermal reversible expansion of a perfect gas

Consider the isothermal reversible expansion of a perfect gas. The expansion is made isothermal by keeping the system in thermal contact with its unchanging surroundings (which may be a constant-temperature bath). Because the equation of state is $pV = nRT$, 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 isothermal reversible expansion of a perfect gas from V_i to V_f at a temperature T is

$$w = -nRT \overbrace{\int_{V_i}^{V_f} \frac{\mathrm{d}V}{V}}^{\text{Integral A.2}} = -nRT\ln\frac{V_f}{V_i} \quad \begin{array}{l}\text{Work of isothermal}\\\text{reversible expansion}\\\text{[perfect gas]}\end{array} \quad (2A.9)$$

When a sample of 1.00 mol Ar, regarded here as a perfect gas, undergoes an isothermal reversible expansion at 20.0 °C from $10.0\,\mathrm{dm}^3$ to $30.0\,\mathrm{dm}^3$ the work done is

$$w = -(1.00\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(293.2\,\mathrm{K})\ln\frac{30.0\,\mathrm{dm}^3}{10.0\,\mathrm{dm}^3}$$

$$= -2.68\,\mathrm{kJ}$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 2A.9 is positive and hence $w < 0$. In this case, the system has done work on the surroundings and there is a corresponding negative contribution to its internal energy. (Note the cautious language: as seen later, there is a compensating influx of energy as heat, so overall the internal energy is constant for the isothermal expansion of a perfect gas.) The equations also show that more work is done for a given change of volume when the temperature is increased: at a higher temperature the greater pressure of the confined gas needs a higher opposing pressure to ensure reversibility and the work done is correspondingly greater.

The result of the calculation can be illustrated by an indicator diagram in which the magnitude of the work done is equal to the area under the isotherm $p = nRT/V$ (Fig. 2A.7). 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 pushing power of the system is wasted. It is not possible to obtain more work than that for
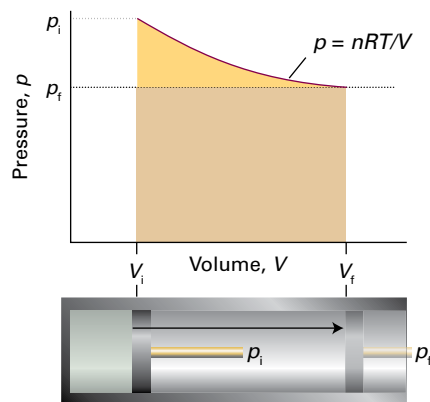

Figure 2A.7 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work done is greater than the irreversible work done.