2

The First Law

The basic concepts

Thermochemistry

State functions and exact differentials

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 have done on it or the heat that it may produce or absorb. The target concept of the chapter is enthalpy, which is a very useful bookkeeping 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 that is released unused 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 thermodynamics, 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; 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.

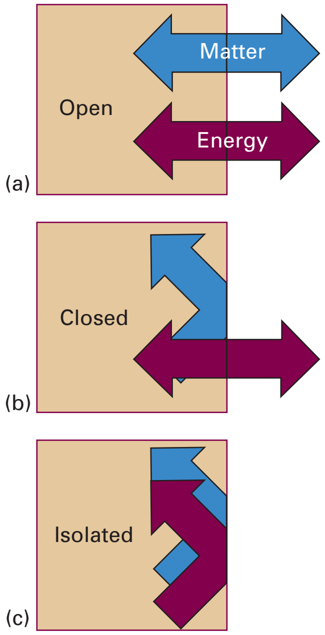


Fig. 2.1 (a) An open system can exchange matter and energy with its surroundings. (b) A closed system can exchange energy with its surroundings, but it cannot exchange matter. (c) An isolated system can exchange neither energy nor matter with its surroundings.

2.1 Work, heat, and energy

Key points **(a) Work is done to achieve motion against an opposing force; energy is the capacity to do work. (b) Heating is the transfer of energy that makes use of disorderly molecular motion; work is the transfer of energy that makes use of organized motion.**

Although thermodynamics deals with observations on bulk systems, it is immeasurably enriched by understanding the molecular origins of these observations. In each case we shall set out the bulk observations on which thermodynamics is based and then describe their molecular interpretations.

(a) Operational definitions

The fundamental physical property in thermodynamics is work: **work** is done to achieve motion against an opposing force. 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. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be passed 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. Boundaries that do permit the transfer of energy as heat are called **diathermic**; those that do not are called **adiabatic**.

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 language, 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 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. 2.2.

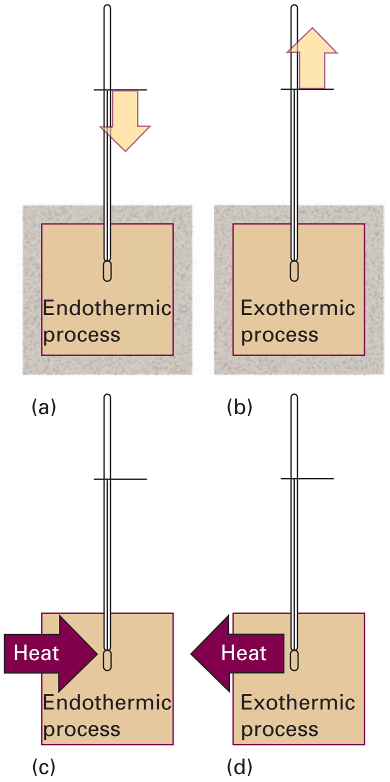


Fig. 2.2 (a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, the temperature rises. (c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature.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

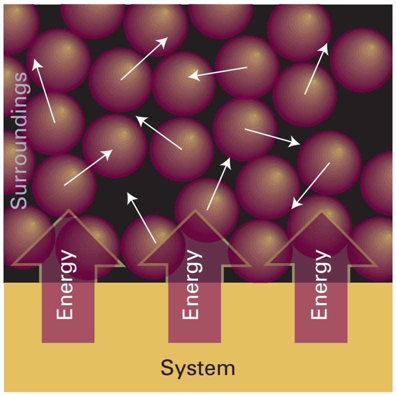


Fig. 2.3 When energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. Transfer of energy from the surroundings to the system makes use of random motion (thermal motion) in the surroundings.

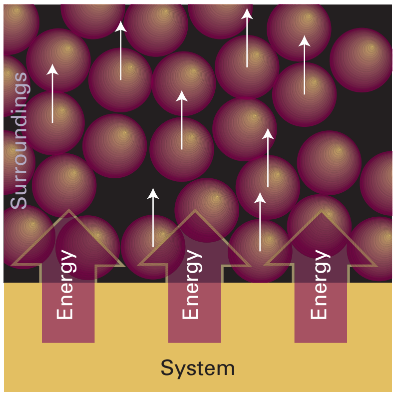


Fig. 2.4 When a system does work, it stimulates orderly motion in the surroundings. For instance, the atoms shown here may be part of a weight that is being raised. The ordered motion of the atoms in a falling weight does work on the system.

(b) The molecular interpretation of heat and work

In molecular terms, heating is the transfer of energy that makes use of disorderly 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 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 in the surroundings (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 electrons in an electric current move in an orderly 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 adiabatic compression of a gas, 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. 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

Key points **Internal energy, the total energy of a system, is a state function. (a) The equipartition theorem can be used to estimate the contribution to the internal energy of classical modes of motion. (b) The First Law states that the internal energy of an isolated system is constant.**

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. 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:

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

Throughout thermodynamics, we use the convention 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** 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, internal energy 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. That the internal energy is a state function has consequences of the greatest importance, as we shall start to unfold in Section 2.10.

The internal energy is an extensive property of a system (Section F.3) and is measured in joules ($1\ \mathrm{J} = 1\ \mathrm{kg\ m^2\ s^{-2}}$, Section F.4). 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 and commonly reported in kilojoules per mole ($\mathrm{kJ\ mol^{-1}}$).

A brief comment

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. That is, the internal energy is the energy 'internal' to the system.

(a) Molecular interpretation of internal energy

A molecule has a certain number of motional 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, leaving its centre of mass unmoved). 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 'equipartition theorem' of classical mechanics was introduced in Section F.5. According to it, the average energy of each quadratic contribution to the energy is $\frac{1}{2}kT$. As we saw in Section F.5, the mean energy of the atoms free to move in three dimensions is $\frac{3}{2}kT$ and the total energy of a monatomic perfect gas is $\frac{3}{2}NkT$, or $\frac{3}{2}nRT$ (because $N = nN_A$ and $R = N_Ak$). We can therefore write

$$U_m(T) = U_m(0) + \tfrac{3}{2}RT \quad \text{(monatomic gas; translation only)} \qquad (2.2a)$$

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, $\frac{3}{2}RT = 3.7\ \mathrm{kJ\ mol^{-1}}$, so translational motion contributes about $4\ \mathrm{kJ\ mol^{-1}}$ to the molar internal energy of a gaseous sample of atoms or molecules.

When the gas consists of 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

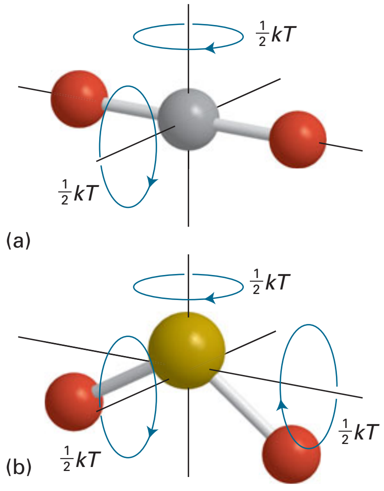


Fig. 2.5 The rotational modes of molecules and the corresponding average energies at a temperature T. (a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

$$U_m(T) = U_m(0) + \tfrac{5}{2}RT \quad \text{(linear molecule; translation and rotation only)} \qquad (2.2b)$$

A nonlinear molecule, such as CH_4 or H_2O, 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. That is,

$$U_m(T) = U_m(0) + 3RT \quad \text{(nonlinear molecule; translation and rotation only)} \qquad (2.2c)$$

The internal energy now increases twice as rapidly with temperature compared with the monatomic gas. Put another way: for a gas consisting of 1 mol of nonlinear molecules to undergo the same rise in temperature as 1 mol of monatomic gas, twice as much energy must be supplied. Molecules do not vibrate significantly at room temperature and, as a first approximation, the contribution of molecular vibrations to the internal energy is negligible except for very large molecules such as polymers and biological macromolecules.

None of the expressions we have derived depends on 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. 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.

(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 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 is expressed as follows:

The internal energy of an isolated system is constant.

First Law of thermodynamics

We cannot 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 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

$$\Delta U = q + w \qquad (2.3)$$

Mathematical statement of the First Law

Equation 2.3 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 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. In other words, we view the flow of energy as work or heat from the system's perspective.

• A brief illustration

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

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

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

2.3 Expansion work

Key points **(a) Expansion work is proportional to the external pressure. (b) Free expansion (against zero pressure) does no work. (c) The work of expansion against constant pressure is proportional to that pressure and to the change in volume. (d) To achieve reversible expansion, the external pressure is matched at every stage to the pressure of the system. (e) The work of reversible, isothermal expansion of a perfect gas is a logarithmic function of the volume.**

The way is 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 2.3 we have

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \tag{2.4}$$

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 of gases (for instance, the thermal decomposition of calcium carbonate or the combustion of octane), 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 used in physics, which states that the work required to move an object a distance dz against an opposing force of magnitude F is

$$\mathrm{d}w = -F\mathrm{d}z \qquad \text{General definition of work done} \qquad [2.5]$$

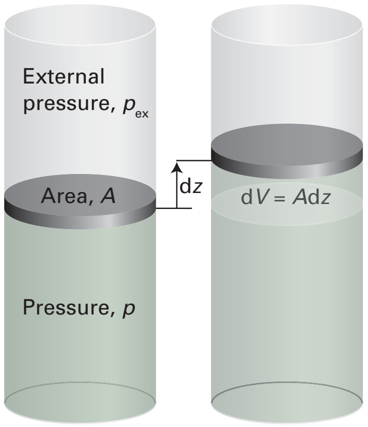


Fig. 2.6 When a piston of area A moves out through a distance dz, it sweeps out a volume $\mathrm{d}V = A\mathrm{d}z$. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{ex}A$.

The negative sign tells us that, when the system moves an object against an opposing force of magnitude F, and there are no other changes, then the internal energy of the system doing the work will decrease. That is, if dz is positive (motion to positive z), dw is negative, and the internal energy decreases (dU in eqn 2.4 is negative provided that $\mathrm{d}q = 0$).

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_{ex}, the magnitude of the force acting on the outer face of the piston is $F = p_{ex}A$. When the system expands through a distance dz against an external pressure p_{ex}, it follows that the work done is $\mathrm{d}w = -p_{ex}A\mathrm{d}z$. The quantity $A\mathrm{d}z$ 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

$$\mathrm{d}w = -p_{ex}\mathrm{d}V \qquad \boxed{\text{Expansion work}} \qquad (2.6a)$$

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

$$w = -\int_{V_i}^{V_f} p_{ex}\mathrm{d}V \qquad (2.6b)$$

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 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 eqn 2.6.

Table 2.1 Varieties of work*

Type of work	dw	Comments	Units†
Expansion	$-p_{ex}\mathrm{d}V$	p_{ex} is the external pressure dV is the change in volume	Pa m^3
Surface expansion	$\gamma\mathrm{d}\sigma$	γ is the surface tension dσ is the change in area	$\mathrm{N\,m}^{-1}$ m^2
Extension	$f\mathrm{d}l$	f is the tension dl is the change in length	N m
Electrical	$\phi\mathrm{d}Q$	ϕ 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 $\mathrm{d}w = -F\mathrm{d}z$, where F is 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.

(b) Free expansion

Free expansion is expansion against zero opposing force. It occurs when $p_{\text{ex}} = 0$. According to eqn 2.6a, $\mathrm{d}w = 0$ for each stage of the expansion. Hence, overall:

$$w = 0 \qquad \text{Work of free expansion} \qquad (2.7)$$

That is, no work is done when a system expands freely. Expansion of this kind occurs when a gas 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 in a container that can expand. We can evaluate eqn 2.6b by taking the constant p_{ex} outside the integral:

$$w = -p_{\text{ex}}\int_{V_{\text{i}}}^{V_{\text{f}}} \mathrm{d}V = -p_{\text{ex}}(V_{\text{f}} - V_{\text{i}})$$

Therefore, if we write the change in volume as $\Delta V = V_{\text{f}} - V_{\text{i}}$,

$$w = -p_{\text{ex}}\Delta V \qquad \text{Expansion work against constant external pressure} \qquad (2.8)$$

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 illustrate 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. 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. 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 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.

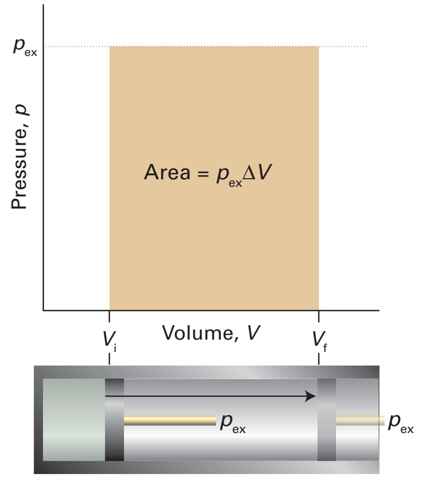
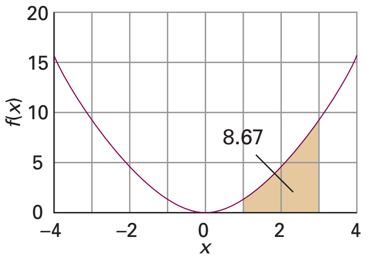


Fig. 2.7 The work done by a gas when it expands against a constant external pressure, p_{ex}, is equal to the shaded area in this example of an indicator diagram.

A brief comment

The value of the integral $\int_a^b f(x)\mathrm{d}x$ 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

$$\int_1^3 x^2\mathrm{d}x = \left(\tfrac{1}{3}x^3 + \text{constant}\right)\Big|_1^3 = \tfrac{1}{3}(3^3 - 1^3) = \tfrac{26}{3} \approx 8.67$$



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 matches the changing upward force due to the pressure of the gas. When we set $p_{\mathrm{ex}} = p$, eqn 2.6a becomes

$$\mathrm{d}w = -p_{\mathrm{ex}}\mathrm{d}V = -p\mathrm{d}V \qquad (2.9\mathrm{a})_{\mathrm{rev}}$$

Reversible expansion work

(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 does so only because p_{ex} has been set 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

$$w = -\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} p\mathrm{d}V \qquad (2.9\mathrm{b})_{\mathrm{rev}}$$

We can evaluate the integral once we know how the pressure of the confined gas depends on its volume. Equation 2.9 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

$$w = -nRT\int_{V_{\mathrm{i}}}^{V_{\mathrm{f}}} \frac{\mathrm{d}V}{V} = -nRT\ln\frac{V_{\mathrm{f}}}{V_{\mathrm{i}}} \qquad (2.10)^{\circ}_{\mathrm{rev}}$$

Reversible, isothermal expansion work of a perfect gas

A brief comment

An integral that occurs throughout thermodynamics is

$$\int \frac{1}{x}\mathrm{d}x = \ln x + \text{constant,}$$

$$\text{so} \qquad \int_a^b \frac{1}{x}\mathrm{d}x = \ln\frac{b}{a}$$

When the final volume is greater than the initial volume, as in an expansion, the logarithm in eqn 2.10 is positive and hence $w < 0$. In this case, the system has done work on the surroundings and there is a corresponding reduction in its internal energy. (Note the cautious language: 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.) 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.

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 $p > p_{\mathrm{ex}}$, 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.

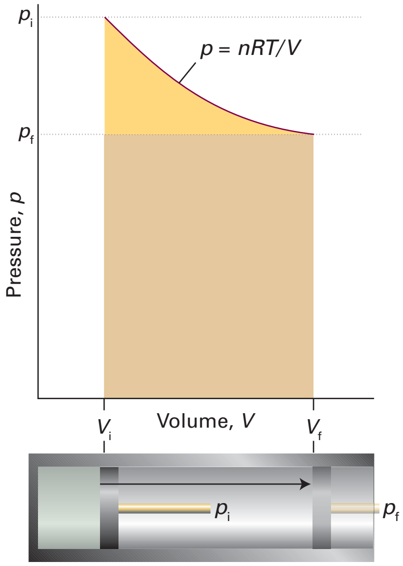


Fig. 2.8 The work done by a perfect gas when it expands reversibly and isothermally is equal to the area under the isotherm $p = nRT/V$. The work done during the irreversible expansion against the same final pressure is equal to the rectangular area shown slightly darker. Note that the reversible work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

interActivity Calculate the work of isothermal reversible expansion of 1.0 mol $CO_2(g)$ at 298 K from 1.0 m^3 to 3.0 m^3 on the basis that it obeys the van der Waals equation of state.

Example 2.1 *Calculating the work of gas production*

Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $FeC1_2(aq)$ and hydrogen in (a) a closed vessel of fixed volume, (b) an open beaker at 25°C.

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 $w = -p_{ex}\Delta V$. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/p_{ex}$, 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 $Fe(s) + 2\,HCl(aq) \rightarrow FeC1_2(aq) + H_2(g)$, 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

Key points **The energy transferred as heat at constant volume is equal to the change in internal energy of the system. (a) Calorimetry is the measurement of heat transactions. (b) The heat capacity at constant volume is the slope of the internal energy with respect to temperature.**

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

$$dU = dq + dw_{exp} + dw_e \qquad (2.11)$$

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

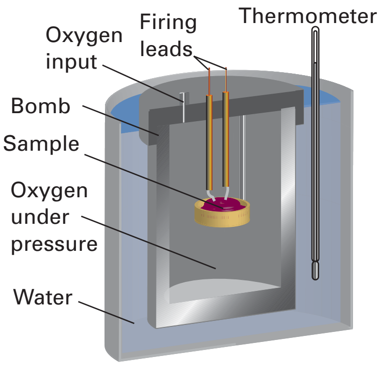


Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a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

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:

$$dU = dq \qquad \text{Heat transferred at constant volume} \tag{2.12a}$$

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

$$\Delta U = q_V \tag{2.12b}$$

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

(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 energy that the reaction releases or absorbs as heat. 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

$$q = C\Delta T \tag{2.13}$$

The calorimeter constant may be measured electrically by passing a constant current, I, from a source of known potential difference, $\Delta\phi$, through a heater for a known period of time, t, for then

$$q = It\Delta\phi \tag{2.14}$$

A brief comment

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 $\Delta\phi$ (measured in volts, V), the total energy supplied in an interval t is $It\Delta\phi$. 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.

● A brief illustration

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 2.14 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 A V s = 1 J. If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36\ \text{kJ})/(5.5\ \text{K}) = 6.5\ \text{kJ K}^{-1}$. ●

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.

(b) Heat capacity

The internal energy of a system 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 system has a constant volume. For example, it 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 as

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

Definition of heat capacity at constant volume

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).

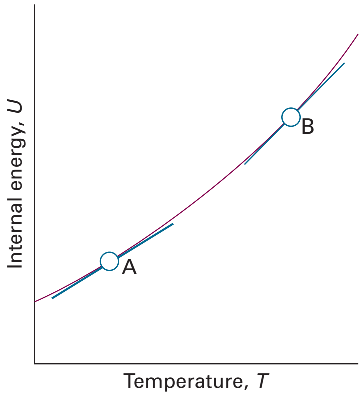


Fig. 2.10 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system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

A brief comment

Partial derivatives are reviewed in *Mathematical background* 2 following this chapter.

- **A brief illustration**

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy derived in Section 2.2a. There we saw that

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

so from eqn 2.15

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

The numerical value is 12.47 J K^{-1} mol^{-1}. ●

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 substance, and is an intensive property (all molar quantities are intensive). Typical values of $C_{V,m}$ for polyatomic gases are close to 25 J K^{-1} 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 4.2 J K^{-1} 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

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

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

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

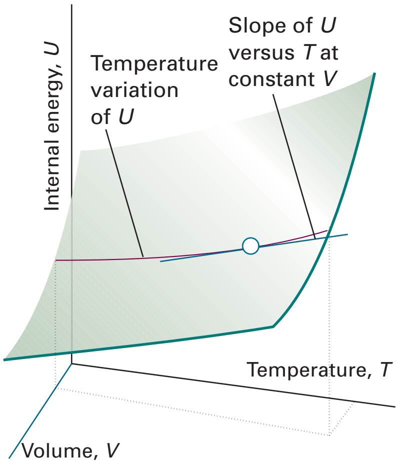


Fig. 2.11 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to T. The slope of this curve at any point is the partial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

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2.12b), the last equation can also be written

$$q_V = C_V \Delta T \tag{2.17}$$

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 4.6.

2.5 Enthalpy

Key points **(a) Energy transferred as heat at constant pressure is equal to the change in enthalpy of a system. (b) Enthalpy changes are measured in a constant-pressure calorimeter. (c) The heat capacity at constant pressure is equal to the slope of enthalpy with temperature.**

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.

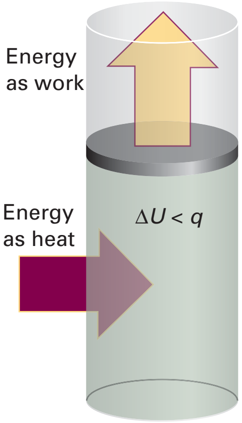


Fig. 2.12 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

(a) The definition of enthalpy

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

$$H = U + pV \quad \boxed{\text{Definition of enthalpy}} \quad [2.18]$$

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 thermochemisty. 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):

$$\mathrm{d}H = \mathrm{d}q \quad \boxed{\text{Heat transferred at constant pressure}} \tag{2.19a}$$

For a measurable change

$$\Delta H = q_p \tag{2.19b}$$

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

For a general infinitesimal change in the state of the system, U changes to $U + \mathrm{d}U$, p changes to $p + \mathrm{d}p$, and V changes to $V + \mathrm{d}V$, so from the definition in eqn 2.18, H changes from $U + pV$ to

$$\begin{aligned} H + \mathrm{d}H &= (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V) \\ &= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V \end{aligned}$$

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

$$H + \mathrm{d}H = H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

and hence that

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

If we now substitute $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$ into this expression, we get

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, we can write $\mathrm{d}w = -p\mathrm{d}V$ and obtain

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

Now we impose the condition that the heating occurs at constant pressure by writing $\mathrm{d}p = 0$. Then

$$\mathrm{d}H = \mathrm{d}q \qquad \text{(at constant pressure, no additional work)}$$

as in eqn 2.19a.

The result expressed in eqn 2.19 states that, when a system is subjected to 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 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**

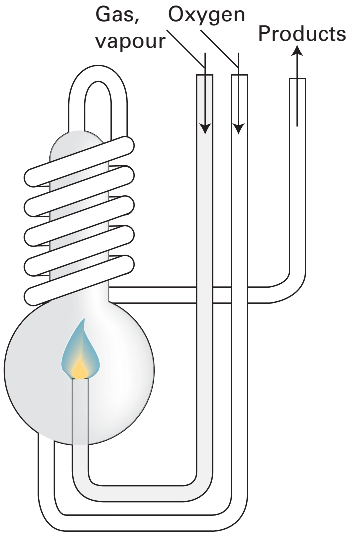


Fig. 2.13 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

(DSC). Changes in enthalpy and internal energy may also be measured by noncalorimetric methods (see Chapter 6).

Example 2.2 *Relating ΔH and ΔU*

The change in molar internal energy when $CaCO_3(s)$ as calcite converts to another form, aragonite, is +0.21 kJ mol^{-1}. Calculate the difference between the molar enthalpy and internal energy changes when the pressure is 1.0 bar given that the densities of the polymorphs 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

$$\begin{aligned}\Delta H_m &= H_m(\text{aragonite}) - H_m(\text{calcite})\\ &= \{U_m(\text{a}) + pV_m(\text{a})\} - \{U_m(\text{c}) + pV_m(\text{c})\}\\ &= \Delta U_m + p\{V_m(\text{a}) - V_m(\text{c})\}\end{aligned}$$

where a denotes aragonite and c calcite. It follows by substituting $V_m = M/\rho$ that

$$\Delta H_m - \Delta U_m = pM\left(\frac{1}{\rho(\text{a})} - \frac{1}{\rho(\text{c})}\right)$$

Substitution of the data, using $M = 100$ g mol^{-1}, gives

$$\begin{aligned}\Delta H_m - \Delta U_m &= (1.0\times10^5\ \text{Pa})\times(100\ \text{g mol}^{-1})\times\left(\frac{1}{2.93\ \text{g cm}^{-3}} - \frac{1}{2.71\ \text{g cm}^{-3}}\right)\\ &= -2.8\times10^5\ \text{Pa cm}^3\ \text{mol}^{-1} = -0.28\ \text{Pa m}^3\ \text{mol}^{-1}\end{aligned}$$

Hence (because 1 Pa m^3 = 1 J), $\Delta H_m - \Delta U_m = -0.28$ J mol^{-1}, which is only 0.1 per cent of the value of ΔU_m. We see that it is usually justifiable to ignore the difference between the molar enthalpy and internal energy of condensed phases, except at very high pressures, when $p\Delta V_m$ 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, $\Delta H = +2.1$ kJ. [$\Delta H - \Delta U = -4.4$ J]

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

$$H = U + pV = U + nRT \tag*{(2.20)°}$$

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

$$\Delta H = \Delta U + \Delta n_g RT \tag*{(2.21)°}$$

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

• A brief illustration

In the reaction $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$, 3 mol of gas-phase molecules is replaced by 2 mol of liquid-phase molecules, so $\Delta n_g = -3$ mol. Therefore, at 298 K, when $RT = 2.48$ kJ mol^{-1}, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H_m - \Delta U_m = (-3\text{ mol}) \times RT \approx -7.4\text{ kJ mol}^{-1}$$

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 $q = It\Delta\phi$), 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 A V s = 1 J. Because 0.798 g of water is (0.798 g)/(18.02 g mol^{-1}) = (0.798/18.02) mol H_2O, 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 $H_2O(l) \rightarrow H_2O(g)$ the change in the amount of gas molecules is $\Delta n_g = +1$ mol, so

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

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.

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}, 6.6×10^2 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

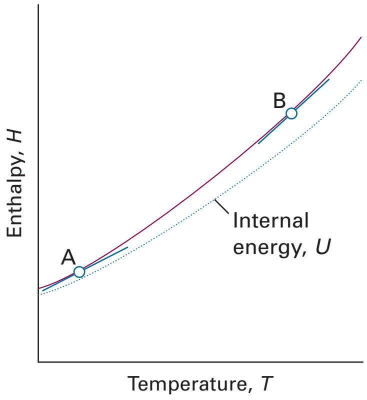


Fig. 2.14 The constant-pressure heat capacity at a particular temperature is the slope of the tangent to a curve of the enthalpy of a system plotted against temperature (at constant pressure). For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,\mathrm{m}}$ is larger than $C_{V,\mathrm{m}}$.

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:

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad \boxed{\text{Definition of heat capacity at constant pressure}} \qquad [2.22]$$

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume and is an extensive property. The **molar heat capacity at constant pressure**, $C_{p,\mathrm{m}}$, 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

$$\mathrm{d}H = C_p\mathrm{d}T \quad \text{(at constant pressure)} \qquad (2.23\text{a})$$

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

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

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

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

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

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

The empirical parameters a, b, and c are independent of temperature (Table 2.2) and are found by fitting this expression to experimental data.

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

	a	$b/(10^{-3}\,\mathrm{K})$	$c/(10^5\,\mathrm{K}^2)$
C(s, graphite)	16.86	4.77	−8.54
CO_2(g)	44.22	8.79	−8.62
H_2O(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 N_2 when it is heated from 25°C to 100°C? Use the heat capacity information in Table 2.2.

Method The heat capacity of N_2 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 relation we require is

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

and the relevant integrals are

$$\int \mathrm{d}x = x + \text{constant} \qquad \int x\,\mathrm{d}x = \tfrac{1}{2}x^2 + \text{constant} \qquad \int \frac{\mathrm{d}x}{x^2} = -\frac{1}{x} + \text{constant}$$

It follows that

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

Substitution of the numerical data results in

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

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

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)? $[\Delta H = \tfrac{1}{4}aT^4]$

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 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:

$$C_p - C_V = nR \qquad (2.26)^\circ$$

Relation between heat capacities of a perfect gas

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

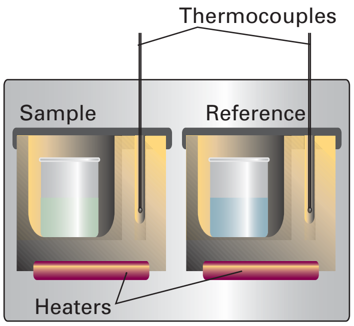


Fig. 2.15 A differential scanning calorimeter. The sample and a reference material are heated in separate but identical metal heat sinks. The output is the difference in power needed to maintain the heat sinks at equal temperatures as the temperature rises.

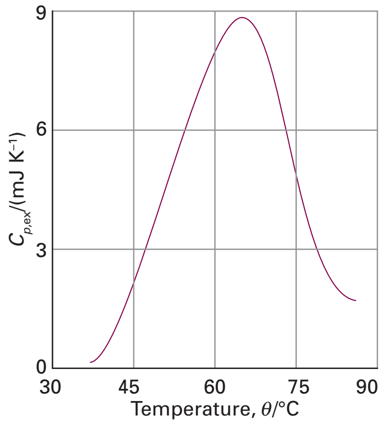


Fig. 2.16 A thermogram for the protein ubiquitin at pH = 2.45. The protein retains its native structure up to about 45°C and then undergoes an endothermic conformational change. (Adapted from B. Chowdhry and S. LeHarne, *J. Chem. Educ.* 74, 236 (1997).)

IMPACT ON BIOCHEMISTRY AND MATERIALS SCIENCE

I2.1 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 that 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. A computer controls the electrical power supply that maintains the same temperature in the sample and reference compartments throughout the analysis (Fig. 2.15).

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. Because $T = T_0 + \alpha t$, $\Delta T = \alpha t$. The chemical or physical process requires the transfer of $q_p + q_{p,\mathrm{ex}}$, where $q_{p,\mathrm{ex}}$ is the excess energy transferred as heat needed to attain the same change in temperature of the sample as the control. The quantity $q_{p,\mathrm{ex}}$ is interpreted in terms of an apparent change in the heat capacity at constant pressure of the sample, C_p, during the temperature scan:

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

where $P_{\mathrm{ex}} = q_{p,\mathrm{ex}}/t$ 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 $C_{p,\mathrm{ex}}$ against T (Fig. 2.16). From eqn 2.23a, the enthalpy change associated with the process is

$$\Delta H = \int_{T_1}^{T_2} C_{p,\mathrm{ex}}\mathrm{d}T$$

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 equal to the area under the plot of $C_{p,\mathrm{ex}}$ 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 conventional calorimeters, which require several grams of material. The technique is used in the chemical industry to characterize polymers in terms of their structural integrity, stability, and nanoscale organization. For example, it is possible to detect the ability of certain polymers such as ethylene oxide (EO) and propylene oxide (PO) to self-aggregate as their temperature is raised. These copolymers are widely used as surfactants and detergents with the amphiphilic (both water- and hydrocarbon-attracting) character provided by the hydrophobic central PO block and the more hydrophilic EO blocks attached on either side. They aggregate to form micelles (clusters) as the temperature is raised because the more hydrophobic central PO block becomes less soluble at higher temperature but the terminal EO blocks retain their strong interaction with water. This enhanced amphiphilic character of the molecules at higher temperature drives the copolymers to form micelles that are spherical in shape. The micellization process is strongly endothermic, reflecting the initial destruction of the hydrogen bonds of the PO block with water, and is readily detected by DSC. Further increases in temperature affect the shape of the micelle, changing from spherical to rod-like. A new but weaker DSC signal at higher temperature reflects a small change in enthalpy as micelles aggregate to form the rod-like structure. The marked decrease in the heat capacity accompanying the sphere-to-rod transition presumably reflects an extensive decrease in the degree of hydration of the polymer.

The technique is also used to assess the stability of proteins, nucleic acids, and membranes. For example, the thermogram shown in Fig. 2.16 indicates that the protein ubiquitin undergoes an endothermic conformational change in which a large number of non-covalent interactions (such as hydrogen bonds) are broken simultaneously and result in denaturation, the loss of the protein's three-dimensional structure. The area under the curve represents the heat absorbed in this process and can be identified with the enthalpy change. The thermogram also reveals the formation of new intermolecular interactions in the denatured form. The increase in heat capacity accompanying the native → denatured transition reflects the change from a more compact native conformation to one in which the more exposed amino acid side chains in the denatured form have more extensive interactions with the surrounding water molecules.

2.6 Adiabatic changes

Key point **For the reversible adiabatic expansion of a perfect gas, pressure and volume are related by an expression that depends on the ratio of heat capacities.**

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 $\Delta U = w_{ad}$. The subscript 'ad' denotes an adiabatic process. Therefore, by equating the two expressions we have obtained for ΔU, we obtain

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

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

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

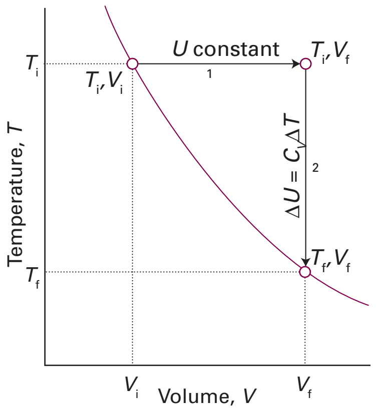


Fig. 2.17 To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect 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 $c = C_{V,\mathrm{m}}/R$. By raising each side of this expression to the power c, an equivalent expression is

$$V_{\mathrm{i}}T_{\mathrm{i}}^{c} = V_{\mathrm{f}}T_{\mathrm{f}}^{c} \qquad (2.28\mathrm{b})^{\circ}_{\mathrm{rev}}$$

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

● **A brief illustration**

Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm^3 to 1.00 dm^3. 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,

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

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

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

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 dm^3 to 2.00 dm^3, the other initial conditions being the same.

[195 K, −56 J, −56 J]

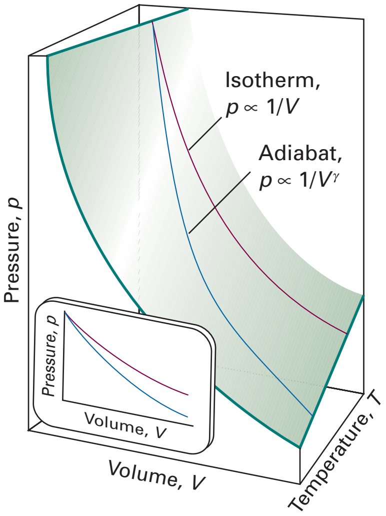


Fig. 2.18 An adiabat depicts the variation of pressure with volume when a gas expands adiabatically. Note that the pressure declines more steeply for an adiabat than it does for an isotherm because the temperature decreases in the former.

interActivity 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

$$p_{\mathrm{f}}V_{\mathrm{f}}^{\gamma} = p_{\mathrm{i}}V_{\mathrm{i}}^{\gamma} \qquad (2.29)^{\circ}_{\mathrm{rev}}$$

Reversible adiabatic expansion of a perfect gas

where $\gamma = C_{p,\mathrm{m}}/C_{V,\mathrm{m}}$. This result is commonly summarized in the form $pV^{\gamma} = \text{constant}$. For a monatomic perfect gas (Section 2.2a), and from eqn 2.26 $C_{p,\mathrm{m}} = \frac{5}{2}R$, so $\gamma = \frac{5}{3}$. For a gas of nonlinear polyatomic molecules (which can rotate as well as translate), $C_{V,\mathrm{m}} = 3R$, 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.

● **A brief illustration**

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

$$p_{\mathrm{f}} = \left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{\gamma} p_{\mathrm{i}} = \left(\frac{1}{2}\right)^{5/3} \times (100\ \mathrm{kPa}) = 31.5\ \mathrm{kPa}$$

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

We now transform the remaining partial derivative. With V regarded as a function of p and T, when these two quantities change the resulting change in V is

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p \qquad (2.56)$$

If (as in eqn 2.56) we require the volume to be constant, $\mathrm{d}V = 0$ implies that

$$\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}T = -\left(\frac{\partial V}{\partial p}\right)_T \mathrm{d}p \qquad \text{at constant volume} \qquad (2.57)$$

On division by $\mathrm{d}T$, this relation becomes

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \qquad (2.58)$$

and therefore

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa_T} \qquad (2.59)$$

Insertion of this relation into eqn 2.55 produces eqn 2.48.

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.

Exercises

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermodynamic 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 ($g = 1.60$ 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 cm^2. 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 cm^2. 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 dm^3 to 44.8 dm^3 (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 dm^3 to 31.7 dm^3 (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 $C_{V,\mathrm{m}} = \frac{3}{2}R$, initially at $p_1 = 1.00$ atm and $T_1 = 300$ 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 $C_{V,\mathrm{m}} = \frac{5}{2}R$, initially at $p_1 = 111$ kPa and $T_1 = 277$ 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 dm^3 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 dm^3. (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 dm^3 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 dm^3. (b) Calculate the work that would be done if the same expansion occurred reversibly.

2.6(a) A sample of 1.00 mol $H_2O(g)$ 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 $CH_3OH(g)$ 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 placed in 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 placed in 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 $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.3665(T/\mathrm{K})$. 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 $C_p/(\mathrm{J\,K^{-1}}) = 20.17 + 0.4001(T/\mathrm{K})$. 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 $\mathrm{dm^3}$ at 273.15 K to 3.0 $\mathrm{dm^3}$.

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 $\mathrm{cm^3}$ at 298.15 K to 2.00 $\mathrm{dm^3}$.

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 $\mathrm{cm^3}$ to 3.00 $\mathrm{dm^3}$. 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 $\mathrm{cm^3}$ to 2.00 $\mathrm{dm^3}$. 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 $\mathrm{dm^3}$ to a final volume of 2.0 $\mathrm{dm^3}$. 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 $\mathrm{cm^3}$ to a final volume of 3.0 $\mathrm{dm^3}$. Take $\gamma = 1.3$.

2.12(a) When 229 J of energy is supplied as heat to 3.0 mol Ar(g) at constant pressure, 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 at constant pressure, 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 O_2 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 O_2(g) at constant pressure is 29.4 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate q, ΔH, and ΔU.

2.13(b) When 2.0 mol CO_2 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 CO_2(g) at constant pressure is 37.11 $\mathrm{J\,K^{-1}\,mol^{-1}}$, calculate q, ΔH, and ΔU.

2.14(a) A sample of 4.0 mol O_2(g) is originally confined in 20 $\mathrm{dm^3}$ 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 CO_2(g) is originally confined in 15 $\mathrm{dm^3}$ 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 $C_V = 20.8\ \mathrm{J\,K^{-1}}$ 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 $C_{p,\mathrm{m}} = 20.8\ \mathrm{J\,K^{-1}\,mol^{-1}}$ 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 $\Delta_{\mathrm{vap}}H^{\ominus} = 26.0\ \mathrm{kJ\,mol^{-1}}$. 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 $\Delta_{\mathrm{vap}}H^{\ominus} = 32.0\ \mathrm{kJ\,mol^{-1}}$. Calculate q, w, ΔH, and ΔU when 0.75 mol is vaporized at 260 K and 765 Torr.

2.17(a) Calculate the lattice enthalpy of SrI_2 from the following data:

	$\Delta H/(\mathrm{kJ\,mol^{-1}})$
Sublimation of Sr(s)	+164
Ionization of Sr(g) to Sr^{2+}(g)	+1626
Sublimation of I_2(s)	+62
Dissociation of I_2(g)	+151
Electron attachment to I(g)	−304
Formation of SrI_2(s) from Sr(s) and I_2(s)	−558

2.17(b) Calculate the lattice enthalpy of $MgBr_2$ from the following data:

	$\Delta H/(\mathrm{kJ\,mol^{-1}})$
Sublimation of Mg(s)	+148
Ionization of Mg(g) to Mg^{2+}(g)	+2187
Vaporization of Br_2(l)	+31
Dissociation of Br_2(g)	+193
Electron attachment to Br(g)	−331
Formation of $MgBr_2$(s) from Mg(s) and Br_2(l)	−524

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

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

2.19(a) The standard enthalpy of combustion of cyclopropane is −2091 $\mathrm{kJ\,mol^{-1}}$ at 25°C. From this information and enthalpy of formation data for CO_2(g) and H_2O(g), calculate the enthalpy of formation of cyclopropane. The enthalpy of formation of propene is +20.42 $\mathrm{kJ\,mol^{-1}}$. Calculate the enthalpy of isomerization of cyclopropane to propene.

2.19(b) From the following data, determine $\Delta_f H^{\ominus}$ for diborane, B_2H_6(g), at 298 K:

(1) $B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g)$ $\quad \Delta_r H^{\ominus} = -2036\ \mathrm{kJ\,mol^{-1}}$

(2) $2\,B(s) + \frac{3}{2}\,O_2(g) \rightarrow B_2O_3(s)$ $\quad \Delta_r H^{\ominus} = -1274\ \mathrm{kJ\,mol^{-1}}$

(3) $H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow H_2O(g)$ $\quad \Delta_r H^{\ominus} = -241.8\ \mathrm{kJ\,mol^{-1}}$

2.20(a) When 120 mg of naphthalene, $C_{10}H_8$(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, C_6H_5OH(s), is burned in the calorimeter under the same conditions?

2.20(b) When 2.25 mg of anthracene, $C_{14}H_{10}$(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, C_6H_5OH(s), is burned in the calorimeter under the same conditions? ($\Delta_c H^{\ominus}(C_{14}H_{10},s) = -7061\ \mathrm{kJ\,mol^{-1}}$.)

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

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

2.22(a) The standard enthalpy of decomposition of the yellow complex H_3NSO_2 into NH_3 and SO_2 is +40 $\mathrm{kJ\,mol^{-1}}$. Calculate the standard enthalpy of formation of H_3NSO_2.

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

2.23(a) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ for reaction (3), (b) $\Delta_f H^\ominus$ for both HCl(g) and H_2O(g) all at 298 K.

(1) $H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$ $\quad \Delta_r H^\ominus = -184.62$ kJ mol^{-1}
(2) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ $\quad \Delta_r H^\ominus = -483.64$ kJ mol^{-1}
(3) $4\,HCl(g) + O_2(g) \rightarrow 2\,Cl_2(g) + 2\,H_2O(g)$

2.23(b) Given the reactions (1) and (2) below, determine (a) $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ for reaction (3), (b) $\Delta_f H^\ominus$ for both HI(g) and H_2O(g) all at 298 K.

(1) $H_2(g) + I_2(s) \rightarrow 2\,HI(g)$ $\quad \Delta_r H^\ominus = +52.96$ kJ mol^{-1}
(2) $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$ $\quad \Delta_r H^\ominus = -483.64$ kJ mol^{-1}
(3) $4\,HI(g) + O_2(g) \rightarrow 2\,I_2(s) + 2\,H_2O(g)$

2.24(a) For the reaction $C_2H_5OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 3\,H_2O(g)$, $\Delta_r U^\ominus = -1373$ kJ mol^{-1} at 298 K, calculate $\Delta_r H^\ominus$.

2.24(b) For the reaction $2\,C_6H_5COOH(s) + 13\,O_2(g) \rightarrow 12\,CO_2(g) + 6\,H_2O(g)$, $\Delta_r U^\ominus = -772.7$ kJ mol^{-1} at 298 K, calculate $\Delta_r H^\ominus$.

2.25(a) Calculate the standard enthalpies of formation of (a) $KClO_3$(s) from the enthalpy of formation of KCl, (b) $NaHCO_3$(s) from the enthalpies of formation of CO_2 and NaOH together with the following information:

$2\,KClO_3(s) \rightarrow 2\,KCl(s) + 3\,O_2(g)$ $\quad \Delta_r H^\ominus = -89.4$ kJ mol^{-1}
$NaOH(s) + CO_2(g) \rightarrow NaHCO_3(s)$ $\quad \Delta_r H^\ominus = -127.5$ kJ mol^{-1}

2.25(b) Calculate the standard enthalpy of formation of NOCl(g) from the enthalpy of formation of NO given in Table 2.8, together with the following information:

$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$ $\quad \Delta_r H^\ominus = +75.5$ kJ mol^{-1}

2.26(a) Use the information in Table 2.8 to predict the standard reaction enthalpy of $2\,NO_2(g) \rightarrow N_2O_4(g)$ at 100°C from its value at 25°C.

2.26(b) Use the information in Table 2.8 to predict the standard reaction enthalpy of $2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$ at 100°C from its value at 25°C.

2.27(a) From the data in Table 2.8, calculate $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ at (a) 298 K, (b) 378 K for the reaction $C(\text{graphite}) + H_2O(g) \rightarrow CO(g) + H_2(g)$. Assume all heat capacities to be constant over the temperature range of interest.

2.27(b) Calculate $\Delta_r H^\ominus$ and $\Delta_r U^\ominus$ at 298 K and $\Delta_r H^\ominus$ at 348 K for the hydrogenation of ethyne (acetylene) to ethene (ethylene) from the enthalpy of combustion and heat capacity data in Tables 2.6 and 2.8. Assume the heat capacities to be constant over the temperature range involved.

2.28(a) Calculate $\Delta_r H^\ominus$ for the reaction $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$ from the information in Table 2.8 in the *Data section*.

2.28(b) Calculate $\Delta_r H^\ominus$ for the reaction $NaCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + NaNO_3(aq)$ from the information in Table 2.8 in the *Data section*.

2.29(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 Cl_2(g), $+241.6$ kJ mol^{-1}; electron gain enthalpy of Cl(g), -3.78 eV; enthalpy of solution of $MgCl_2$(s), -150.5 kJ mol^{-1}; enthalpy of hydration of Cl^-(g), -383.7 kJ mol^{-1}.

2.29(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 Br_2(g), $+192.9$ kJ mol^{-1}; electron gain enthalpy of Br(g), -331.0 kJ mol^{-1}; enthalpy of solution of $CaBr_2$(s), -103.1 kJ mol^{-1}; enthalpy of hydration of Br^-(g), -97.5 kJ mol^{-1}.

2.30(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.

2.30(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.

2.31(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 dm^3 to 24.8 dm^3 at 298 K. What are the values of q and w?

2.31(b) Repeat Exercise 2.31(a) for argon, from an initial volume of 1.00 dm^3 to 22.1 dm^3 at 298 K.

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

$$V = V'\{0.75 + 3.9\times10^{-4}(T/\text{K}) + 1.48\times10^{-6}(T/\text{K})^2\}$$

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

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

$$V = V'\{0.77 + 3.7\times10^{-4}(T/\text{K}) + 1.52\times10^{-6}(T/\text{K})^2\}$$

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

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

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

2.34(a) Given that $\mu = 0.25$ 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.

2.34(b) Given that $\mu = 1.11$ 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.

Chapter 2

E2.1(a)	On Earth: 2.6×10^{3} J needed, on the moon: 4.2×10^{2} J needed
E2.2(a)	-1.0×10^{2} J
E2.3(a)	(a) $w=-1.57$ kJ, $q=+1.57$ kJ (b) $w=-1.13$ kJ, $q=+1.13$ kJ (c) 0
E2.4(a)	$p_2=1.33$ atm, $w=0$, $q=\Delta U=+1.25$ kJ
E2.5(a)	(a) -88 J (b) -167 J
E2.6(a)	$\Delta H=q=-40.656$ kJ, $w=3.10$ kJ, $\Delta U=-37.55$ kJ
E2.7(a)	$w=-1.5$ kJ
E2.8(a)	(a) $q=\Delta H=+2.83\times10^{4}$ J $=+28.3$ kJ, $w=-1.45$ kJ, $\Delta U=+26.8$ kJ (b) $\Delta H=+28.3$ kJ, $\Delta U=+26.8$ kJ, $w=0$, $q=+26.8$ kJ
E2.9(a)	$13\bar{1}$ K
E2.10(a)	$w=-194$ J
E2.11(a)	22 kPa
E2.12(a)	$C_{p,\mathrm{m}}=30\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $C_{V,\mathrm{m}}=22\ \mathrm{J\,K^{-1}\,mol^{-1}}$
E2.13(a)	$q_p=+2.2$ kJ, $\Delta H=+2.2$ kJ, $\Delta U=+1.6$ kJ
E2.14(a)	$w=-3.2$ kJ, $\Delta U=-3.2$ kJ, $\Delta T=-38$ K, $\Delta H=-4.5$ kJ
E2.15(a)	$V_\mathrm{f}=0.00944\ \mathrm{m^3}$, $T_\mathrm{f}=288$ K, $w=-4.6\times10^{2}$ J
E2.16(a)	$q=+13.0$ kJ, $w=-1.0$ kJ, $\Delta U=12.0$ kJ

E2.17(a) $\Delta_L H^\ominus(\mathrm{SrI_2,s}) = 1953\ \mathrm{kJ\ mol^{-1}}$

E2.18(a) $-4564.7\ \mathrm{kJ\ mol^{-1}}$

E2.19(a) $\Delta_f H[(\mathrm{CH_2})_3,\mathrm{g}] = +53\ \mathrm{kJ\ mol^{-1}}$, $\Delta_r H = -33\ \mathrm{kJ\ mol^{-1}}$

E2.20(a) $\Delta_c U^\ominus = -5152\ \mathrm{kJ\ mol^{-1}}$, $C = 1.58\ \mathrm{kJ\ K^{-1}}$, $\Delta T = 205\ \mathrm{K}$

E2.21(a) $+65.49\ \mathrm{kJ\ mol^{-1}}$

E2.22(a) $-383\ \mathrm{kJ\ mol^{-1}}$

E2.23(a) (a) $\Delta_r H^\ominus(3) = -114.40\ \mathrm{kJ\ mol^{-1}}$, $\Delta_r U = -111.92\ \mathrm{kJ\ mol^{-1}}$
(b) $\Delta_f H^\ominus(\mathrm{HCl,g}) = -92.31\ \mathrm{kJ\ mol^{-1}}$,
$\Delta_f H^\ominus(\mathrm{H_2O,g}) = -241.82\ \mathrm{kJ\ mol^{-1}}$

E2.24(a) $-1368\ \mathrm{kJ\ mol^{-1}}$

E2.25(a) (a) $-392.1\ \mathrm{kJ\ mol^{-1}}$ (b) $-946.6\ \mathrm{kJ\ mol^{-1}}$

E2.26(a) $-56.98\ \mathrm{kJ\ mol^{-1}}$

E2.27(a) (a) $\Delta_r H^\ominus(298\ \mathrm{K}) = +131.29\ \mathrm{kJ\ mol^{-1}}$,
$\Delta_r U^\ominus(298\ \mathrm{K}) = +128.81\ \mathrm{kJ\ mol^{-1}}$
(b) $\Delta_r H^\ominus(378\ \mathrm{K}) = +132.56\ \mathrm{kJ\ mol^{-1}}$,
$\Delta_r U^\ominus(378\ \mathrm{K}) = +129.42\ \mathrm{kJ\ mol^{-1}}$

E2.28(a) $-218.66\ \mathrm{kJ\ mol^{-1}}$

E2.29(a) $-1892\ \mathrm{kJ\ mol^{-1}}$

E2.30(a) $0.71\ \mathrm{K\ atm^{-1}}$

E2.31(a) $\Delta U = 131\ \mathrm{J\ mol^{-1}}$, $q = +8.05\times 10^3\ \mathrm{J\ mol^{-1}}$, $w = -7.92\times 10^3\ \mathrm{J\ mol^{-1}}$

E2.32(a) $1.31\times 10^{-3}\ \mathrm{K^{-1}}$

E2.33(a) $1.\bar{1}\times 10^3\ \mathrm{atm}$

E2.34(a) $\left(\dfrac{\partial H_\mathrm{m}}{\partial p}\right)_T = -7.2\ \mathrm{J\ atm^{-1}\ mol^{-1}}$, $q(\text{supplied}) = +8.1\ \mathrm{kJ}$