

the reversible process because increasing the external pressure even infinitesimally at any stage results in compression. It can be inferred from this discussion that, because some pushing power is wasted when $p > p_{\text{ex}}$, the maximum work available from a system operating between specified initial and final states is obtained when the change takes place reversibly.

2A.4 Heat transactions

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

$$dU = dq + dw_{\text{exp}} + dw_{\text{add}} \quad (2A.10)$$

where dw_{add} is work in addition ('add' for additional) to the expansion work, dw_{exp} . For instance, dw_{add} might be the electrical work of driving a current of electrons through a circuit. A system kept at constant volume can do no expansion work, so in that case $dw_{\text{exp}} = 0$. 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 $dw_{\text{add}} = 0$ too. Under these circumstances:

$$dU = dq \quad \text{Heat transferred at constant volume} \quad (2A.11a)$$

This relation can also be expressed as $dU = dq_v$, where the subscript implies the constraint of constant volume. For a measurable change between states *i* and *f* along a path at constant volume,

$$\int_i^f dU = \int_i^f dq_v$$

which is summarized as

$$\Delta U = q_v \quad (2A.11b)$$

Note that the integral over dq is not written as Δq because q , unlike U , is not a state function. It follows from eqn 2A.11b that measuring the energy supplied as heat to a system at constant volume is equivalent to measuring the change in internal energy of the system.

(a) Calorimetry

Calorimetry is the study of the transfer of energy as heat during a physical or chemical process. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring q_v (and therefore ΔU) is an **adiabatic bomb calorimeter** (Fig. 2A.8). The process to be studied—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

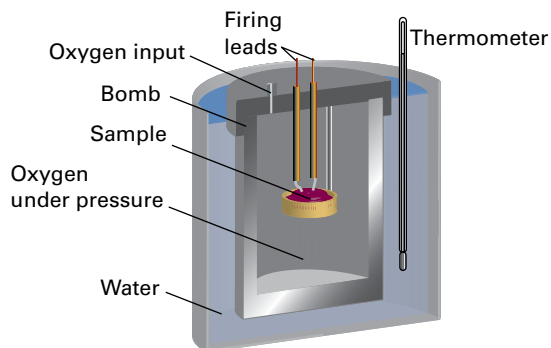


Figure 2A.8 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

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, q_v and hence ΔU can be determined by measuring ΔT . The conversion of ΔT to q_v is best achieved by calibrating the calorimeter using a process of known output and determining the **calorimeter constant**, the constant C in the relation

$$q = C\Delta T \quad (2A.12)$$

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 (*The chemist's toolkit* 8)

$$q = It\Delta\phi \quad (2A.13)$$

Brief illustration 2A.4

If a current of 10.0 A from a 12 V supply is passed for 300 s, then from eqn 2A.13 the energy supplied as heat is

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

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

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 energy as heat.

The chemist's toolkit 8 Electrical charge, current, power, and energy

Electrical charge, Q , is measured in *coulombs*, C. The fundamental charge, e , the magnitude of charge carried by a single electron or proton, is approximately 1.6×10^{-19} 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 the electric charge is that of electrons (as it is for the current in a metal), then a current of 1 A represents the flow of 6×10^{18} electrons ($10 \mu\text{mol e}^-$) per second.

When a current I flows through a potential difference $\Delta\phi$ (measured in volts, V, with $1 \text{ V} = 1 \text{ J A}^{-1}$), the power, P , is

$$P = I\Delta\phi$$

It follows that if a constant current flows for a period t the energy supplied is

$$E = Pt = It\Delta\phi$$

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. That energy may be supplied as either work (to drive a motor) or as heat (through a 'heater'). In the latter case

$$q = It\Delta\phi$$

(b) Heat capacity

The internal energy of a system increases when its temperature is raised. This increase depends on the conditions under which the heating takes place. Suppose the system has a constant volume. If the internal energy is plotted against temperature, then a curve like that in Fig. 2A.9 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

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{Heat capacity at constant volume [definition]} \quad (2A.14)$$

(Partial derivatives and the notation used here are reviewed in *The chemist's toolkit 9*.) The internal energy varies with the temperature and the volume of the sample, but here only its variation with the temperature is important, because the volume is held constant (Fig. 2A.10), as signified by the subscript V .

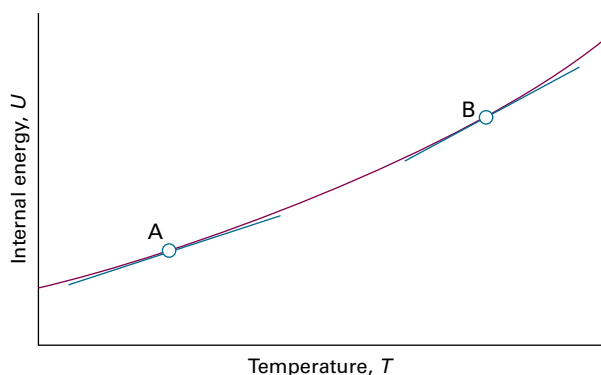


Figure 2A.9 The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature. Note that, for the system illustrated, the heat capacity is greater at B than at A.

Brief illustration 2A.5

In *Brief illustration 2A.1* it is shown that the translational contribution to the molar internal energy of a perfect monatomic gas is $\frac{3}{2}RT$. Because this is the only contribution to the internal energy, $U_m(T) = \frac{3}{2}RT$. It follows from eqn 2A.14 that

$$C_{V,m} = \frac{\partial}{\partial T} \left\{ \frac{3}{2}RT \right\} = \frac{3}{2}R$$

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

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). For certain applications it is useful to know the

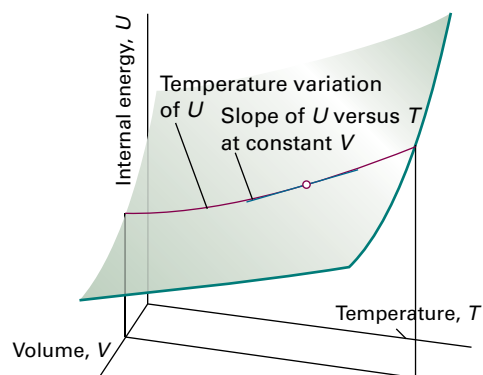


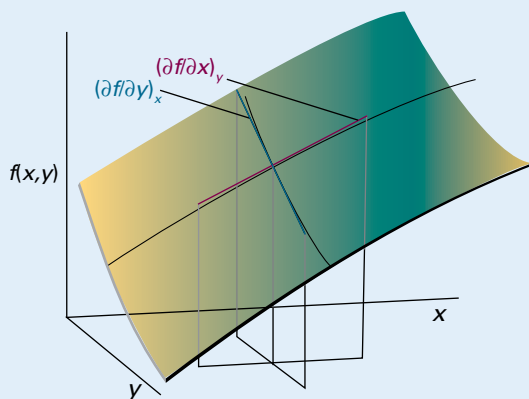
Figure 2A.10 The internal energy of a system varies with volume and temperature, perhaps as shown here by the surface. The variation of the internal energy with temperature at one particular constant volume is illustrated by the curve drawn parallel to the temperature axis. The slope of this curve at any point is the partial derivative $(\partial U/\partial T)_V$.

The chemist's toolkit 9 Partial derivatives

A **partial derivative** of a function of more than one variable, such as $f(x,y)$, is the slope of the function with respect to one of the variables, all the other variables being held constant (Sketch 1). Although a partial derivative shows how a function changes when one variable changes, it may be used to determine how the function changes when more than one variable changes by an infinitesimal amount. Thus, if f is a function of x and y , then when x and y change by dx and dy , respectively, f changes by

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

where the symbol ∂ ('curly d') is used (instead of d) to denote a partial derivative and the subscript on the parentheses indicates which variable is being held constant.



Sketch 1

The quantity df is also called the **differential** of f . Successive partial derivatives may be taken in any order:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$$

specific heat capacity (more informally, the 'specific heat') of a substance, which is the heat capacity of the sample divided by its mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to $4.2 \text{ J K}^{-1} \text{ g}^{-1}$. In general, heat capacities depend on the temperature and decrease at low temperatures. However, over small ranges of temperature at and above room temperature, the variation is quite small and for approximate calculations heat capacities can be treated as almost independent of temperature.

The heat capacity is used to relate a change in internal energy to a change in temperature of a constant-volume system. It follows from eqn 2A.14 that

For example, suppose that $f(x,y) = ax^3y + by^2$ (the function plotted in Sketch 1) then

$$\left(\frac{\partial f}{\partial x}\right)_y = 3ax^2y \quad \left(\frac{\partial f}{\partial y}\right)_x = ax^3 + 2by$$

Then, when x and y undergo infinitesimal changes, f changes by

$$df = 3ax^2y dx + (ax^3 + 2by) dy$$

To verify that the order of taking the second partial derivative is irrelevant, form

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial(3ax^2y)}{\partial y}\right)_x = 3ax^2$$

$$\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \left(\frac{\partial(ax^3 + 2by)}{\partial x}\right)_y = 3ax^2$$

Now suppose that z is a variable on which x and y depend (for example, x , y , and z might correspond to p , V , and T). The following relations then apply:

Relation 1. When x is changed at constant z :

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Relation 2

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

Relation 3

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

Combining Relations 2 and 3 results in the **Euler chain relation**:

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

Euler chain relation

$$dU = C_V dT$$

Internal energy change on heating [constant volume] (2A.15a)

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, then

$$\Delta U = \int_{T_1}^{T_2} C_V dT = C_V \int_{T_1}^{T_2} dT = C_V \overbrace{(T_2 - T_1)}^{\Delta T}$$

A measurable change of temperature, ΔT , brings about a measurable change in internal energy, ΔU , with

$$\Delta U = C_V \Delta T \quad \text{Internal energy change on heating [constant volume]} \quad (2A.15b)$$

Because a change in internal energy can be identified with the heat supplied at constant volume (eqn 2A.11b), the last equation can also be written as

$$q_V = C_V \Delta T \quad (2A.16)$$

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 (by electrical heating, for example) under constant volume conditions 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).

Brief illustration 2A.6

Suppose a 55 W electric heater immersed in a gas in a constant-volume adiabatic container was on for 120 s and it was found that the temperature of the gas rose by 5.0°C (an increase equivalent to 5.0 K). The heat supplied is (55 W) \times (120 s) = 6.6 kJ (with 1 J = 1 W s), so the heat capacity of the sample is

$$C_V = \frac{6.6 \text{ kJ}}{5.0 \text{ K}} = 1.3 \text{ kJ K}^{-1}$$

Checklist of concepts

- 1. **Work** is the process of achieving motion against an opposing force.
- 2. **Energy** is the capacity to do work.
- 3. An **exothermic process** is a process that releases energy as heat.
- 4. An **endothermic process** is a process in which energy is acquired as heat.
- 5. **Heat** is the process of transferring energy as a result of a temperature difference.
- 6. In molecular terms, work is the transfer of energy that makes use of organized motion of atoms in the surroundings and heat is the transfer of energy that makes use of their disorderly motion.
- 7. **Internal energy**, the total energy of a system, is a state function.
- 8. The internal energy increases as the temperature is raised.
- 9. The **equipartition theorem** can be used to estimate the contribution to the internal energy of each classically behaving mode of motion.
- 10. The **First Law** states that the internal energy of an isolated system is constant.
- 11. Free expansion (expansion against zero pressure) does no work.
- 12. A **reversible change** is a change that can be reversed by an infinitesimal change in a variable.
- 13. To achieve **reversible expansion**, the external pressure is matched at every stage to the pressure of the system.
- 14. The energy transferred as heat at constant volume is equal to the change in internal energy of the system.
- 15. **Calorimetry** is the measurement of heat transactions.

Checklist of equations

Property	Equation	Comment	Equation number
First Law of thermodynamics	$\Delta U = q + w$	Convention	2A.2
Work of expansion	$dw = -p_{\text{ex}} dV$		2A.5a
Work of expansion against a constant external pressure	$w = -p_{\text{ex}} \Delta V$	$p_{\text{ex}} = 0$ for free expansion	2A.6
Reversible work of expansion of a gas	$w = -nRT \ln(V_f/V_i)$	Isothermal, perfect gas	2A.9
Internal energy change	$\Delta U = q_V$	Constant volume, no other forms of work	2A.11b
Electrical heating	$q = It\Delta\phi$		2A.13
Heat capacity at constant volume	$C_V = (\partial U/\partial T)_V$	Definition	2A.14

TOPIC 2B Enthalpy

► Why do you need to know this material?

The concept of enthalpy is central to many thermodynamic discussions about processes, such as physical transformations and chemical reactions taking place under conditions of constant pressure.

► What is the key idea?

A change in enthalpy is equal to the energy transferred as heat at constant pressure.

► What do you need to know already?

This Topic makes use of the discussion of internal energy (Topic 2A) and draws on some aspects of perfect gases (Topic 1A).

The change in internal energy is not equal to the energy transferred as heat when the system is free to change its volume, such as when it is able to expand or contract under conditions of constant pressure. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work (Fig. 2B.1), so dU is less than dq . 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’.

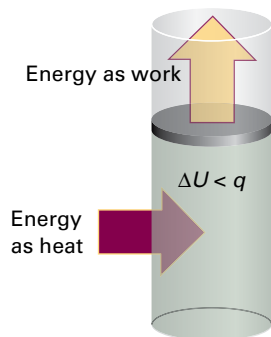


Figure 2B.1 When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

2B.1 The definition of enthalpy

The enthalpy, H , is defined as

$$H = U + pV \quad \text{Enthalpy [definition]} \quad (2B.1)$$

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.

(a) Enthalpy change and heat transfer

An important consequence of the definition of enthalpy in eqn 2B.1 is that it can be shown that the change in enthalpy is equal to the energy supplied as heat under conditions of constant pressure.

How is that done? 2B.1 Deriving the relation between enthalpy change and heat transfer at constant pressure

In a typical thermodynamic derivation, as here, a common way to proceed is to introduce successive definitions of the quantities of interest and then apply the appropriate constraints.

Step 1 Write an expression for $H + dH$ in terms of the definition of H

For a general infinitesimal change in the state of the system, U changes to $U + dU$, p changes to $p + dp$, and V changes to $V + dV$, so from the definition in eqn 2B.1, H changes by dH to

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

The last term is the product of two infinitesimally small quantities and can be neglected. Now recognize that $U + pV = H$ on the right (in blue), so

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

and hence

$$dH = dU + pdV + Vdp$$

Step 2 Introduce the definition of dU

Because $dU = dq + dw$ this expression becomes

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

Step 3 Apply the appropriate constraints

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, then $dw = -pdV$, which cancels the other pdV term, leaving

$$dH = dq + Vdp$$

At constant pressure, $dp = 0$, so

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

The constraint of constant pressure is denoted by a p , so this equation can be written

$$dH = dq_p \quad \text{Heat transferred at constant pressure [infinitesimal change]} \quad (2B.2a)$$

This equation states that, provided there is no additional (non-expansion) work done, *the change in enthalpy is equal to the energy supplied as heat at constant pressure.*

Step 4 Evaluate ΔH by integration

For a measurable change between states i and f along a path at constant pressure, the preceding expression is integrated as follows

$$\int_i^f dH = \int_i^f dq_p$$

Note that the integral over dq is not written as Δq because q , unlike H , is not a state function and $q_f - q_i$ is meaningless. The final result is

$$\Delta H = q_p \quad \text{Heat transferred at constant pressure [measurable change]} \quad (2B.2b)$$

Brief illustration 2B.1

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 the water, it is found that 0.798 g of water is vaporized. The enthalpy change is

$$\begin{aligned} \Delta H = q_p &= It\Delta\phi = (0.50 \text{ A}) \times (300 \text{ s}) \times (12 \text{ V}) \\ &= 0.50 \times 300 \text{ J} \times 12 \end{aligned}$$

where $1 \text{ A V s} = 1 \text{ J}$. Because 0.798 g of water is $(0.798 \text{ g}) / (18.02 \text{ g mol}^{-1}) = (0.798/18.02) \text{ mol H}_2\text{O}$, the enthalpy of vaporization per mole of H_2O is

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

(b) Calorimetry

An enthalpy change can be measured calorimetrically by monitoring the temperature change that accompanies a physical or chemical change at constant pressure. A calorimeter for

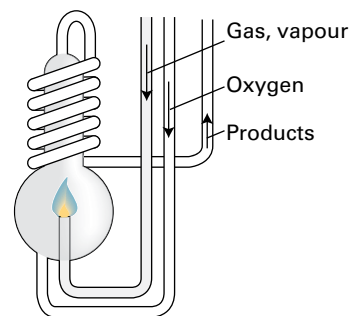


Figure 2B.2 A constant-pressure flame calorimeter consists of this component immersed in a stirred water bath. Combustion occurs as a known amount of reactant is passed through to fuel the flame, and the rise of temperature is monitored.

studying processes at constant pressure is called an **isobaric calorimeter**. A simple example is a thermally insulated vessel open to the atmosphere: the energy released as heat 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. 2B.2). The most sophisticated way to measure enthalpy changes, however, is to use a *differential scanning calorimeter* (DSC), as explained in Topic 2C. Changes in enthalpy and internal energy may also be measured by non-calorimetric methods (Topic 6C).

One route to ΔH is to measure the internal energy change by using a bomb calorimeter (Topic 2A), 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.

Example 2B.1 Relating ΔH and ΔU

The change in molar internal energy when $\text{CaCO}_3(\text{s})$ as calcite converts to its polymorph aragonite, is $+0.21 \text{ kJ mol}^{-1}$. Calculate the difference between the molar enthalpy and internal energy changes when the pressure is 1.0 bar. The mass densities of the polymorphs are 2.71 g cm^{-3} (calcite) and 2.93 g cm^{-3} (aragonite).

Collect your thoughts The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2B.1). You need to express the difference between the two quantities in terms of the pressure and the difference of their molar volumes. The latter can be calculated

from their molar masses, M , and their mass densities, ρ , by using $\rho = M/V_m$.

The solution 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 $M = 100.09 \text{ g mol}^{-1}$, gives

$$\begin{aligned}\Delta H_m - \Delta U_m &= (1.0 \times 10^5 \text{ Pa}) \times (100.09 \text{ g mol}^{-1}) \\ &\times \left(\frac{1}{2.93 \text{ g cm}^{-3}} - \frac{1}{2.71 \text{ g cm}^{-3}} \right) \\ &= -2.8 \times 10^5 \text{ Pa cm}^3 \text{ mol}^{-1} = -0.28 \text{ Pa m}^3 \text{ mol}^{-1}\end{aligned}$$

Hence (because $1 \text{ Pa m}^3 = 1 \text{ J}$), $\Delta H_m - \Delta U_m = -0.28 \text{ J mol}^{-1}$, which is only 0.1 per cent of the value of ΔU_m .

Comment. 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 2B.1 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.

Answer: $\Delta H - \Delta U = -4.4 \text{ J}$

In contrast to processes involving condensed phases, the values of the changes in internal energy and enthalpy might differ significantly for processes involving gases. The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H :

$$H = U + pV = U + nRT \quad (2B.3)$$

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

$$\Delta H = \Delta U + \Delta n_g RT \quad \text{Relation between } \Delta H \text{ and } \Delta U \text{ [isothermal process, perfect gas]} \quad (2B.4)$$

where Δn_g is the change in the amount of gas molecules in the reaction. For molar quantities, replace Δn_g by Δv_g .

Brief illustration 2B.2

In the reaction $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$, 3 mol of gas-phase molecules are replaced by 2 mol of liquid-phase molecules,

so $\Delta n_g = -3 \text{ mol}$ and $\Delta v_g = -3$. Therefore, at 298 K, when $RT = 2.5 \text{ kJ mol}^{-1}$, the enthalpy and internal energy changes taking place in the system are related by

$$\Delta H_m - \Delta U_m = (-3) \times RT \approx -7.5 \text{ kJ mol}^{-1}$$

Note that the difference is expressed in kilojoules, not joules as in Example 2B.1. The enthalpy change is smaller than the change in internal energy because, although energy escapes from the system as heat when the reaction occurs, the system contracts as the liquid is formed, so energy is restored to it as work from the surroundings.

2B.2 The variation of enthalpy with temperature

The enthalpy of a substance increases as its temperature is raised. The reason is the same as for the internal energy: molecules are excited to states of higher energy so their total energy increases. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (e.g. whether the pressure or the volume is constant).

(a) Heat capacity at constant pressure

The most frequently encountered condition in chemistry is constant pressure. The slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure** (or *isobaric heat capacity*), C_p , at a given temperature (Fig. 2B.3). More formally:

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad \text{Heat capacity at constant pressure [definition]} \quad (2B.5)$$

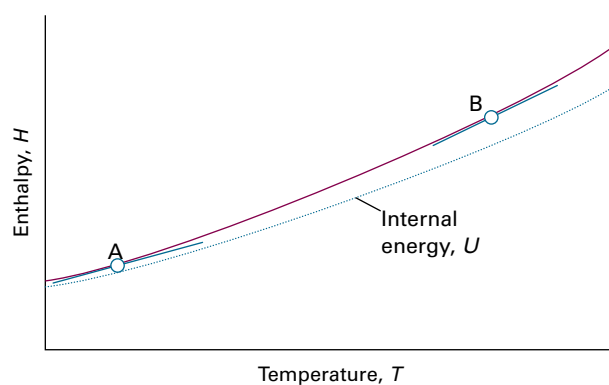


Figure 2B.3 The constant-pressure heat capacity at a particular temperature is the slope of the tangent to a curve of the enthalpy of a system plotted against temperature (at constant pressure). For gases, at a given temperature the slope of enthalpy versus temperature is steeper than that of internal energy versus temperature, and $C_{p,m}$ is larger than $C_{v,m}$.

The heat capacity at constant pressure is the analogue of the heat capacity at constant volume (Topic 2A) and is an extensive property. The **molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of substance; it is an intensive property.

The heat capacity at constant pressure relates the change in enthalpy to a change in temperature. For infinitesimal changes of temperature, eqn 2B.5 implies that

$$dH = C_p dT \text{ (at constant pressure)} \quad (2B.6a)$$

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

$$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p \int_{T_1}^{T_2} dT = C_p \overbrace{(T_2 - T_1)}^{\Delta T}$$

which can be summarized as

$$\Delta H = C_p \Delta T \text{ (at constant pressure)} \quad (2B.6b)$$

Because a change in enthalpy can be equated to the energy supplied as heat at constant pressure, the practical form of this equation is

$$q_p = C_p \Delta T \quad (2B.7)$$

This expression shows how to measure the constant-pressure 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 is an excellent approximation 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 for other substances, a convenient approximate empirical expression is

$$C_{p,m} = a + bT + \frac{c}{T^2} \quad (2B.8)$$

The empirical parameters a , b , and c are independent of temperature (Table 2B.1) and are found by fitting this expression to experimental data.

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

	a	$b/(\text{10}^{-3} \text{ K}^{-1})$	$c/(\text{10}^5 \text{ K}^2)$
C(s, graphite)	16.86	4.77	-8.54
CO ₂ (g)	44.22	8.79	-8.62
H ₂ O(l)	75.29	0	0
N ₂ (g)	28.58	3.77	-0.50

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

Example 2B.2 Evaluating an increase in enthalpy with temperature

What is the change in molar enthalpy of N₂ when it is heated from 25 °C to 100 °C? Use the heat capacity information in Table 2B.1.

Collect your thoughts The heat capacity of N₂ changes with temperature significantly in this range, so you cannot use eqn 2B.6b (which assumes that the heat capacity of the substance is constant). Therefore, use eqn 2B.6a, substitute eqn 2B.8 for the temperature dependence of the heat capacity, and integrate the resulting expression from 25 °C (298 K) to 100 °C (373 K).

The solution For convenience, denote the two temperatures T_1 (298 K) and T_2 (373 K). The required relation is

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

By using Integral A.1 in the *Resource section* for each term, it follows that

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

Substitution of the numerical data results in

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

Comment. If a constant heat capacity of 29.14 J K⁻¹ mol⁻¹ (the value given by eqn 2B.8 for $T = 298 \text{ K}$) had been assumed, then the difference between the two enthalpies would have been calculated as 2.19 kJ mol⁻¹, only slightly different from the more accurate value.

Self-test 2B.2 At very low temperatures the heat capacity of a solid is proportional to T^3 , and $C_{p,m} = aT^3$. 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)?

$$\int_0^T aT^3 dT = \frac{a}{4} T^4$$

(b) The relation between heat capacities

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 work. 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 in most cases the heat capacity at constant pressure of a system is larger than its heat capacity at constant volume. As shown in Topic 2D, there is a simple relation between the two heat capacities of a perfect gas:

$$C_p - C_v = nR \quad \text{Relation between heat capacities [perfect gas]} \quad (2B.9)$$

It follows that the molar heat capacity of a perfect gas is about $8 \text{ J K}^{-1} \text{ mol}^{-1}$ larger at constant pressure than at constant volume. Because the molar constant-volume heat capacity of a monatomic gas is about $\frac{3}{2}R = 12 \text{ J K}^{-1} \text{ mol}^{-1}$ (Topic 2A),

the difference is highly significant and must be taken into account. The two heat capacities are typically very similar for condensed phases, and for them the difference can normally be ignored.

Checklist of concepts

- 1. Energy transferred as heat at constant pressure is equal to the change in **enthalpy** of a system.
- 2. Enthalpy changes can be measured in a constant-pressure calorimeter.
- 3. The **heat capacity at constant pressure** is equal to the slope of enthalpy with temperature.

Checklist of equations

Property	Equation	Comment	Equation number
Enthalpy	$H = U + pV$	Definition	2B.1
Heat transfer at constant pressure	$dH = dq_p$ $\Delta H = q_p$	No additional work	2B.2
Relation between ΔH and ΔU at a temperature T	$\Delta H = \Delta U + \Delta n_g RT$	Molar volumes of the participating condensed phases are negligible	2B.4
Heat capacity at constant pressure	$C_p = (\partial H / \partial T)_p$	Definition	2B.5
Relation between heat capacities	$C_p - C_v = nR$	Perfect gas	2B.9