Thermochemistry

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

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

$$\text{exothermic process: } \Delta H < 0 \qquad \text{endothermic process: } \Delta H > 0$$

2.7 Standard enthalpy changes

Key points **(a) The standard enthalpy of transition is equal to the energy transferred as heat at constant pressure in the transition. (b) A thermochemical equation is a chemical equation and its associated change in enthalpy. (c) Hess's law states that the standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided.**

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. In most of our discussions we shall consider the **standard enthalpy change**, $\Delta H^{\ominus}$, the change in enthalpy for a process in which the initial and final substances are in their standard states:

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

Specification of standard state

A brief comment
The definition of standard state is more sophisticated for a real gas (*Further information 3.2*) and for solutions (Sections 5.10 and 5.11).

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

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

$$\mathrm{H_2O(l)} \rightarrow \mathrm{H_2O(g)} \qquad \Delta_{\text{vap}}H^{\ominus}(373\ \text{K}) = +40.66\ \text{kJ mol}^{-1}$$

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

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

(a) Enthalpies of physical change

The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{\text{trs}}H^{\ominus}$ (Table 2.3). The **standard**

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

	T_f/K	Fusion	T_b/K	Vaporization
Ar	83.81	1.188	87.29	6.506
C_6H_6	278.61	10.59	353.2	30.8
H_2O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

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

Table 2.4 Enthalpies of transition

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

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

enthalpy of vaporization, $\Delta_{vap}H^{\ominus}$, is one example. Another is the **standard enthalpy of fusion**, $\Delta_{fus}H^{\ominus}$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta_{fus}H^{\ominus}(273\ \mathrm{K}) = +6.01\ \mathrm{kJ\ mol^{-1}}$$

As in this case, it is sometimes convenient to know the standard enthalpy change at the transition temperature as well as at the conventional temperature of 298 K. The different types of enthalpies encountered in thermochemistry are summarized in Table 2.4. We shall meet them again in various locations throughout the text.

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

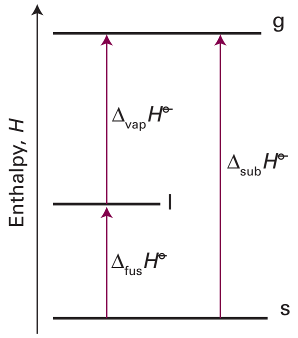
$$H_2O(s) \rightarrow H_2O(g) \qquad \Delta_{sub}H^{\ominus}$$

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

$$\begin{array}{rll} & H_2O(s) \rightarrow H_2O(l) & \Delta_{fus}H^{\ominus} \\ & H_2O(l) \rightarrow H_2O(g) & \Delta_{vap}H^{\ominus} \\ \text{Overall: } & H_2O(s) \rightarrow H_2O(g) & \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus} \end{array}$$

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

$$\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus} \tag{2.30}$$

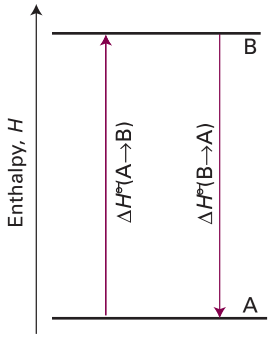


1

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

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

$$\Delta H^{\ominus}(A \rightarrow B) = -\Delta H^{\ominus}(B \rightarrow A) \tag{2.31}$$



2

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

The vaporization of a solid often involves a large increase in energy, especially when the solid is ionic and the strong Coulombic interaction of the ions must be overcome in a process such as

$$MX(s) \rightarrow M^+(g) + X^-(g)$$

The **lattice enthalpy**, ΔH_L, is the change in standard molar enthalpy for this process. The lattice enthalpy is equal to the lattice internal energy at $T = 0$; at normal temperatures they differ by only a few kilojoules per mole, and the difference is normally neglected.

Experimental values of the lattice enthalpy are obtained by using a **Born–Haber cycle**, a closed path of transformations starting and ending at the same point, one step of which is the formation of the solid compound from a gas of widely separated ions.

● A brief illustration

A typical Born–Haber cycle, for potassium chloride, is shown in Fig. 2.19. It consists of the following steps (for convenience, starting at the elements):

	$\Delta H^{\ominus}$/(kJ mol^{-1})	
1. Sublimation of K(s)	$+89$	[dissociation enthalpy of K(s)]
2. Dissociation of $\frac{1}{2}$ $Cl_2(g)$	$+122$	[$\frac{1}{2}\times$ dissociation enthalpy of $Cl_2(g)$]
3. Ionization of K(g)	$+418$	[ionization enthalpy of K(g)]
4. Electron attachment to Cl(g)	-349	[electron gain enthalpy of Cl(g)]
5. Formation of solid from gas	$-\Delta H_L$/(kJ mol^{-1})	
6. Decomposition of compound	$+437$	[negative of enthalpy of formation of KCl(s)]

Because the sum of these enthalpy changes is equal to zero, we can infer from

$$89 + 122 + 418 - 349 - \Delta H_L/(\text{kJ mol}^{-1}) + 437 = 0$$

that $\Delta H_L = +717$ kJ mol^{-1}. ●

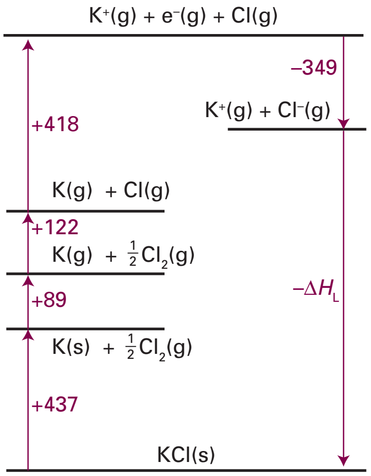


Fig. 2.19 The Born–Haber cycle for KCl at 298 K. Enthalpies changes are in kilojoules per mole.

Some lattice enthalpies obtained in the same way as in the *brief illustration* are listed in Table 2.5. They are large when the ions are highly charged and small, for then they are close together and attract each other strongly. We examine the quantitative relation between lattice enthalpy and structure in Section 19.6.

Table 2.5* Lattice enthalpies at 298 K

	$\Delta H_L/(\text{kJ mol}^{-1})$
NaF	787
NaBr	751
MgO	3850
MgS	3406

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

(b) Enthalpies of chemical change

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

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H^{\ominus} = -890\ \text{kJ}$$

$\Delta H^{\ominus}$ is the change in enthalpy when reactants in their standard states change to products in their standard states:

Pure, separate reactants in their standard states
→ pure, separate products in their standard states

Except in the case of ionic reactions in solution, the enthalpy changes accompanying mixing and separation are insignificant in comparison with the contribution from the reaction itself. For the combustion of methane, the standard value refers to the reaction in which 1 mol CH_4 in the form of pure methane gas at 1 bar reacts completely with 2 mol O_2 in the form of pure oxygen gas at 1 bar to produce 1 mol CO_2 as pure carbon dioxide gas at 1 bar and 2 mol H_2O as pure liquid water at 1 bar; the numerical value is for the reaction at 298.15 K.

Alternatively, we write the chemical equation and then report the **standard reaction enthalpy**, $\Delta_r H^{\ominus}$ (or 'standard enthalpy of reaction'). Thus, for the combustion of methane, we write

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta_r H^{\ominus} = -890\ \text{kJ mol}^{-1}$$

For a reaction of the form $2\,A + B \rightarrow 3\,C + D$ the standard reaction enthalpy would be

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

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

$$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu H_m^{\ominus} - \sum_{\text{Reactants}} \nu H_m^{\ominus} \qquad [2.32]$$

Definition of standard reaction enthalpy

where in each case the molar enthalpies of the species are multiplied by their (dimensionless and positive) stoichiometric coefficients, ν.

Some standard reaction enthalpies have special names and a particular significance. For instance, the **standard enthalpy of combustion**, $\Delta_c H^{\ominus}$, is the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 gas and liquid H_2O if the compound contains C, H, and O, and to N_2 gas if N is also present. An example is the combustion of glucose:

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l) \qquad \Delta_c H^{\ominus} = -2808\ \text{kJ mol}^{-1}$$

The value quoted shows that 2808 kJ of heat is released when 1 mol $C_6H_{12}O_6$ burns under standard conditions (at 298 K). More values are given in Table 2.6.

(c) Hess's law

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

Table 2.6* Standard enthalpies of formation and combustion of organic compounds at 298 K

	$\Delta_f H^\ominus/(\text{kJ mol}^{-1})$	$\Delta_c H^\ominus/(\text{kJ mol}^{-1})$
Benzene, $C_6H_6(l)$	+49.0	−3268
Ethane, $C_2H_6(g)$	−84.7	−1560
Glucose, $C_6H_{12}O_6(s)$	−1274	−2808
Methane, $CH_4(g)$	−74.8	−890
Methanol, $CH_3OH(l)$	−238.7	−726

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

Hess's law

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

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

Example 2.5 *Using Hess's law*

The standard reaction enthalpy for the hydrogenation of propene

$$CH_2{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_3(g)$$

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

$$CH_3CH_2CH_3(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

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

Method The skill to develop is the ability to assemble a given thermochemical equation from others. Add or subtract the reactions given, together with any others needed, so as to reproduce the reaction required. Then add or subtract the reaction enthalpies in the same way. Additional data are in Table 2.6.

Answer The combustion reaction we require is

$$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$$

This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus/(\text{kJ mol}^{-1})$
$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$	−124
$C_3H_8(g) + 5\,O_2(g) \rightarrow 3\,CO_2(g) + 4\,H_2O(l)$	−2220
$H_2O(l) \rightarrow H_2(g) + \tfrac{1}{2}\,O_2(g)$	+286
$C_3H_6(g) + \tfrac{9}{2}\,O_2(g) \rightarrow 3\,CO_2(g) + 3\,H_2O(l)$	−2058

Self-test 2.6 Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane. [−205 kJ mol^{-1}]

Table 2.7 Thermochemical properties of some fuels

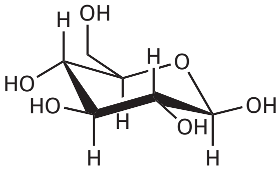
Fuel	Combustion equation	$\Delta_c H^\ominus$/(kJ mol^{-1})	Specific enthalpy/(kJ g^{-1})	Enthalpy density/(kJ dm^{-3})
Hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	−286	142	13
Methane	$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$	−890	55	40
Octane	$C_8H_{18}(l) + \frac{25}{2}O_2(g)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

IMPACT ON BIOLOGY

I2.2 Food and energy reserves

The thermochemical properties of fuels and foods are commonly discussed in terms of their *specific enthalpy*, the enthalpy of combustion per gram of material. Thus, if the standard enthalpy of combustion is $\Delta_c H^\ominus$ and the molar mass of the compound is M, then the specific enthalpy is $\Delta_c H^\ominus/M$. Table 2.7 lists the specific enthalpies of several fuels.

A typical 18–20 year old man requires a daily input of about 12 MJ; a woman of the same age needs about 9 MJ. If the entire consumption were in the form of glucose (**3**; which has a specific enthalpy of 16 kJ g^{-1}), that would require the consumption of 750 g of glucose for a man and 560 g for a woman. In fact, digestible carbohydrates have a slightly higher specific enthalpy (17 kJ g^{-1}) than glucose itself, so a carbohydrate diet is slightly less daunting than a pure glucose diet, as well as being more appropriate in the form of fibre, the indigestible cellulose that helps move digestion products through the intestine.



3 α-D-Glucose (α-D-Glucopyranose)

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

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

The heat released by the oxidation of foods needs to be discarded in order to maintain body temperature within its typical range of 35.6–37.8°C. A variety of mechanisms contribute to this aspect of homeostasis, the ability of an organism to counteract environmental changes with physiological responses. The general uniformity of temperature throughout the body is maintained largely by the flow of blood. When heat needs to be dissipated rapidly, warm blood is allowed to flow through the capillaries of the skin, so producing flushing. Radiation is one means of discarding heat; another is evaporation and the energy demands of the enthalpy of vaporization of water. Evaporation removes about 2.4 kJ per gram of water perspired. When vigorous exercise promotes sweating (through the influence of heat selectors on the hypothalamus), 1–2 dm^3 of perspired water can be produced per hour, corresponding to a heat loss of 2.4–5.0 MJ h^{-1}.

2.8 Standard enthalpies of formation

Key points **Standard enthalpies of formation are defined in terms of the reference states of elements. (a) The standard reaction enthalpy is expressed as the difference of the standard enthalpies of formation of products and reactants. (b) Computer modelling is used to estimate standard enthalpies of formation.**

The **standard enthalpy of formation**, $\Delta_f H^\ominus$, of a substance is the standard reaction enthalpy for the formation of the compound from its elements in their reference states:

> The **reference state** of an element is its most stable state at the specified temperature and 1 bar.

Specification of reference state

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

$$6\,C(s,\text{ graphite}) + H_2(g) \rightarrow C_6H_6(l)$$

and is +49.0 kJ mol^{-1}. The standard enthalpies of formation of elements in their reference states are zero at all temperatures because they are the enthalpies of such 'null' reactions as $N_2(g) \rightarrow N_2(g)$. Some enthalpies of formation are listed in Tables 2.6 and 2.8.

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

$$\Delta_f H^\ominus(H^+, aq) = 0 \qquad [2.33]$$

Convention for ions in solution

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

Table 2.8* Standard enthalpies of formation of inorganic compounds at 298 K

	$\Delta_f H^\ominus$/(kJ mol^{-1})
$H_2O(l)$	−285.83
$H_2O(g)$	−241.82
$NH_3(g)$	−46.11
$N_2H_4(l)$	+50.63
$NO_2(g)$	+33.18
$N_2O_4(g)$	+9.16
NaCl(s)	−411.15
KCl(s)	−436.75

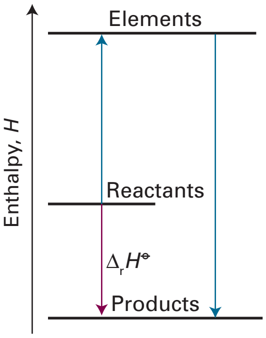
* More values are given in the *Data section*.

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

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

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu \Delta_f H^\ominus - \sum_{\text{Reactants}} \nu \Delta_f H^\ominus \qquad (2.34a)$$

Procedure for calculating standard reaction enthalpy



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A brief comment

Stoichiometric *numbers*, which have a sign, are denoted ν_J or $\nu(J)$. Stoichiometric *coefficients*, which are all positive, are denoted simply ν (with no subscript).

where in each case the enthalpies of formation of the species that occur are multiplied by their stoichiometric coefficients. A more sophisticated way of expressing the same result is to introduce the **stoichiometric numbers** ν_J (as distinct from the stoichiometric coefficients) which are positive for products and negative for reactants. Then we can write

$$\Delta_r H^\ominus = \sum_J \nu_J \Delta_f H^\ominus(J) \tag{2.34b}$$

● A brief illustration

According to eqn 2.34a, the standard enthalpy of the reaction $2\,HN_3(l) + 2\,NO(g) \rightarrow H_2O_2(l) + 4\,N_2(g)$ is calculated as follows:

$$\begin{aligned}\Delta_r H^\ominus &= \{\Delta_f H^\ominus(H_2O_2,l) + 4\Delta_f H^\ominus(N_2,g)\} - \{2\Delta_f H^\ominus(HN_3,l) + 2\Delta_f H^\ominus(NO,g)\}\\ &= \{-187.78 + 4(0)\}\ \text{kJ mol}^{-1} - \{2(264.0) + 2(90.25)\}\ \text{kJ mol}^{-1}\\ &= -896.3\ \text{kJ mol}^{-1}\end{aligned}$$

To use eqn 2.34b we identify $\nu(HN_3) = -2$, $\nu(NO) = -2$, $\nu(H_2O_2) = +1$, and $\nu(N_2) = +4$, and then write

$$\Delta_r H^\ominus = -2\Delta_f H^\ominus(HN_3,l) - 2\Delta_f H^\ominus(NO,g) + \Delta_f H^\ominus(H_2O_2,l) + 4\Delta_f H^\ominus(N_2,g)$$

which gives the same result. ●

(b) Enthalpies of formation and molecular modelling

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

$$\text{A–B(g)} \rightarrow \text{A(g)} + \text{B(g)} \qquad \Delta H(\text{A–B})$$

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

Computer-aided molecular modelling has largely displaced this more primitive approach. Commercial software packages use the principles developed in Chapter 10 to calculate the standard enthalpy of formation of a molecule drawn on the computer screen. These techniques can be applied to different conformations of the same molecule. In the case of methylcyclohexane, for instance, the calculated conformational energy difference ranges from 5.9 to 7.9 kJ mol^{-1}, with the equatorial conformer having the lower standard enthalpy of formation. These estimates compare favourably with the experimental value of 7.5 kJ mol^{-1}. However, good agreement between calculated and experimental values is relatively rare. Computational methods almost always predict correctly which conformer is more stable but do not always predict the correct magnitude of the conformational energy difference. The most reliable technique for the determination of enthalpies of formation remains calorimetry, typically by using enthalpies of combustion.

2.9 The temperature dependence of reaction enthalpies

Key point The temperature dependence of a reaction enthalpy is expressed by Kirchhoff's law.

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature (Fig. 2.20). In many cases heat capacity data are more accurate than reaction enthalpies. Therefore, providing the information is available, the procedure we are about to describe is more accurate than the direct measurement of a reaction enthalpy at an elevated temperature.

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

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \mathrm{d}T \qquad (2.35)$$

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

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus \mathrm{d}T \qquad (2.36a)$$

Kirchhoff's law

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

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,\mathrm{m}}^\ominus - \sum_{\text{Reactants}} \nu C_{p,\mathrm{m}}^\ominus \qquad (2.36b)$$

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

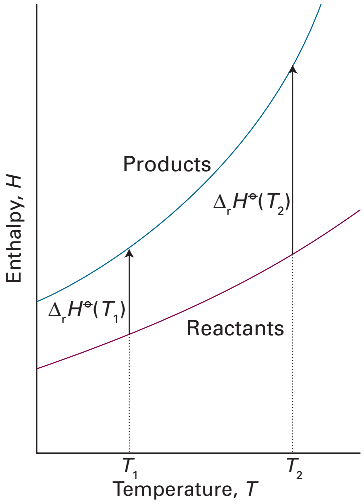

Fig. 2.20 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

Example 2.6 *Using Kirchhoff's law*

The standard enthalpy of formation of $H_2O(g)$ at 298 K is -241.82 kJ mol^{-1}. Estimate its value at 100°C given the following values of the molar heat capacities at constant pressure: $H_2O(g)$: 33.58 J K^{-1} mol^{-1}; $H_2(g)$: 28.82 J K^{-1} mol^{-1}; $O_2(g)$: 29.36 J K^{-1} mol^{-1}. Assume that the heat capacities are independent of temperature.

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

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

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

Answer The reaction is $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$, so

$$\Delta_r C_p^\ominus = C_{p,\mathrm{m}}^\ominus(H_2O,g) - \{C_{p,\mathrm{m}}^\ominus(H_2,g) + \tfrac{1}{2}C_{p,\mathrm{m}}^\ominus(O_2,g)\} = -9.92\ \mathrm{J\,K^{-1}\,mol^{-1}}$$