

## 1 Energy changes in inorganic reactions

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### 1.1 Introduction

Knowledge of inorganic substances and their reactions has been greatly systematised by the recognition and classification of the sorts of forces which hold atoms together. Based on the nuclear model of the atom, and involving simple ideas of electron sharing and transfer, the largely qualitative ‘electronic theory of valency’ expounded by G. N. Lewis, N. V. Sidgwick and others during the 1920s provided a new and more fundamental basis for the empirical framework of periodicity so strikingly demonstrated by Mendeleev and Lothar Meyer fifty years before. Such was the success of the early electronic theory, however, that for a long time inorganic chemists were content to interpret the monovalence of sodium simply as a consequence of ‘the stability of the valence octet’, and to shrug off the rather bewildering chemistry of the transition elements as an unfortunate complication associated with their incomplete electron shells. Over the same period, chemists expert in thermodynamics had developed what seemed to be their own esoteric science – a formidable discipline in which quantities like  $\Delta U$ ,  $\Delta H$  and  $\Delta G$  appeared, often enough in a context of heat engines, perfect gases adiabatically expanding, and systems of weightless and frictionless pistons. The inorganic chemists, for their part, appeared to recognise the existence of reactions variously exothermic and endothermic, and of some reactions which did not ‘proceed to completion’, but otherwise they pursued an essentially independent approach to chemistry.

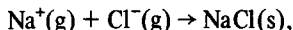
Today, one of the features of modern inorganic chemistry is the willingness of its exponents to be quantitative. While it would be foolhardy to assert that there has been a happy and fruitful reconciliation of the points of view of the thermodynamicists and the inorganic chemists, the latter have certainly come to realise that the reactivity of the elements and compounds within their domain of interest can no longer be expressed in purely descriptive terms. Thus an attempt is made to afford statements like ‘gold is an unreactive element’, ‘mercury compounds are easily reduced’, ‘the bonds in the iodine molecule are readily broken’, or ‘potassium chloride is a stable salt’ the

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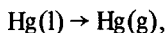
## 1. Energy changes in inorganic reactions

2

precision of a thermodynamic context. Inevitably such an attempt leads to a consideration of the *energy changes* which accompany not only laboratory-bench reactions, but also those which are not easily accessible experimentally, like



and those which, like



are sometimes differentiated as 'physical' changes.

The term 'energy' is one which is widely and sometimes vaguely used. It is therefore important to be quite certain of the significance of the various thermodynamic quantities, notably  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ , which are commonly encountered in quantitative descriptions of energy changes. The main purpose of this chapter is to introduce, discuss, and illustrate these quantities.

1.2 The change in internal energy  $\Delta U$ 

## 1.2.1 Absolute energy and energy changes

The total energy of a substance, called its *internal energy* and symbolised  $U$ , is the sum of all the different sorts of energy which a substance can be said to possess. Some of the components of the total energy can be precisely defined, while others still await recognition and definition. For most of the purposes of chemistry – as distinct, say, from the purposes of nuclear physics – only those parts of the total energy which are susceptible to change in the course of chemical reactions are of interest. For example, the *nuclei* of atoms pass unchanged through purely chemical processes, so that any energy associated with the nucleus alone, or with the particles which compose it, remains constant in quantity. Processes in which the nuclei are affected – such as radioactive emissions – are of course of interest to nuclear chemists and radiochemists, but will not be discussed here. The only chemically significant components of the energy are therefore those associated with the translational, rotational and vibrational movements of the molecules (or other structural units capable of these types of motion) and with the various interactions, both intermolecular and intramolecular, which exist between positively charged nuclei and negatively charged electrons. The remainder of the energy not only remains constant but also resists any sort of complete and useful analysis.

The only significant – and indeed the only measurable – energy quantity is the *difference* between the energy of the products and the energy of the reactants for the reaction or process considered, i.e. the energy change  $\Delta U$ :

$$\Delta U = U_{\text{products}} - U_{\text{reactants}}.$$

Nevertheless it is possible to recognise the *components* of the absolute energies (i.e. the components of  $U_{\text{products}}$  and of  $U_{\text{reactants}}$ ) which undergo

## 1.2. The change in internal energy, $\Delta U$

3

change in chemical reactions, and it is therefore useful to discuss them. In particular, it is important to have a feeling for the relative *magnitudes* of the various components of the total energy, since some of them make only minor contributions to the total change in energy for chemical reactions conducted under ordinary conditions.

### 1.2.2 Components of the internal energy

*Translational energy*,  $U_{\text{trans}}$ , is energy associated with translational motion in three dimensions. It is possessed (at temperatures above the absolute zero) only by chemical species capable of this sort of motion, like gas molecules (e.g.  $\text{H}_2$ ) or atoms (e.g. He), and by the molecules in liquids. In the solid state, translational energy is normally absent. Atoms and molecules free to move in three dimensions are said to possess three translational degrees of freedom.

*Rotational energy*,  $U_{\text{rot}}$ , is energy associated with rotation about a centre of gravity, and is absent in monatomic gases (e.g. He). Diatomic gases (e.g.  $\text{H}_2$ , CO) and linear polyatomic gas molecules (e.g. HCN,  $\text{N}_2\text{O}$ , BrCN,  $\text{CO}_2$ ), which rotate about two axes perpendicular to the line joining the nuclei, are said to possess two rotational degrees of freedom and, at temperatures above the absolute zero, a corresponding rotational energy. In solids, the possibility of rotation depends on the crystal components and the nature of the bonding. For example, the non-polar molecules of solid nitrogen and hydrogen, and the ammonium ions in solid ammonium chloride, exhibit rotation. In cases where the components are locked in position by virtue of the crystal geometry (as in solid carbon dioxide), or by intermolecular bonding (as in ice or ammonium fluoride), rotational energy is either absent or of little significance.

*Vibrational energy*,  $U_{\text{vib}}$ , is energy associated with the motion of the constituent atoms of a molecule (or polyatomic ion) towards and away from one another. Molecules possess  $3n - 6$  vibrational degrees of freedom ( $n$  = the number of atoms in the molecule) if they are non-linear, or  $3n - 5$  vibrational degrees of freedom if they are linear. Vibrational energy is possessed by all diatomic and polyatomic molecules and ions in the gaseous, liquid and solid states. Crystals consisting of monatomic ions, like sodium chloride, exhibit only lattice vibrations, i.e. vibrations of the crystal lattice as a whole. Unlike translational and rotational motions, which cease at 0 K, vibrational motion persists at this temperature and substances therefore possess a vibrational *zero-point energy*.

*Electronic energy*,  $U_{\text{el}}$ , is energy associated with the interacting systems of positively charged nuclei and negatively charged electrons, in terms of which substances are adequately described for chemical purposes. (Note again that this description of matter would hardly satisfy a physicist, to whom the intimate structure of the nuclei is of great importance.) It is the change in

## 1. Energy changes in inorganic reactions

4

electronic energy which commonly dominates the total energy change for a chemical reaction. Electronic energy has also been called 'chemical binding energy'; the general term 'bond energy', however, is sometimes defined in such a way as to include translational, rotational and vibrational components. This is examined in section 1.3.1.

Translational, rotational and vibrational energies can be measured in relation to their values at 0 K, where  $U_{\text{trans}} = 0$ ,  $U_{\text{rot}} = 0$ , and  $U_{\text{vib}}$  = the zero-point energy. In the case of the electronic energy  $U_{\text{el}}$ , the choice of a reference standard is more arbitrary. The electronic energy in the hydrogen molecule  $\text{H}_2$ , for example, can be assessed by comparing the energy of the  $\text{H}_2$  molecule with either the energy of the infinitely separated nuclei and electrons (2 protons + 2 electrons) or, as is usually the case, the energy of the infinitely separated hydrogen atoms. In either case, the electronic energy of the hydrogen molecule  $\text{H}_2$  is *lower* than the energy of the system chosen for comparison.

The relative magnitudes of the contributions made by  $U_{\text{trans}}$ ,  $U_{\text{rot}}$ ,  $U_{\text{vib}}$  and  $U_{\text{el}}$  can now be discussed.

## 1.2.3 Quantisation of the energy

At the outset it must be noted that these various forms of energy are *quantised*, that is to say, there exists for each sort of energy a range of permitted values or *energy levels*. The magnitude of the contribution of each sort of energy, therefore, will be determined by the extent to which each of the available energy levels is occupied under the conditions studied. This in turn depends on the size of the energy quanta, i.e. on the separations between the permitted levels, in a way which will be described in the next section. Experimental information about the sizes of energy quanta is most complete for isolated gas molecules free of intermolecular interactions, i.e. for ideal gases.

Briefly, translational quanta are minute (of the order  $10^{-20}$  kJ mol<sup>-1</sup>), and typical rotational quanta are about 0.02 kJ mol<sup>-1</sup>; vibrational quanta usually fall within the range 5–40 kJ mol<sup>-1</sup>, while quanta of the electronic energy are commonly much larger.

Some typical energy quanta determined spectroscopically for the carbon monoxide (CO) molecule are as follows. The energy of the first allowed transition is shown in each case. The electronic transition corresponds to the excitation of an electron from a sigma-type bonding orbital ( $x\sigma$ ) into a pi-type antibonding orbital ( $\nu\pi$ ).

		$\Delta U/(\text{kJ mol}^{-1})$
Electronic:	$[\text{KK}(z\sigma)^2(y\sigma)^2(x\sigma)^2(w\pi)^4]$ $\rightarrow [\text{KK}(z\sigma)^2(y\sigma)^2(x\sigma)^1(w\pi)^4(\nu\pi)^1]$	577
Vibrational:	$\nu = 0 \rightarrow \nu = 1$	25.1
Rotational:	$J = 0 \rightarrow J = 1$	0.046

1.2. The change in internal energy,  $\Delta U$ 

5

## 1.2.4 Components of the energy of an ideal gas

The distribution of the molecules of an ideal gas among the various energy levels depends on the size of the quanta in the following way.

If the number of molecules which occupy a given energy level  $U_n$  is  $N_n$ , and the number of molecules which occupy the lowest level  $U_0$  is  $N_0$ , then the difference between the two energy levels, i.e. the quantum absorbed in the transition  $U_0 \rightarrow U_n$ , is  $U_n - U_0$ . The ratio of molecules occupying the upper state to molecules occupying the lowest state,  $N_n/N_0$ , is given by the Boltzmann expression

$$N_n/N_0 = \exp [-(U_n - U_0)/kT], \quad (1.1)$$

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature. The ratio  $N_n/N_0$  obviously depends on the size of the difference  $U_n - U_0$  compared with the size of  $kT$ . The magnitude of  $kT$  (and of its molar equivalent,  $RT$ ;  $R$  is the gas constant) at various temperatures is as follows:

	$kT$ /(J molecule <sup>-1</sup> )	$RT$ /(kJ mol <sup>-1</sup> )
0 K	0	0
298 K (25°C)	$4.12 \times 10^{-21}$	2.48
1273 K (1000°C)	$1.76 \times 10^{-20}$	10.59

It is not difficult to deduce from (1.1) that, if  $U_n - U_0$  is large compared with  $kT$  (or with  $RT$ , if molar energies are considered), then the ratio  $N_n/N_0$  is very small. This means that, for the sorts of energy whose level-spacings or quanta are much bigger than  $kT$  (or  $RT$ ), only the lowest level will be occupied to any significant extent. This is essentially the situation with the vibrational and electronic energies of most molecules.

For example, it has been stated above that vibrational quanta lie in the range 5–40 kJ mol<sup>-1</sup>; if 25 kJ mol<sup>-1</sup> is chosen as a typical separation between the lowest vibrational level and the first excited level, then

$$U_n - U_0 = 25 \text{ kJ mol}^{-1}.$$

Since at room temperature (298 K)  $RT = 2.48 \text{ kJ mol}^{-1}$ ,

$$(U_n - U_0)/RT = 25/2.48 \approx 10,$$

from which it follows that the ratio  $N_n/N_0 = 4.5 \times 10^{-5}$ , i.e. for every 100 000 molecules in the lowest vibrational level (possessing only zero-point energy) there are only four or five in the first excited state (and still fewer in the higher levels).

For most molecules at room temperature the lowest electronic state is even more highly favoured.

The situation is quite different for translational and rotational levels.

## 1. Energy changes in inorganic reactions

6

Table 1.1. Zero-point energies/(kJ mol<sup>-1</sup>)

H <sub>2</sub>	N <sub>2</sub>	NH <sub>3</sub>	CH <sub>4</sub>	AsF <sub>3</sub>	BiCl <sub>3</sub>	SiF <sub>4</sub>	TiCl <sub>4</sub>	NaCl	KHF <sub>2</sub>
26	14	85	113	17	7	34	15	7.5	4.2

Rotational levels are separated by about 0.02 kJ mol<sup>-1</sup> for most molecules, and translational quanta are quite minute. In these cases many excited states will be extensively occupied at room temperature, in addition to the lowest state. Indeed, in order to get estimates of the magnitudes of the translational and rotational energies of gases at room temperature, it may be assumed that the gases are ideal and that the energy is distributed classically, i.e. the energy is  $\frac{1}{2}kT$  for each translational and rotational degree of freedom.

Since gas molecules possess three translational degrees of freedom, the translational energy  $U_{\text{trans}}$  of a gas is  $\frac{3}{2}kT$  per molecule, or  $\frac{3}{2}RT$  per mole, which is 3.72 kJ mol<sup>-1</sup> at 298 K.

For linear molecules, which possess two rotational degrees of freedom, the rotational energy  $U_{\text{rot}} = kT$  per molecule or  $RT$  per mole, which is 2.48 kJ mol<sup>-1</sup> at 298 K. For non-linear molecules, which possess three rotational degrees of freedom, the rotational energy  $U_{\text{rot}} = \frac{3}{2}kT$  per molecule, or  $\frac{3}{2}RT$  per mole, which is 3.72 kJ mol<sup>-1</sup> at 298 K.

*Example: hydrogen gas*

The significant components of the internal energy of a mole of hydrogen gas (H<sub>2</sub>) at 298 K are as follows:

(a)  $U_{\text{trans}} = 3.72 \text{ kJ mol}^{-1}$  ( $= \frac{3}{2}RT$  per mole).

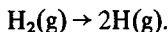
(b)  $U_{\text{rot}} = 2.48 \text{ kJ mol}^{-1}$  ( $= RT$  per mole).

(c)  $U_{\text{vib}}$ . It can be assumed that the H<sub>2</sub> molecule will be essentially in its lowest vibrational state at 298 K. This does not mean that its vibrational energy is zero, because all molecules retain one half-quantum of vibrational energy ( $\frac{1}{2}h\nu_0$ , where  $h$  is Planck's constant and  $\nu_0$  is the fundamental vibration frequency) for each vibrational degree of freedom, even at the absolute zero of temperature. Since H<sub>2</sub> has only one vibrational degree of freedom ( $3n - 5 = 1$ , when  $n = 2$ ), its vibrational energy will be one half-quantum at 0 K, and close to this value at 298 K. The zero-point energy of H<sub>2</sub> is 26 kJ mol<sup>-1</sup>. The zero-point energies of some other substances are shown in Table 1.1; the values were calculated from the experimental vibration frequencies by taking one half of the energy for each fundamental and summing.

(d)  $U_{\text{el}}$ . This is the energy associated with the interactions of the two protons and two electrons which constitute the hydrogen molecule. It can be conveniently measured as the difference between the energy of the H<sub>2</sub> molecule on the one hand, and two separated hydrogen atoms on the other, i.e. as  $\Delta U$  for the reaction

1.2. The change in internal energy,  $\Delta U$ 

7

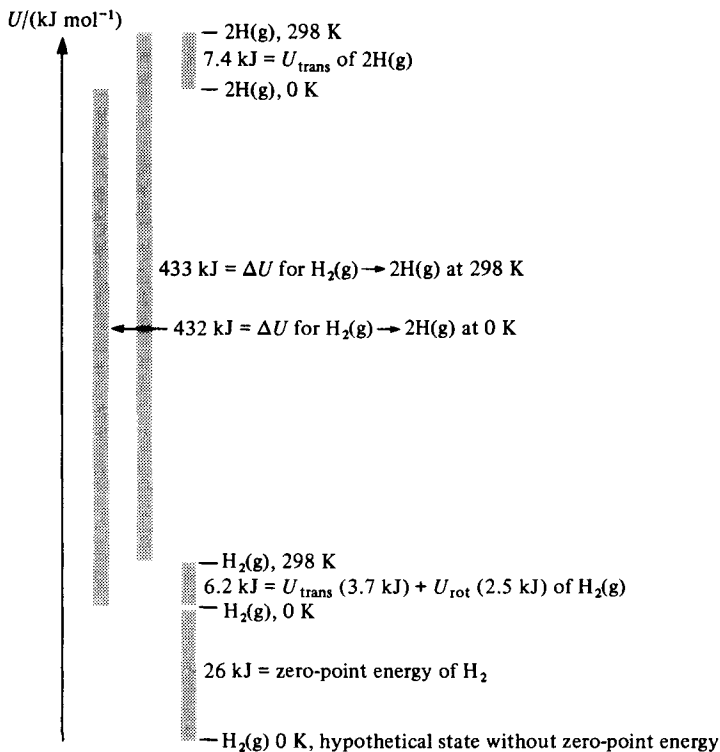


If the reaction temperature were 0 K, then the energy change for the dissociation of  $\text{H}_2$  molecules into atoms would be  $\Delta U_0 = +432 \text{ kJ mol}^{-1}$ , which represents the difference in energy between (a) one mole of  $\text{H}_2$  molecules without translational or rotational energy, but possessing the zero-point energy of vibration, and (b) two moles of hydrogen atoms without translational, rotational or vibrational energy; both the reactants and the products are assumed to be in their lowest electronic states.

$\Delta U_0$  for the above dissociation is normally called the *bond-dissociation energy* (see Section 4.1.2) of the hydrogen molecule. To obtain the true total of the electronic energy, however (i.e.  $\Delta U$  for the hypothetical dissociation in which translational, rotational and vibrational energies are completely absent from both the reactants and the products), the zero-point energy must be added to the experimental  $\Delta U_0$ .

If the reaction temperature is 298 K, the experimental value for the change in internal energy on dissociation is  $\Delta U_{298} = +433 \text{ kJ mol}^{-1}$ , which differs only slightly from the value at 0 K.

Fig. 1.1. Internal energy differences for various states of the system  $\text{H}_2/2\text{H}$  (not to scale)





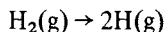
## 1. Energy changes in inorganic reactions

8

The internal energy relationships for the  $\text{H}_2/2\text{H}$  system are summarised diagrammatically in Figure 1.1. It should now be clear that the representation of the total energy of the hydrogen molecule as a series of terms, viz

$$U_{\text{total}} = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{el}},$$

is a device of limited value, as  $U_{\text{total}}$  is in fact only that part of the energy susceptible to alteration in a chemical reaction and each of the contributing terms is in fact an *energy difference* of some sort:  $U_{\text{trans}}$ , for example, is the difference between the translational energy at the temperature specified and that at 0 K, while  $U_{\text{el}}$  is the difference between the energy of  $\text{H}_2$  and that of  $2\text{H}$  under specified conditions. It is therefore more meaningful to define the specific process



and enumerate the changes in the different sorts of energy which occur. Thus at 298 K,

$$\begin{aligned} \Delta U &= \Delta U_{\text{trans}} + \Delta U_{\text{rot}} + \Delta U_{\text{vib}} + \Delta U_{\text{el}} \\ &= +3.7 - 2.5 - 26 + 458 \\ &= +433 \text{ kJ mol}^{-1}. \end{aligned}$$

It can be seen that for this system the electronic energy makes by far the greatest contribution to  $\Delta U$ , and that the translational and rotational components have very little effect on the energy change.

1.2.5 Heat capacity at constant volume,  $C_v$ 

In the case of the hydrogen system discussed above, the increase in internal energy between 0 K and 298 K for both  $\text{H}_2$  molecules and H atoms was calculated assuming that (a) both  $\text{H}_2$  and H are ideal gases in their lowest electronic states; (b)  $\text{H}_2$  possesses no vibrational energy other than the zero-point energy; and (c) translational and rotational components of the total energy contribute  $\frac{1}{2}RT$  per mole for each degree of freedom. These assumptions can be tested experimentally, since, for substances generally, the increase in internal energy accompanying a rise in temperature can be measured. Provided the volume is kept constant (to ensure that no pressure/volume change work is done by the substance in the course of expansion) and provided that no electrical or other work is involved, the amount of heat absorbed by a substance under these conditions is equal to the increase in internal energy. Thus the *heat capacity* at constant volume  $C_v$  of a substance is the rate at which the internal energy changes with temperature, i.e.

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v,$$

and is measured by determining experimentally the temperature rise which accompanies a given input of heat.



1.2. The change in internal energy,  $\Delta U$ 

9

Table 1.2. Heat capacities at 298 K,  
 $C_v / (\text{J K}^{-1} \text{mol}^{-1})$ 

	Experimental	'Theoretical'
He	12.5	12.5
Ar	12.5	12.5
H <sub>2</sub>	20.5	20.8
O <sub>2</sub>	21.1	20.8
N <sub>2</sub>	20.8	20.8
Cl <sub>2</sub>	25.5	20.8
CO	20.9	20.8
HCl	20.8	20.8
CO <sub>2</sub>	28.8	20.8
N <sub>2</sub> O	30.4	20.8
SO <sub>2</sub>	31.6	24.9
NH <sub>3</sub>	27.2	24.9

The values of the heat capacity  $C_v$  at 298 K for a number of gases are listed in Table 1.2; these figures represent the heat absorbed (and hence the increase in internal energy) in  $\text{J mol}^{-1}$ , when the temperature rises by 1 K at 298 K. Also shown are the 'theoretical' heat capacities: i.e. for monatomic gases, the increase in  $U$  will be wholly translational and equal to  $\frac{3}{2}R$  per kelvin, which is  $12.5 \text{ J mol}^{-1}$ ; for diatomic and linear polyatomic gases, the energy of two rotational degrees of freedom ( $R$ ) must be added, viz  $12.5 + 8.3 = 20.8 \text{ J mol}^{-1}$ ; for non-linear polyatomic gases, the rotational contribution is  $\frac{3}{2}R$ , so that the increase in  $U = 3R = 24.9 \text{ J mol}^{-1}$ . Some discrepancies between the experimental and calculated values are evident; they can be attributed to deviations from ideality, and to extra contributions of vibrational energy resulting from the existence of vibrational energy levels sufficiently low-lying to be significantly occupied at room temperature. Heat capacities, including those of solids and liquids, are discussed again for constant-pressure conditions in Section 1.3.2.

1.3 The change in enthalpy  $\Delta H$ 1.3.1 Relationship to the change in internal energy  $\Delta U$ 

A great many chemical reactions are carried out under conditions of constant pressure, i.e. in circumstances in which the amount of heat absorbed or evolved will reflect not only the change in internal energy, but also the amount of work done in the course of expansion or contraction, should a change of volume occur.

As long as no other sort of work is involved, the amount of heat absorbed or evolved under conditions of constant pressure is called the change in *enthalpy* and is symbolised  $\Delta H$ . Then

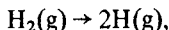
$$\Delta H = \Delta U + P\Delta V,$$

where  $P$  is the constant pressure and  $\Delta V$  the volume change.

## 1. Energy changes in inorganic reactions

10

For example, for the reaction



we have seen that  $\Delta U$  at 298 K = +433 kJ mol<sup>-1</sup>, and this is equal to the heat absorbed if the reaction is carried out at constant volume. If the reaction is carried out at a constant pressure of one atmosphere and at 298 K, the work done in doubling the volume against the constant pressure will be reflected in an additional absorption of heat. Then, if the gases are ideal,

$$P\Delta V = \Delta n RT \quad (\Delta n = \text{the change in the number of moles of gas})$$

and with  $\Delta n = 1$ ,

$$\begin{aligned} P\Delta V &= 1 \times 8.314 \times 298.2 \text{ J mol}^{-1} \\ &= 2.5 \text{ kJ mol}^{-1}, \end{aligned}$$

so that

$$\begin{aligned} \Delta H_{298} &= \Delta U + P\Delta V \\ &= 433 + 2.5 \\ &= 436 \text{ kJ mol}^{-1}. \end{aligned}$$

Since many reactions are carried out at room temperature (say 298 K) and in open vessels (i.e. at constant atmospheric pressure), the quantity  $\Delta H_{298}$  is for some purposes of more interest than either  $\Delta U_{298}$  or  $\Delta U_0$ .

The components of  $\Delta H_{298}$  for the reaction  $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$  can now be set down. They are, in kilojoules per mole of  $\text{H}_2$ ,

$$\begin{aligned} \Delta H_{298} &= P\Delta V + \Delta U_{\text{trans}} + \Delta U_{\text{rot}} + \Delta U_{\text{zero-point}} + \Delta U_{\text{el}} \\ &= +2.5 + 3.7 - 2.5 - 26 + 458 \\ &= 436 \text{ kJ mol}^{-1}. \end{aligned}$$

These figures are of interest because  $\Delta H_{298}$  for an atomisation reaction such as the above is commonly used as a measure of bond strength, the *bond enthalpy* or ‘thermochemical bond energy’, as discussed in Section 4.1.2. When used in this way, it is salutary to remember that  $\Delta H_{298}$  is a composite quantity, only one term of which – albeit the dominating one in the above instance, namely  $\Delta U_{\text{el}}$  – is strictly a measure of what is usually acknowledged to be the essence of the bond itself: the interaction between electrons and nuclei. The terms  $P\Delta V$ ,  $\Delta U_{\text{trans}}$  and  $\Delta U_{\text{rot}}$  are seldom of much significance numerically, but the contribution of the zero-point energy is often overlooked.

As will be seen in subsequent chapters, quantities commonly recorded as values of  $\Delta H_{298}$  are, as their names imply, enthalpies of formation (dealt with in the next section), enthalpies of atomisation (Chapter 2), and enthalpies of