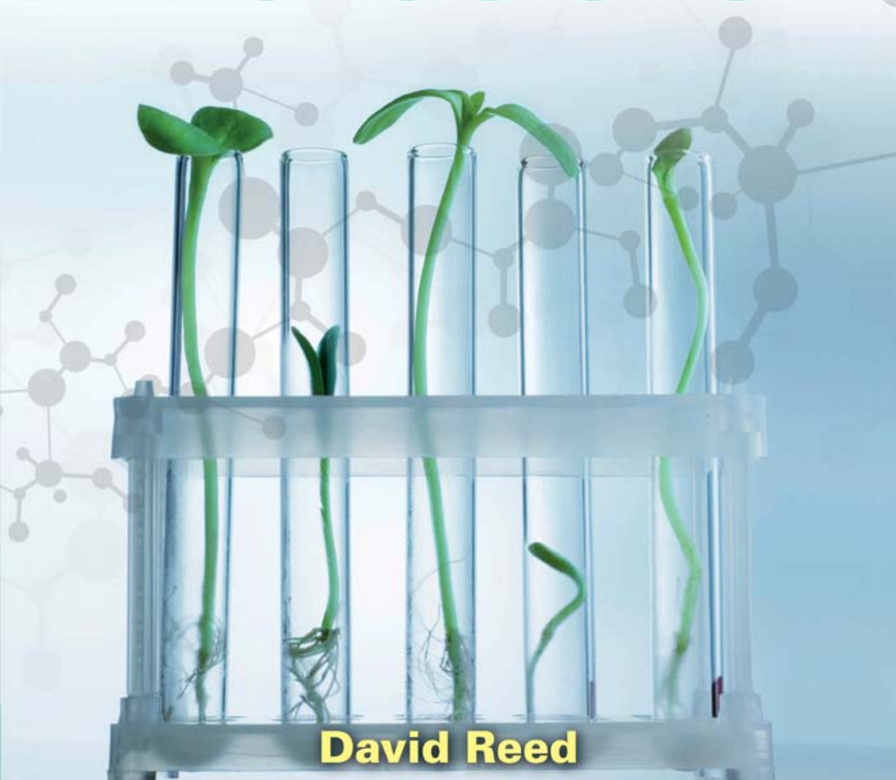
CHEMISTRY FOR BIOLOGISTS



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Chemistry for Biologists

4.4 Spontaneous processes, entropy and free energy

Thus far the discussions have looked at the concepts of energy and how these relate to chemical processes. These will now be extended to develop the ideas of thermodynamics to answer the question of 'why does a reaction go?'

A reaction that 'goes' is said to be a 'spontaneous' reaction, and although it is often the case that many spontaneous processes, including chemical reactions, are exothermic, this is not always true, so there must be a different criterion for a reaction to be spontaneous.

- Examples of spontaneous processes that involve no energy change:
  - The expansion of a gas from one container into an evacuated chamber (Figure 4.5). This costs no energy but will always happen.
  - The flow of heat from a hot object to a cold object within an insulated container. For example, a pack of cola will always get colder if it is placed in an insulated container of ice even though the total amount of heat inside the box remains effectively constant.
- Examples of spontaneous processes that are *endo*thermic:
  - Dissolution of certain salts (e.g. NH_4NO_3) in water chills it – heat is drawn from the surroundings to the system.
  - Evaporation of volatile liquids cools the surface on which they lie. For example, ethyl bromide, C_2H_5Br, used in local anaesthesia, evaporates rapidly when placed on skin, and cools it. For this process, $\Delta H_{vap} = +27.4\ \mathrm{kJ\ mol^{-1}}$ (ΔH_{vap} is the enthalpy of vaporisation).

The common factor in each of these cases is a greater dispersal of either energy (as heat) or of matter.

Dispersal of matter also increases on going from solid to liquid to gas phases of matter. The flow of heat from one body to another cooler body always results in greater dispersal of heat. In both cases the degree of dispersal (or of disorder) is quantified by the *entropy*, *S*, which has units of energy/temperature or $\mathrm{J\,K^{-1}}$.

Entropy, *S*, like enthalpy, is a *state function*, independent of history, so its value can be determined for a given substance (chemical composition), in a given state (gas, liquid, solid, solution…) and under external factors such as temperature or pressure. (*Note that values are given at some standard temperature (usually 298K) and pressure and purity*.)

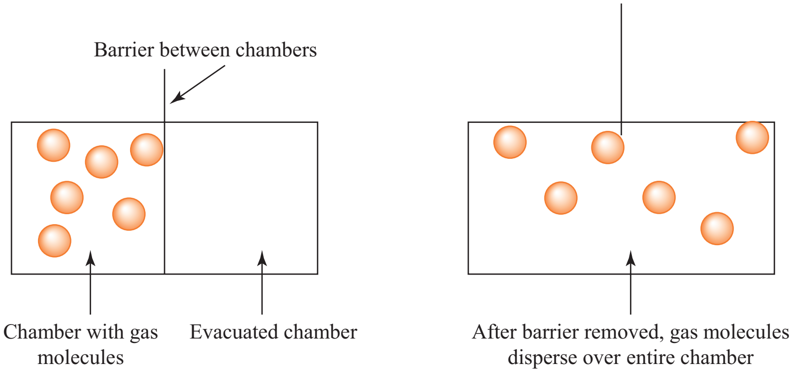

Figure 4.5 Expansion of a gas.

A few generalisations can be made:

- Entropy values increase as the volume of gas increases.
- Entropy values increase as the state of the material changes from solid to liquid to gas.
- Entropy values increase in the *surroundings* if heat, *q*, is passed *from* the *system*.

Box 4.8 contains information about entropy and defines the standard entropy change for a reaction.

Box 4.8

`Some information and definitions`

- At the absolute zero of temperature, the entropy of a perfectly crystalline solid is zero (this is referred to as the third law of thermodynamics).
- The standard molar entropy value for a substance is the entropy content of one mole of the substance at a pressure of 1 bar*, and is recorded as an absolute value, being shown as S^θ.
- ΔS_{surr} is the entropy change in the surroundings, ΔS_{sys} is the entropy change in the system.
- $\Delta S_{sys} + \Delta S_{surr}$ = entropy change in the universe.
- Also, the definition for ΔS_{sys} for a chemical reaction is:

$$\Delta S_{sys} = \text{total entropy of products} - \text{total entropy of reactants}$$

$$\Delta S^\theta = \Sigma \Delta S_f^\theta(\text{products}) - \Sigma \Delta S_f^\theta(\text{reactants})$$

*Remember 1 bar = 100 000 N m^{-2}.

It is possible to make a precise prediction that if the heat transfer from the system to the surroundings is done very (infinitely) slowly, under what are referred to as reversible conditions, then:

$$\Delta S_{surr} = -q_{sys}/T = -\Delta H_{sys}/T$$

(because, for a reaction at constant pressure, $q_{sys} = \Delta H_{sys}$).

In any real system it is impossible to achieve the idealised reversible conditions, and the result of this is some of the heat is effectively wasted, so the entropy change is less than the reversible case:

$$\Delta S_{surr} < -\Delta H_{sys}/T$$

We will now explore how this helps to predict whether a reaction is spontaneous.

4.4.1 The second law of thermodynamics

One way of stating this law is: ‘the entropy of the universe increases in any spontaneous process’. This can be represented as:

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

It is unrealistic to try to monitor ‘the universe’, or indeed ΔS_{surr}. It has been seen, however, that this term arises from the transfer of heat from the system, so on substituting for ΔS_{surr} with $-\Delta H_{sys}/T$ in the relationship:

$$S_{\mathrm{sys}} + \Delta S_{\mathrm{surr}} > 0$$

this then gives

$$\Delta S_{\mathrm{sys}} - \Delta H_{\mathrm{sys}}/T > 0$$

(From now on the focus will be on the properties of the system, so the subscript 'sys' will be dropped, and its usage will be taken to be implicit.)

Thus the following relationships, which are variants of one another, all hold:

$$\Delta S - \Delta H/T > 0 \text{ or } T\Delta S - \Delta H > 0 \text{ or } \Delta H - T\Delta S < 0$$

The person who developed this concept, J. Willard Gibbs (1839–1903), gave his name to a quantity that accounts for this balance and this is called the free energy or, more commonly, the *Gibbs free energy*:

$$\Delta G = \Delta H - T\Delta S \qquad [4.7]$$

In summary:

- If $\Delta G < 0$, the reaction goes. It is said to be spontaneous.
- If $\Delta G > 0$, the reaction does not go. It is said to be non-spontaneous.

Gibbs free energy is often defined as the maximum energy available to do useful work, and the difference between it and the enthalpy value is the energy 'discarded' as entropy in the system. This relationship forms the basis of predicting whether any chemical or fundamental biological process can go or not.

Note that it does not predict how fast a process will go. (This is the subject of Chapter 9, on reaction rates.)

It is now possible to produce Table 4.1, which summarises the impact of enthalpy and entropy changes on whether or not a reaction is spontaneous. So, for any reaction, if ΔH and ΔS are known (details can usually be derived from standard tables), then it is possible to calculate ΔG, and thereby determine whether the reaction 'goes' – whether it is spontaneous or not. Box 4.9 contains a definition and description of the standard free energy change for a reaction.

Table 4.1 Thermodynamic properties and reaction spontaneity

ΔH	ΔS	ΔG	*Spontaneous*
Negative	Positive	Negative	Yes
Positive	Negative	Positive	No
Negative	Negative	Depends on relative values of ΔH, ΔS	Favoured at lower T
Positive	Positive	Depends on relative values of ΔH, ΔS	Favoured at higher T

Example 4.4 The boiling point of water

It is possible to calculate the boiling point of water by using standard thermodynamic parameters (taken from the *CRC Handbook**) for the transition of water to steam, which is given by:

$$H_2O\,(l) \rightarrow H_2O\,(g)$$

Box 4.9

Standard free energy change, ΔG^{θ}

The value of ΔG^{θ} simply refers to the difference in free energy of the reactants and products in their standard states, in the proportions in which they appear in the equation for the reaction to form one mole of product. It can be calculated from:

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

Just as there is a standard enthalpy for formation given by ΔH_f^{θ}, so there is a standard free energy of formation, the symbol for which is ΔG_f^{θ}. ΔG_f^{θ} is the standard free energy of formation of a compound from its elements in their reference states.

The standard reaction free energy may be calculated from ΔG_f^{θ} values of the reaction components. Thus, for a reaction:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

The standard free energy change for this reaction is given by:

$$\Delta G^{\theta} = c\Delta G_f^{\theta}(\text{C}) + d\Delta G_f^{\theta}(\text{D}) - a\Delta G_f^{\theta}(\text{A}) - b\Delta G_f^{\theta}(\text{B})$$

which is summarised by:

$$\Delta G^{\theta} = \Sigma\Delta G_{\text{f}}^{\theta}(\text{products}) - \Sigma\Delta G_{\text{f}}^{\theta}(\text{reactants})$$

But ΔG^{θ} only applies to a reaction going from pure unmixed reactants to pure unmixed products. It is far more usual to wish to know about the thermodynamics of mixtures and reactions that do not form pure products, or which only reach an equilibrium ratio of reactants to products. (This will be explored more completely in the next chapter.)

The enthalpy change is $\Delta H = +44.0\,\text{kJ mol}^{-1}$ and the entropy change is $\Delta S = 117.9\,\text{J K}^{-1}\,\text{mol}^{-1}$. At the boiling point, T_b, the process of going from liquid to gas crosses over from $\Delta G > 0$ to $\Delta G < 0$; that is, from a non-spontaneous to a spontaneous process. In other words, at T_b, $\Delta G = 0$.

Remembering the relationship $\Delta G = \Delta H - T\Delta S$, then assuming at the point where $T = T_b$, the free energy change $\Delta G = 0$, this relationship can be rewritten as:

$$0 = \Delta H - T_b\Delta S$$

This rearranges to give:

$$\Delta H = T_b\Delta S$$

and hence can give T_b,

$$T_b = \frac{\Delta H}{\Delta S}$$

**The CRC Handbook of Chemistry and Physics*, also known as the 'Rubber Book', is a repository of physical and chemical data.

Putting in the values for ΔH and ΔS, *noting that ΔH is quoted in kJ and ΔS in J, therefore it is necessary to convert both to the same units, usually to J.* So,

$$T_b = 44\,000/117.9 = 373.1\,\text{K} \; (= 100\,°\text{C})$$

Example 4.5 The decomposition of the mineral calcium carbonate, $CaCO_3$

This decomposition is represented by the reaction:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

This reaction can be studied at two different temperatures, namely 'room' temperature, 25 °C/298 K, and a very high temperature, 2000 °C/2273 K, using the standard thermodynamic values for enthalpy and entropy of $\Delta H = +173.0\,\text{kJ}\,\text{mol}^{-1}$ and $\Delta S = 160.5\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$ respectively. As indicated in the preceding example, it is important to be consistent with the units.

At 'low' temperature (e.g. 298 K):

$$\Delta G = \Delta H - T\Delta S = 173\,000 - (298)160.5 = +125.2\,\text{kJ}\,\text{mol}^{-1}$$

so it does not go (it is non-spontaneous).

If the system is warmed to a high temperature, e.g. 2273 K:

$$\Delta G = \Delta H - T\Delta S = 173\,000 - (2273)160.5 = -191.8\,\text{kJ}\,\text{mol}^{-1}$$

so it *does* go.

Example 4.6 Dissolution of NH_4NO_3 in water at 298 K

This process is endothermic, with an enthalpy of solution, $\Delta H = +26.4\,\text{kJ}\,\text{mol}^{-1}$ and an entropy change of $\Delta S = 108.2\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}$. Therefore:

$$\Delta G = \Delta H - T\Delta S = 26\,400 - (298)108.2 = -5843\,\text{J}\,\text{mol}^{-1} = -5.8\,\text{kJ}\,\text{mol}^{-1}$$

In other words, this is compatible with dissolution at room temperature.

4.4.2 Free energy and ATP: coupling of reactions

During the discussion of enthalpy (Section 4.3.4), the hydrolysis of ATP to produce ADP was discussed, as summarised below:

$$\text{ATP} + H_2O \rightarrow \text{ADP} + \text{phosphate} \qquad \Delta H^{\theta} = -29\,\text{kJ}\,\text{mol}^{-1}.$$

The standard free energy change for this process is $\Delta G^{\theta} = -31\,\text{kJ}\,\text{mol}^{-1}$. In order that organisms do not exhaust their supply of ATP, this process needs to be reversed, that is:

$$\text{ADP} + \text{phosphate} \rightarrow \text{ATP} + H_2O$$

However, as the re-creation of ATP is the reverse of its hydrolysis, the standard free energy change, ΔG^{θ}, for the process is $+31\,\text{kJ}\,\text{mol}^{-1}$, which appears to go against the second law of thermodynamics, since this indicates the reaction is not spontaneous. *This is overcome by coupling this unfavourable reaction to a favourable one such that the overall free energy change is negative.*

One such favourable reaction is the conversion of glucose to lactic acid. Lactic acid is responsible for a burning sensation in the muscles involved with intense exercise. The conversion of glucose to lactic acid is summarised below:

$$C_6H_{12}O_6 \rightarrow 2CH_3CH(OH)CO_2H \qquad \Delta G = -197\,\text{kJ mol}^{-1}$$

In practice, 1 mole of glucose degrades together with the regeneration of two moles of ADP, with the overall process being summarised by:

$$2ADP + 2\text{ phosphate} + C_6H_{12}O_6 \rightarrow 2ATP + 2H_2O + 2CH_3CH(OH)CO_2H$$

The free energy change for the whole process is calculated from the simple summation below, which is a Hess's law calculation, applied this time to Gibbs free energy (recall Gibbs free energy is a state function):

$$C_6H_{12}O_6 \longrightarrow CH_3CH(OH)CO_2H \qquad \Delta G_{(I)} = -197\,\text{kJ mol}^{-1}$$

and

$$2ADP + 2\text{ phosphate} \longrightarrow 2ATP + 2H_2O \qquad 2\Delta G_{(II)} = (2 \times 31)\,\text{kJ mol}^{-1}$$

gives

$$C_6H_{12}O_6 + 2ADP + 2\text{ phosphate} \longrightarrow 2ATP + 2H_2O + CH_3CH(OH)CO_2H \quad \Delta G_{(III)}$$

Therefore:

$$\Delta G_{(III)} = \Delta G_{(I)} + 2\Delta G_{(II)}$$

$$\Delta G_{(III)} = -197\,\text{kJ mol}^{-1} + (2 \times 31)\,\text{kJ mol}^{-1} = -135\,\text{kJ mol}^{-1}$$

(*A detailed analysis of how this happens will be given in Chapter 12 on metabolism.*)

4.4.3 Biological example: thermodynamic rationale of micelle behaviour

Micelles result from an aggregation of a particular type of a group of compounds called lipids, discussed briefly here. (A more complete look at lipids will follow in Chapter 7.)

The sodium salts of long-chain carboxylic acids (soaps) are almost completely miscible in water. Except in extremely dilute solutions, however, they dissolve as micelles, which are spherical clusters of carboxylate ions that are dispersed throughout the aqueous phase. The non-polar (and thus hydrophobic, which means water-hating) alkyl chains remain in the non-polar environment (in the interior of the micelles) while the polar (and therefore hydrophilic, or water-loving) carboxylate groups are exposed to the polar environment of the aqueous medium. A diagrammatic representation of both a soap and a cross-section of a spherical micelle is shown in Figure 4.6.

In dilute solutions the hydrophobic tails of the long chain acids are surrounded by 'cages' of water molecules, then as the concentration of the acid salt increases, the micelles are formed. In thermodynamic terms,

- the process is generally very slightly endothermic (ΔH is usually about 1–2 kJ mol^{-1});
- the ΔS for micelle formation is generally negative (micelles are more organised than a collection of individual molecules).