

# Chapter 2 Entropy: how far?

- There are a number of possible answers to this question including:
    - the reaction of pure ethanoic acid with solid ammonium carbonate
    - the reaction of solid hydrated barium hydroxide with solid ammonium chloride
    - dissolving ammonium nitrate in water
  - The entropy of a perfect crystal of helium at absolute zero is zero, as is that of a perfect crystal of sodium chloride. This is because of the third law of thermodynamics: 'All perfect crystals have zero entropy at absolute zero'. This applies to both elements and compounds.
- e* This is not to be confused with enthalpy — the standard enthalpy of formation of an *element* is zero, but that of a compound is not.
- Both are solutions of molecular substances, so the solution of the substance with the more complex structure will have the greater entropy. Glucose has 24 atoms in each molecule whereas carbon dioxide has only three, so the glucose solution is more random and has greater entropy.
  - The comparison is with a *solution* of carbon dioxide, not with gaseous carbon dioxide.
    - As any substance is heated, its entropy increases. Aqueous sodium chloride at 50°C has a higher entropy than it does at 25°C.
  - This is shown by the Maxwell-Boltzmann distribution of energies of the particles; those at the higher temperature are more spread out than those at the lower temperature.
  - For a solution to 'unmix', the second law of thermodynamics would have to be broken. The *total* entropy of the dissolved copper sulfate is greater than that of separate solid copper sulfate and water. This is because the total entropy change is made up of the entropy change of the system (the difference between the entropies of the solution and of the solid and the water) and the entropy change of the surroundings ( $-\Delta H/T$ )
    - $$\Delta S_{\text{system}} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} = 2 \times 192 - (192 + 3 \times 131) = -201 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{\text{surr}} = -\Delta H/T = -(-92\,000/298) = +309 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = -201 + 309 = +108 \text{ J K}^{-1} \text{ mol}^{-1}$$

This is a positive number and so the reaction is thermodynamically feasible at 298 K.
- e* Be careful when using the Edexcel or Nuffield data booklets. The values given for the standard entropies of all the *diatomic* gaseous elements are based on  $\frac{1}{2}$  mol of the diatomic elements. This applies to elements such as hydrogen, nitrogen and chlorine. The value for nitrogen is given as 95.8, which is for  $\frac{1}{2}$  N<sub>2</sub>, so for N<sub>2</sub> the value is  $2 \times 95.8 = 192 \text{ J K}^{-1} \text{ mol}^{-1}$  (to 3 significant figures).
- $$\Delta S_{\text{system}} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} = 40 + 214 - 93 = +161 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{\text{surr}} = -\Delta H/T = -(+178\,000/298) = -597 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = +161 - 597 = -436 \text{ J K}^{-1} \text{ mol}^{-1}$$

This is a negative number and so the reaction is not thermodynamically feasible at 298 K.
- e* There are three important points here.
- The values for the standard entropy of *elements* in some data books is per atom in the molecule. The data in Table 2.2 are the standard entropies per *molecule*, i.e. for 1 mol of nitrogen gas, N<sub>2</sub>, at a temperature of 298 K.

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- As is usual in questions containing data about entropy and  $\Delta H$ , make sure that both are in joules. This means that the  $\Delta H$  value has to be multiplied by 1000.
- Note that the first reaction is feasible at this temperature even though the entropy change for the system is negative. This is because the reaction is exothermic and the heat change outweighs the negative entropy change. The second reaction is not feasible even though the entropy change of the system is positive. The reaction is too endothermic for the reaction to be feasible at 298 K.

**6 a**  $\Delta H^\circ = \Sigma \Delta H_f^\circ(\text{products}) - \Sigma \Delta H_f^\circ(\text{reactants}) = -860 + 10 \times -286 + 2 \times -46 - (-3245 + 2 \times -315) = +63 \text{ kJ mol}^{-1}$

**b**  $\Delta S_{\text{system}} = \Delta S_{\text{total}} - \Delta S_{\text{surr}} = \Delta S_{\text{total}} + \Delta H/T = 150 + 63\,000/298 = +361 \text{ J K}^{-1} \text{ mol}^{-1} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}} = 130 + 700 + 386 - (x + 184)$

Entropy of hydrated barium hydroxide,  $x = 130 + 700 + 386 - 184 - 361 = +671 \text{ J K}^{-1} \text{ mol}^{-1}$

**e** Do not forget the stoichiometric numbers when calculating both  $\Delta H$  and  $\Delta S_{\text{system}}$ .

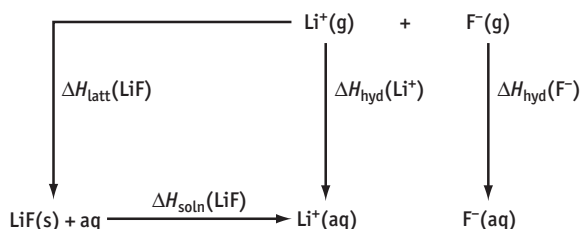
**7**  $\Delta S_{\text{system}} = 70 - (131 + \frac{1}{2} \times 205) = -164 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta S_{\text{surr}} = -\Delta H/T = -(-286\,000/298) = +960 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta S_{\text{total}} = -164 + 960 = +796 \text{ J K}^{-1} \text{ mol}^{-1}$  which is positive, so the reactants are thermodynamically unstable relative to the products (reaction thermodynamically feasible). For  $M^{2+}$ : charge/radius =  $2/0.31 = 65$ . For  $Q^{3+}$ : charge/radius =  $3/0.095 = 32$ .  $M^{2+}$  has the larger charge density, so its hydration energy will be more exothermic.

**e** Do not say that the reaction is thermodynamically unstable, but relate the stability of the reactants to the products.

**8** The Hess's law diagram is:



$$\Delta H_{\text{latt}}(\text{LiF(s)}) + \Delta H_{\text{soln}}(\text{LiF(s)}) = \Delta H_{\text{hyd}}(\text{Li}^+(\text{g})) + \Delta H_{\text{hyd}}(\text{F}^-(\text{g}))$$

$$\Delta H_{\text{soln}}(\text{LiF(s)}) = \Delta H_{\text{hyd}}(\text{Li}^+(\text{g})) + \Delta H_{\text{hyd}}(\text{F}^-(\text{g})) - \Delta H_{\text{latt}}(\text{LiF(s)})$$

$$= -519 + (-506) - (-1022) = -3 \text{ kJ mol}^{-1}$$

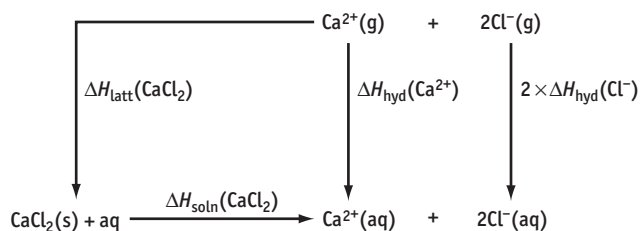
The enthalpy change is so small that the solubility of lithium fluoride cannot be predicted. The solubility will be determined almost entirely by  $\Delta S_{\text{system}}$ .

**e** You can work out the enthalpy of solution of an ionic solid using the formula:

$$\Delta H_{\text{soln}} = \text{sum of hydration enthalpies of the ions} - \text{lattice energy}$$

Remember that if there are two anions in the formula, a value of  $2 \times \Delta H_{\text{hyd}}(\text{anion})$  must be used. This is the case with hydroxides and halides of the group 2 metals.

9 The Hess's law diagram is:



$$\Delta H_{\text{latt}}(\text{CaCl}_2(\text{s})) + \Delta H_{\text{soln}}(\text{CaCl}_2(\text{s})) = \Delta H_{\text{hyd}}(\text{Ca}^{2+}(\text{g})) + 2 \times \Delta H_{\text{hyd}}(\text{Cl}^{-}(\text{g}))$$

$$2 \times \Delta H_{\text{hyd}}(\text{Cl}^{-}(\text{g})) = \Delta H_{\text{latt}}(\text{CaCl}_2(\text{s})) + \Delta H_{\text{soln}}(\text{CaCl}_2(\text{s})) - \Delta H_{\text{hyd}}(\text{Ca}^{2+}(\text{g}))$$

$$= -2237 + (-83) - (-1650) = -670$$

$$\Delta H_{\text{hyd}}(\text{Cl}^{-}(\text{g})) = \frac{1}{2} \times (-670) = -335 \text{ kJ mol}^{-1}$$

e The calculation gives first a value of twice the hydration enthalpy of chloride ions, so you need to divide it by two.

10 The value of the hydration enthalpy depends on the charge and the ionic radius. A small radius results in a large hydration energy, as does a high charge. For  $\text{M}^{2+}$ : charge/radius =  $2/0.031 = 65$ . For  $\text{Q}^{3+}$ : charge/radius =  $3/0.095 = 32$ .  $\text{M}^{2+}$  has the larger charge density, so its hydration energy will be more exothermic.

e M is beryllium in period 2 and Q is thallium in period 6. In most A-level questions, the more positive ion would also have the smaller radius, so that the effects of size and charge are in the same direction.

11 a Solubility is a balance between  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surr}}$ . The value of  $\Delta S_{\text{surr}}$  depends on the value of  $\Delta H$  and the temperature. The compound that has the more positive, or less negative,  $\Delta S_{\text{system}}$  will be the more soluble. The compound that has the more exothermic  $\Delta H$  and hence the more positive  $\Delta S_{\text{surr}}$ , will be the more soluble.

- The change in  $\Delta S_{\text{system}}$  going from  $\text{MgF}_2$  to  $\text{CaF}_2$  depends on the difference in the entropy values of the aqueous cations.
- $\Delta S_{\text{system}}$  becomes less negative by  $83 \text{ J K}^{-1} \text{ mol}^{-1}$ , tending to make  $\text{CaF}_2$  more soluble than  $\text{MgF}_2$ .
- $\Delta H$  becomes more endothermic by  $31\,000 \text{ J}$  and so  $\Delta S_{\text{surr}}$  becomes more negative by  $31\,000/298 = 104 \text{ J K}^{-1} \text{ mol}^{-1}$ , tending to make  $\text{CaF}_2$  less soluble than  $\text{MgF}_2$ .

As the change in  $\Delta S_{\text{surr}}$  is greater than the change in  $\Delta S_{\text{system}}$ , calcium fluoride will be less soluble than magnesium fluoride.

e The value of  $S$  of the anion (the fluoride ion) is the same for both fluorides and so is not relevant to the explanation.

b The change in  $\Delta S_{\text{system}}$  going from  $\text{AgBr}$  to  $\text{AgI}$  depends on the difference in the entropy values of the aqueous anions:

$\Delta S_{\text{system}}$  becomes more positive by  $54 \text{ J K}^{-1} \text{ mol}^{-1}$ , tending to make  $\text{AgI}$  more soluble than  $\text{AgBr}$ .

$\Delta H$  becomes more endothermic by  $27\,000 \text{ J}$  and so  $\Delta S_{\text{surr}}$  becomes more negative by  $27\,000/298 = 91 \text{ J K}^{-1} \text{ mol}^{-1}$ , tending to make  $\text{AgI}$  less soluble than  $\text{AgBr}$ .

As the change in  $\Delta S_{\text{surr}}$  is greater than the change in  $\Delta S_{\text{system}}$ , silver iodide is less soluble than silver bromide.

e The value of  $S$  of the cation (the silver ion) is the same for both halides and so is not relevant to the explanation.

e These calculations show that when comparing similar ionic compounds, it is the change in the value of the enthalpy of solution that is more significant than the change in entropy of the ions.

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- 12 a** As a substance is heated, the motion of the particles becomes more random, so its entropy increases. Thus, liquid water at 25°C has a lower entropy than liquid water at 35°C.
- b** The molecules in a liquid have short-range order, but those in the gas phase are randomly arranged. Therefore, liquid water at 100°C has lower entropy than gaseous water at the same temperature, i.e. there is an increase in entropy (disorder) when water at 100°C boils.
- 13 a** The reaction is going from 1½ mol of gas to 1 mol of gas and so the entropy of the system decreases.
- b** A solid (highly ordered) and ions in solution (fairly disordered) react to form a gas (highly disordered), ions in solution and a liquid (fairly disordered). Thus, there is an increase in entropy ( $\Delta S_{\text{system}}$  is positive).
- c** An ordered solid forms another ordered solid plus a highly disordered gas. Therefore, there is an increase in entropy.
- d** The reaction involves univalent ions dissolving, so the water is only slightly ordered. The solid is dispersed through the liquid resulting in a large increase in disorder (entropy). The second factor is larger than the first and so there is an increase in the entropy of the system.
- e** In this example an anhydrous ionic compound containing 2+ ions is dissolving. This causes a large increase in order of the water, which may be larger than the increase in entropy of the solid becoming dispersed through the liquid. Unless the values are given, it is impossible to predict which factor will be dominant.
- e** Do not make the mistake of thinking that all dissolving results in an increase in the entropy of the system.  $\Delta H_{\text{solution}}$  for calcium sulfate is exothermic, but calcium sulfate is only slightly soluble. Thus  $\Delta S_{\text{total}}$  must be slightly negative and, as  $\Delta H$  is favourable,  $\Delta S_{\text{system}}$  must be unfavourable and therefore negative.

**14 a** 
$$\Delta S_{\text{system}} = \Delta S_{\text{products}} - \Delta S_{\text{reactants}} = 2 \times (+256) - (+325)$$
$$= +187 \text{ J K}^{-1} \text{ mol}^{-1}$$

**b** 
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H}{T} = \frac{57.4}{(273 + 85)} = \frac{57.4}{358} = -0.160 \text{ kJ K}^{-1} \text{ mol}^{-1}$$
$$= -160 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{total}} = +187 + (-160) = +27 \text{ J K}^{-1} \text{ mol}^{-1}$$

- e** Beware of units.  $\Delta S_{\text{system}}$  is in joules, whereas  $\Delta H$ , and hence  $\Delta S_{\text{surr}}$  are in kilojoules.
- c** The total entropy change is positive, so the reaction is feasible (and will take place as long as the activation energy is not too high).
- d**  $\Delta S_{\text{total}}$  is positive at this temperature, so the reactants are thermodynamically unstable relative to the products.
- 15 a** A change is favoured by exothermic (negative)  $\Delta H$  and positive  $\Delta S_{\text{system}}$ .
- Change W is favourable on both counts and so is likely to take place.
- Change X has a favourable  $\Delta H$  (negative) but an unfavourable  $\Delta S_{\text{system}}$  (negative). However:
- $$\Delta S_{\text{surr}} = -\Delta H/T = -(-170)/298 = +0.570 \text{ kJ K}^{-1} \text{ mol}^{-1} = +570 \text{ J K}^{-1} \text{ mol}^{-1}$$
- This outweighs the unfavourable  $\Delta S_{\text{system}}$  of  $-500 \text{ J K}^{-1} \text{ mol}^{-1}$ , so the reaction is likely to take place.
- Change Y has an unfavourable  $\Delta H$  (positive) and an unfavourable  $\Delta S_{\text{system}}$  (negative) and so will never take place.

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Change Z has an unfavourable  $\Delta H$  ( $+170 \text{ kJ mol}^{-1}$ ), but a favourable  $\Delta S_{\text{system}}$  ( $+500 \text{ J K}^{-1} \text{ mol}^{-1}$ ):

$$\Delta S_{\text{surr}} = -\Delta H/T = -(+170\,000/298) \text{ kJ K}^{-1} \text{ mol}^{-1} = -570 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = +500 + (-570) = -70 \text{ J K}^{-1} \text{ mol}^{-1}$$

$\Delta S_{\text{total}}$  is negative and so the reaction will not happen at this temperature.

- e** Note that the enthalpy changes are quoted in kJ, but the entropy values are given in J.  
You should not state that a reaction *will* happen, as the system might be kinetically stable because of a high activation energy.
- b** Only change Z becomes more favourable as the temperature increases. The value of  $-\Delta H/T$  becomes less negative as the temperature rises and eventually it is smaller than the positive  $\Delta S_{\text{system}}$ .  $\Delta S_{\text{total}}$  becomes positive, making the reaction feasible. The reactants become thermodynamically unstable relative to the products above this higher temperature.
- e** The temperature at which the reactants change from being thermodynamically stable to being thermodynamically unstable is when  $\Delta S_{\text{total}} = 0$ . At this point  $\Delta S_{\text{system}} - \Delta H/T = 0$ , or  $T = \Delta H/\Delta S_{\text{system}} = 170 \times 10^3/500 = 340 \text{ K} = 67^\circ\text{C}$
- 16** As this is an endothermic reaction,  $\Delta S_{\text{surr}}$  is negative. However, the reaction is spontaneous and so  $\Delta S_{\text{total}}$  must be positive. This can only be the case if  $\Delta S_{\text{system}}$  is positive (and more positive than  $58\,000/323 = 180 \text{ J K}^{-1} \text{ mol}^{-1}$ ).
- e** An endothermic enthalpy of reaction suggests a lack of reaction unless it is outweighed by a positive change in the entropy of the reactants and products.
- 17 a** Both ethanoic acid and methanol are liquids, but ethanoic acid is a more complex molecule and so its standard entropy value will be greater.
- b**  $\Delta S_{\text{system}} = S(\text{ethanoic acid}) - (S(\text{carbon monoxide}) + S(\text{methanol})) = 160 - (198 + 127) = -165 \text{ J K}^{-1} \text{ mol}^{-1}$
- c**  $\Delta S_{\text{surr}} = -\Delta H/T = -(-137\,000/298) = +460 \text{ J K}^{-1} \text{ mol}^{-1}$
- d**  $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = -165 + (+460) = +295 \text{ J K}^{-1} \text{ mol}^{-1}$   
This is a positive number and so the reaction will be spontaneous at a temperature of 298 K.
- e** As the reaction is thermodynamically spontaneous, the reactants are thermodynamically unstable with respect to the products. As the reaction does not take place at room temperature but is thermodynamically feasible, the activation energy must be high, making the reactants kinetically inert with respect to the products.
- 18 e** Type Boltzmann into Google and you will get many references. Boltzmann's tombstone is inscribed with  $S = k \log W$  (but it should have been  $\log_e W$  or  $\ln W$ , rather than the ambiguous  $\log W$ ).

Summary worksheet ([www.hodderplus.co.uk/philipallan](http://www.hodderplus.co.uk/philipallan))

- 1 C** A solid and a solution are reacting to produce a solution, a liquid and a gas. It is the large randomness of the gas produced that causes the entropy change of the system to be positive. Options **A** and **D** both have a gas reacting to form a solid; in option **B** a gas turns into a liquid. So options **B**, **C** and **D** will result in an increase in order and, therefore, a decrease in entropy of the system.
- 2 C**  $\Delta S_{\text{surr}} = -\Delta H/T = -(-123\,000/298) = +413 \text{ J K}^{-1} \text{ mol}^{-1}$
- In options **A** and **B**, the temperature in °C has not been converted into degrees kelvin. In options **D** and **B** the sign is wrong in the expression for  $\Delta S_{\text{surr}}$ .
- 3 B** To be thermodynamically spontaneous,  $\Delta S_{\text{total}}$  must be positive. This is helped by a negative  $\Delta H$  and a positive  $\Delta S_{\text{system}}$ , as in option **B**. Option **C** has a negative  $\Delta S_{\text{total}}$  at all temperatures. Option **A** will be spontaneous if  $\Delta S_{\text{system}}$  outweighs the unfavourable (endothermic)  $\Delta H$ , which will only happen at high temperatures. Option **D** will be spontaneous if  $\Delta H$  outweighs the unfavourable (negative)  $\Delta S_{\text{system}}$ , which it will only at low temperatures.
- 4 A** An increase in temperature shifts the position of equilibrium to the right in endothermic reactions only. Thus options **B** and **D** must be incorrect. Option **C** cannot be correct because the reaction will not be spontaneous as both  $\Delta H$  and  $\Delta S_{\text{system}}$  are unfavourable.
- 5 A**  $\Delta S_{\text{system}} = S_{\text{product}} - \Sigma S_{\text{reactants}} = 240 - (198 + 2 \times 131) = -220 \text{ J K}^{-1} \text{ mol}^{-1}$
- In options **C** and **D** the entropy of hydrogen has not been multiplied by 2, which ignores the stoichiometry of the reaction. Options **B** and **D** both used  $S_{\text{reactants}} - S_{\text{products}}$ .
- 6 D** Gaseous water has a higher entropy than liquid water, so option **B** cannot be correct. Of the three gases, ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , has the most complex formula and so has the highest entropy.
- 7 A** The extent of ordering of the solvent around the ions depends on the charge density of the ions. All are chlorides, so it is the relative charge densities of the cations that matter. The cations are all 2+, but  $\text{Mg}^{2+}$  has the smallest radius and so surrounds itself with more layers of water molecules than the others.
- e** In questions about a group in the periodic table, the answer will always be the element at the top or the bottom of the group. Thus options **B** and **C** need not be considered.