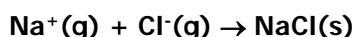


Topic 4 – Lattice Enthalpy & Entropy

Revision Notes

1) Lattice enthalpy

- Lattice enthalpy is a measure of the strength of an ionic bond
- Lattice enthalpy is defined as the enthalpy change that accompanies the formation of one mole of a solid compound from its constituent gaseous ions e.g.



2) Born-Haber cycles

a) General

- Born-Haber cycles show the steps involved in forming an ionic solid either directly from its elements or indirectly via the formation of gaseous atoms and ions
- The indirect route involves the following steps: atomisation of the metal, ionisation of the metal, atomisation of the non-metal, electron affinity of the non-metal and lattice formation. It is recommended that this sequence is followed every time a cycle is drawn
- Born-Haber cycles allow missing enthalpy values to be calculated using Hess's Law (which states that enthalpy change is independent of route)

b) Equations for Born-Haber Cycles

The steps involved in forming NaCl(s) by both routes and their associated enthalpy changes are shown below.

- | | | |
|---|------|--|
| • Formation, ΔH_f | e.g. | $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$ |
| • Atomisation of the metal, ΔH_{at} | e.g. | $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$ |
| • Ionisation of the metal, ΔH_{i1} | e.g. | $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$ |
| • Atomisation of the non-metal, ΔH_{i1} | e.g. | $\frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$ |
| • Electron affinity of the non-metal, ΔH_{ea1} | e.g. | $\text{Cl}(\text{g}) + \text{e}^- \rightarrow \text{Cl}^-(\text{g})$ |
| • Lattice formation, ΔH_{latt} | e.g. | $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$ |

Hess's Law says:

$$\Delta H_f = \Delta H_{\text{at}}(\text{Na}) + \Delta H_{\text{i1}} + \Delta H_{\text{at}}(\text{Cl}) + \Delta H_{\text{ea1}} + \Delta H_{\text{latt}}$$

- Atomisation enthalpies of non-metals are per atom e.g. 121 kJ mol⁻¹ for Cl, so twice this for $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$
- A Group II metal has two ionisation enthalpies which will be shown as separate steps in the cycle. The second ionisation enthalpy is larger than the first because the electron is lost from a particle that is already positive which means that the outer electron is more firmly attracted to the nucleus
- A Group VI non-metal has two electron affinities which will be shown as separate steps in the cycle. The first electron affinity is exothermic but the second is endothermic because the negative ion repels the negatively charged electron
- Lattice formation is an exothermic process, ΔH_{latt} is negative

3) Enthalpies of Solution

- A different type of Born-Haber cycle shows the steps involved in forming an aqueous solution of an ionic solid
- In this cycle there are 2 routes from gaseous ions to dissolved solid
- One route involves lattice formation followed by dissolving. The other route involves hydration of the ions (i.e. gaseous ions to dissolved ions)

The steps involved in forming NaCl(aq) by both routes and their associated enthalpy changes are shown below.

- | | |
|---|--|
| • Lattice enthalpy, ΔH_{latt} | e.g. $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$ |
| • Enthalpy of solution, ΔH_{sol} | e.g. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ |
| • Hydration of the metal ion, ΔH_{hyd} | e.g. $\text{Na}^+(\text{g}) \rightarrow \text{Na}^+(\text{aq})$ |
| • Hydration of the non-metal ion, ΔH_{hyd} | e.g. $\text{Cl}^-(\text{g}) \rightarrow \text{Cl}^-(\text{aq})$ |

Hess's Law says:

$$\Delta H_{\text{latt}} + \Delta H_{\text{sol}} = \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-)$$

Hydration enthalpies are for 1 mole of ions. In the case of MgCl₂, which often appears in exam questions, $\Delta H_{\text{hyd}}(\text{Cl}^-)$ needs to be multiplied by 2

4) Effect of ionic charge and ionic radius

- As ionic charge increases, lattice enthalpy becomes more exothermic e.g. MgCl₂ has a more exothermic lattice enthalpy than NaCl because Mg²⁺ has a higher charge than Na⁺. This is due to a stronger electrostatic attraction between the positive and negative ions
- As ionic radius decreases, lattice enthalpy becomes more exothermic e.g. MgO has a more exothermic lattice enthalpy than CaO because Mg²⁺ has a smaller ionic radius than Ca²⁺. In MgO the ions are closer together so the positive and negative ions are more strongly attracted to one another
- The same factors apply when comparing hydration enthalpies but in this case the comparison is between the attraction of the ions to the appropriate end of a water molecule

5) Entropy and Free-energy

- As a general rule, once an exothermic reaction has started it produces enough energy to keep itself going e.g. burning methane
- Similarly, an endothermic reaction requires constant heating and will stop if the heat is removed e.g. thermal decomposition of copper carbonate
- However, some endothermic reactions will keep going without being heated e.g. NaHCO₃ and HCl. The enthalpy change is not the only factor to be considered when deciding whether a reaction is possible

a) Entropy

- Entropy is measure of the disorder of a system. It has the symbol S and units of $\text{J K}^{-1} \text{mol}^{-1}$ (note that this is J not kJ)
- Considering the states of matter, a solid is the most ordered and has the lowest entropy. A gas is the most disordered state and has the highest entropy
- At absolute zero ($-273\text{ }^{\circ}\text{C}$ or 0 K), particles stop moving and have zero entropy

b) Entropy changes

- Entropy changes are calculated using the following formula

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

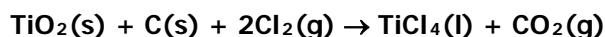
- A reaction that produces a gas will have a positive entropy change because disorder has increased
- Melting and boiling have positive entropy changes. Boiling has a bigger entropy change than melting because gases are much more disordered than liquids and solids

c) Feasibility

- For a chemical reaction to be feasible (possible) the amount of disorder in the universe must not decrease
- Fortunately, we do not have to do measurements on the universe to find out whether a reaction is feasible. Instead we define a quantity called the free energy change, ΔG , and it can be shown that disorder in the universe does not decrease if ΔG is less than or equal to zero for the reaction
- ΔG is calculated using the following formula

$$\Delta G = \Delta H - T\Delta S \quad (T \text{ is temperature in K})$$

Example



For this reaction, $\Delta H = -258\text{ kJ mol}^{-1}$ and $\Delta S = -35.6\text{ J K}^{-1} \text{mol}^{-1}$. Calculate ΔG at 298 K and state whether the reaction is feasible or not.

We need to remember the difference in units between ΔH and ΔS and divide ΔS by 1000 to express it in $\text{kJ K}^{-1} \text{mol}^{-1}$

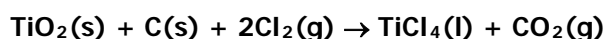
$$\begin{aligned} \Delta G &= -258 - (298 \times -35.6/1000) \\ &= -258 - (-10.6) \\ &= -247\text{ kJ mol}^{-1} \end{aligned}$$

Feasible at 298 K as ΔG is negative

c) **Temperature Dependence of Feasibility**

- An exothermic reaction with a positive entropy change will be feasible at all temperatures (ΔH negative and $T\Delta S$ positive, ΔG always negative)
- An endothermic reaction with a negative entropy change will be infeasible at all temperatures (ΔH positive and $T\Delta S$ negative, ΔG always positive)
- An endothermic reaction with an increase in entropy will be feasible at high temperatures (ΔH positive and $T\Delta S$ positive. At high T , $T\Delta S$ outweighs ΔH making ΔG negative)
- An exothermic reaction with a reduction in entropy will become feasible at low temperatures (ΔH negative and $T\Delta S$ negative. At low T , ΔH outweighs $T\Delta S$ making ΔG negative) – **see example below**
- In the last two cases, the temperature at which the reaction becomes feasible is when **$\Delta G = 0$** (i.e. $\Delta H = T\Delta S$, or $T = \Delta H/\Delta S$)

Example



For this reaction, $\Delta H = -258 \text{ kJ mol}^{-1}$ and $\Delta S = -35.6 \text{ J K}^{-1} \text{ mol}^{-1}$

Calculate the temperature at which this reaction ceases to be feasible

Again we need to remember the difference in units between ΔH and ΔS . This time multiply ΔH by 1000 to express it in J mol^{-1}

$$\begin{aligned} T &= \Delta H/\Delta S \\ &= (-258 \times 1000)/-35.6 \\ &= 7247\text{K} \end{aligned}$$