

Topic 10 – Thermodynamics

Revision Notes

1) Enthalpy Changes

- An enthalpy change is a change in heat energy measured at constant pressure.
- Enthalpy changes refer to the chemicals **not** the surroundings.
- The symbol for an enthalpy change is ΔH (Δ = change, H = heat energy)
- The units for enthalpy change are kJ mol^{-1}

2) Entropy and Free-energy

- As a general rule, once an exothermic reaction has started it produces enough energy to keep it 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. NaHCO_3 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**

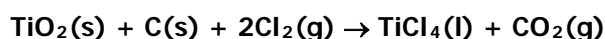
- For a chemical reaction to be feasible (possible) the amount of disorder in the universe must not decrease
- Fortunately, we do not have to do measurements on the universe to find out whether a reaction is feasible. Instead we define a quantity called the free energy change, ΔG , and it can be shown 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

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

- It follows from this formula that feasibility is dependent on temperature
- An exothermic reaction with a positive entropy change will be feasible at all temperatures
- An endothermic reaction with a negative entropy change will be infeasible at all temperatures
- An exothermic reaction with a reduction in entropy will become feasible at low temperatures (when ΔH outweighs $T\Delta S$) – **see example below**
- An endothermic reaction with an increase in entropy will become feasible at high temperatures (when $T\Delta S$ outweighs ΔH)
- 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

$$\begin{aligned} T &= \Delta H/\Delta S \\ &= (-258 \times 1000)/-35.6 \quad (\text{common mistake is to leave out } \times 1000) \\ &= 7247\text{K} \quad (\text{infeasible above this temperature}) \end{aligned}$$

- For changes of state, such as melting and boiling, $\Delta G = 0$ and the two states are in equilibrium

3) 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 $\text{NaCl}(\text{s})$ 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_{LE} e.g. $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$

Hess's Law says:

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

- 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 due to the attraction between the nucleus and the external electron
- The second electron affinity is endothermic because the negative ion repels the negatively charged electron
- Lattice formation is an exothermic process, ΔH_{LE} is negative; lattice dissociation is endothermic, ΔH_{LE} is positive. Both lattice enthalpies have the same numerical value but have opposite signs

4) Enthalpies of Solution

The steps involved in forming $\text{NaCl}(\text{aq})$ are shown below.

- Solution, ΔH_{sol} e.g. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- Lattice dissociation or formation, ΔH_{latt} e.g. $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$
or $\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NaCl}(\text{s})$
- 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. $\text{Cl}^-(\text{g}) \rightarrow \text{Cl}^-(\text{aq})$

If given lattice formation enthalpy use:

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

If given lattice dissociation enthalpy, either change sign to -ve and do above calculation or leave sign +ve and use:

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

5) Effect of ionic charge and ionic radius

- As ionic charge increases, lattice enthalpy becomes more exothermic e.g. MgCl_2 has a more exothermic lattice enthalpy than NaCl because Mg^{2+} 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 Mg^{2+} has a smaller ionic radius than Ca^{2+} . 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

6) Perfect Ionic Model

- Lattice enthalpy (LE) is a measure of the strength of attraction between ions. The more negative the lattice enthalpy of formation, the stronger the attraction and the stronger the ionic bonding.
- The lattice enthalpy values obtained by using Born-Haber cycles are determined by experiment and reflect the actual value.
- It is also possible to calculate the lattice enthalpy by visualizing the ionic lattice as made up of perfectly spherical ions in a lattice (the perfect ionic model).
- In some ionic compounds, the experimental lattice enthalpy of formation is more negative than predicted by the perfect ionic model i.e. the compound is more stable than expected. (When considering lattice enthalpy of dissociation, the experimental value will be more positive than the calculated value.)
- This discrepancy is caused by covalent character which exists in the ionic lattice. This covalent character makes the forces in the lattice stronger than purely ionic forces (i.e. there is extra bonding)
- The covalent character is caused by polarisation of ions
- The extent of the polarisation depends on how much the cation pulls on the electrons; the polarising power, and on how much the anion allows the electrons to be pulled away; the polarisability.
- Polarising power is increased by higher positive charge and smaller cation.
- Polarisability is increased by higher negative charge and larger anion

Compound	Experimental LE value / kJmol^{-1}	Theoretical LE value / kJmol^{-1}	Difference in LE values / kJmol^{-1}
MgF_2	-2957	-2913	44
MgI_2	-2327	-1944	383

- In the above example, F^- is small and not significantly polarized by Mg^{2+} whereas I^- is large and more polarisable leading to increased covalent character and a more negative LE than predicted by the perfect ionic model.

6) Dissolving

- When positive ions dissolve, there is an attraction between the ion and the δ^- O of a water molecule
- When negative ions dissolve, there is an attraction between the ion and the δ^+ H of a water molecule
- These are called ion-dipole attractions

