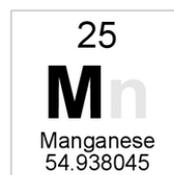
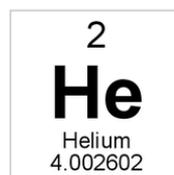
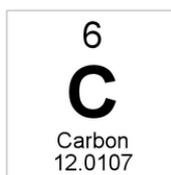
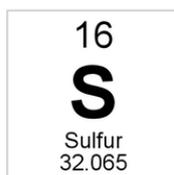
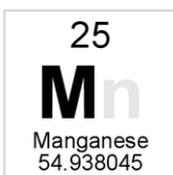


Energetics HL

IB CHEMISTRY HL



15.1 Energy cycles

Understandings:

- Representative equations (e.g $M^{+}_{(g)} \rightarrow M^{+}_{(aq)}$) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond and solution.
- Enthalpy of solution, hydration enthalpy and lattice enthalpy are related in an energy cycle.

Applications and skills:

- Construction of Born-Haber cycles for group 1 and 2 oxides and chlorides.
- Construction of energy cycles from hydration, lattice and solution enthalpy. For example, dissolution of solid NaOH or NH_4Cl in water.
- Calculation of enthalpy changes from Born-Haber or dissolution energy cycles.
- Relate size and charge of ions to lattice and hydration enthalpies.
- Perform lab experiments which could include single replacement reactions in aqueous solutions.

Guidance:

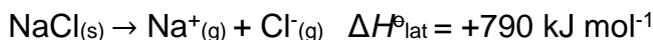
- Polarizing effect of some ions producing covalent character in some largely ionic substances will not be assessed.
- The following enthalpy/energy terms should be covered: ionization, atomization, electron affinity, lattice, covalent bond, hydration and solution.
- Value for lattice enthalpies (section 18), enthalpies of aqueous solutions (section 19) and enthalpies of hydration (section 20).

Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Construct Born-Haber cycles for group 1 and 2 oxides and chlorides			
Calculate the lattice enthalpy and enthalpy of formation from a Born-Haber cycle			
Explain the factors that affect the value of the lattice enthalpy			
Construct energy cycles for the enthalpy change of solution			
Calculate the enthalpy change of solution from an energy cycle			
Explain the factors that affect the value of the hydration enthalpy			

Lattice enthalpy ($\Delta H^{\circ}_{\text{lat}}$)

- Lattice enthalpy ($\Delta H^{\circ}_{\text{lat}}$) is the enthalpy change when one mole of solid ionic compound is separated into its gaseous ions under standard conditions.



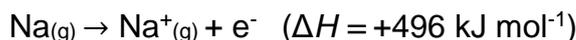
- Note that $\Delta H^{\circ}_{\text{lat}}$ is endothermic and has a positive ΔH .
- A Born-Haber cycle is an enthalpy cycle that can be used to calculate the lattice enthalpy or enthalpy of formation of an ionic compound.

Some important definitions:

- Enthalpy of atomisation ($\Delta H^{\circ}_{\text{atom}}$)** – the enthalpy change when one mole of gaseous atoms is formed from an element in its standard state (endothermic).



- First ionisation energy (ΔH°_i)** – the energy required to remove one mole of electrons from one mole of gaseous atoms (endothermic).



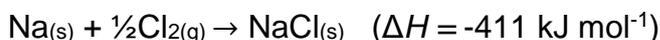
- Bond dissociation enthalpy (E)** – the enthalpy change when one mole of bonds is broken in the gaseous state (endothermic).



- First electron affinity ($\Delta H^{\circ}_{e^{-}}$)** – the enthalpy change when one mole of electrons are added to one mole of gaseous atoms (exothermic).

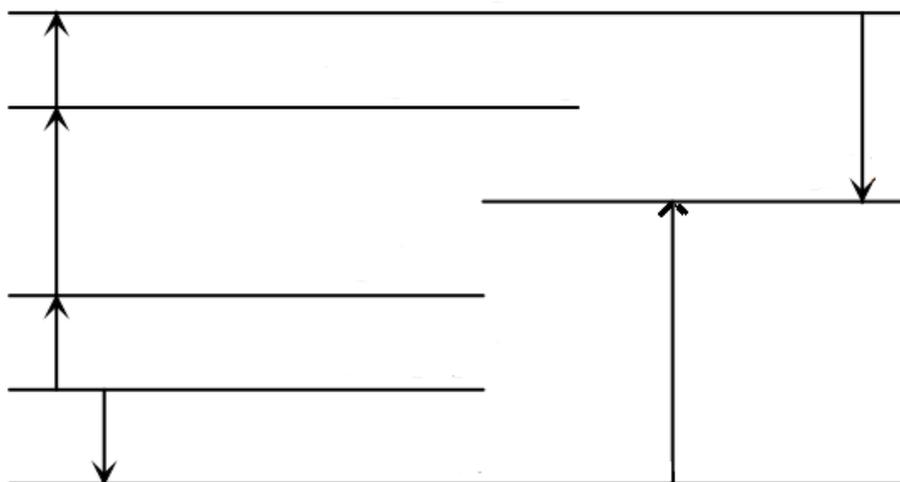


- Standard enthalpy change of formation (ΔH°_f)** – the enthalpy change when one mole of a compound is formed from its elements in their standard states under standard conditions.



Exercises:

- Using the values given above, construct a Born-Haber cycle using the template below and calculate the $\Delta H_{\text{lat}}^{\ominus}$ for NaCl.



- Using the values given in the table below, construct a Born-Haber cycle and calculate the $\Delta H_{\text{f}}^{\ominus}$ for CaF_2

$\Delta H_{\text{atom}} \text{Ca}_{(\text{s})}$ (enthalpy of atomization)	+179 kJ mol ⁻¹
$E \text{F}_{2(\text{g})}$ (bond dissociation enthalpy)	+158 kJ mol ⁻¹
$\Delta H_{\text{i}}^{\ominus} \text{Ca}_{(\text{g})}$ (1 st ionisation energy)	+590 kJ mol ⁻¹
$\Delta H_{\text{i}}^{\ominus} \text{Ca}^{+}_{(\text{g})}$ (2 nd ionisation energy)	+1150 kJ mol ⁻¹
$\Delta H_{\text{e}}^{\ominus} \text{F}_{(\text{g})}$ (first electron affinity)	-328 kJ mol ⁻¹
$\Delta H_{\text{lat}} \text{CaF}_{2(\text{s})}$ (lattice enthalpy)	+2651 kJ mol ⁻¹

Factors that affect lattice enthalpy

- There are two factors that affect the value of the lattice enthalpy, the charge on the ions and the ionic radius of the ions.
- Ions with a higher charge have a stronger force of attraction, therefore a higher lattice enthalpy.
- Smaller ions have a stronger force of attraction, therefore a higher lattice enthalpy.

Exercises:

1. Which has the higher lattice enthalpy, MgCl_2 or NaCl ?

2. Which has the higher lattice enthalpy, NaBr or KBr ?

3. Arrange the following in order of increasing magnitude of lattice enthalpy (lowest first).

MgO NaCl KCl MgS

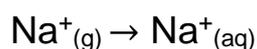
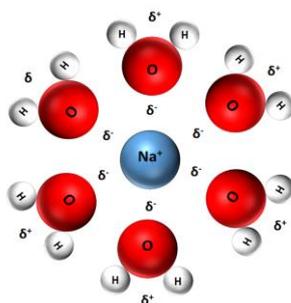
Enthalpies of solution and hydration

Enthalpy of solution $\Delta H^{\circ}_{\text{sol}}$

- The enthalpy change of solution ($\Delta H^{\circ}_{\text{sol}}$) is the enthalpy change when one mole of an ionic substance dissolves in water to give a solution of infinite dilution.
- A solution of infinite dilution is one where there is a sufficiently large excess of water that adding any more does not cause any further heat to be absorbed or evolved.

Enthalpy of hydration $\Delta H^{\circ}_{\text{hyd}}$

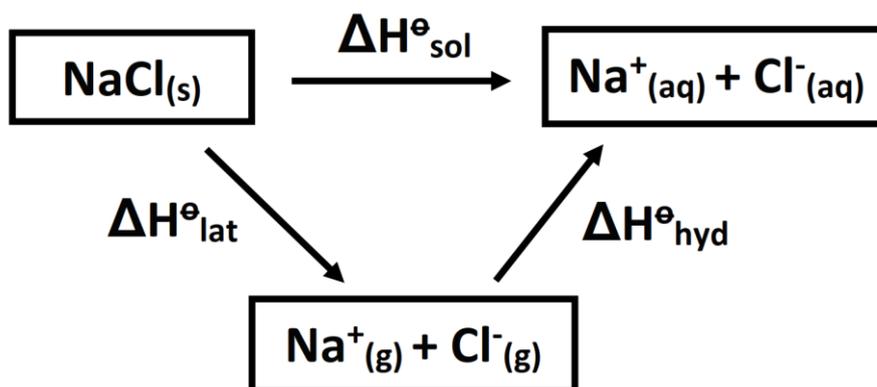
- The enthalpy of hydration ($\Delta H^{\circ}_{\text{hyd}}$) is the enthalpy change when one mole of gaseous ions dissolve in water to give a solution of infinite dilution.
- When a gaseous ion is hydrated, ion-dipole forces occur between the gaseous ion and the dipoles of the water molecule.
- The formation of ion-dipole forces releases energy so ΔH_{hyd} values are always negative.
- The higher the charge on the ion and the smaller the ionic radius, the more exothermic the value of the ΔH_{hyd} .



Dissolving

- The dissolving process can be broken down into two steps.
- The solid ionic compound is broken down into its gaseous ions ($\Delta H^{\circ}_{\text{lat}}$).
- The gaseous ions are hydrated by water molecules ($\Delta H^{\circ}_{\text{hyd}}$).
- This can be represented as the enthalpy cycle shown below.

Enthalpy cycle for the dissolving of $\text{NaCl}_{(s)}$



$$\Delta H^{\circ}_{\text{sol}} = \Delta H^{\circ}_{\text{lat}} + \Delta H^{\circ}_{\text{hyd}}$$

Exercises:

1. Construct an enthalpy cycle and calculate the enthalpy change of solution ($\Delta H^{\circ}_{\text{sol}}$) for calcium fluoride (CaF_2).

$\Delta H^{\circ}_{\text{hyd}} \text{Ca}^{2+}$ (kJ mol^{-1})	-1616
$\Delta H^{\circ}_{\text{hyd}} \text{F}^{-}$ (kJ mol^{-1})	-504
$\Delta H^{\circ}_{\text{lat}} (\text{CaF}_2)$ (kJ mol^{-1})	+2651

2. Construct an enthalpy cycle and calculate the lattice enthalpy ($\Delta H^{\circ}_{\text{lat}}$) for NaOH.

$\Delta H^{\circ}_{\text{hyd}} \text{Na}^{+}$ (kJ mol^{-1})	-424
$\Delta H^{\circ}_{\text{hyd}} \text{OH}^{-}$ (kJ mol^{-1})	-519
$\Delta H^{\circ}_{\text{sol}} (\text{NaOH})$ (kJ mol^{-1})	-44.5

15.2 Entropy and spontaneity

Understandings:

- Entropy (S) refers to the distribution of available energy among the particles. The more ways the energy can be distributed the higher the entropy.
- Gibbs free energy (G) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS), and absolute temperature (T).
- Entropy of gas > liquid > solid under same conditions.

Applications and skills:

- Prediction of whether a change will result in an increase or decrease in entropy by considering the states of the reactants and products.
- Calculation of entropy changes (ΔS) from given standard entropy values (S^\ominus).
- Application of $\Delta G = \Delta H - T\Delta S$
- Relation of ΔG to position of equilibrium.

Guidance:

- Examine various reaction conditions that affect ΔG .
- ΔG is a convenient way to take into account both the direct entropy change resulting from the transformation of the chemicals, and the indirect entropy change of the surroundings as a result of the gain/loss of heat energy.

Syllabus checklist

Objective	I am confident with this	I need to review this	I need help with this
Predict, by looking at the state symbols of reactants and products, whether a reaction has an increase or decrease in entropy.			
Calculate changes in entropy using standard entropy values			
Calculate the ΔG for a reaction using the equation using the equation $\Delta G = \Delta H - T\Delta S$			
Explain the effect of ΔH , ΔS and T on the spontaneity of a chemical reaction			

Spontaneity

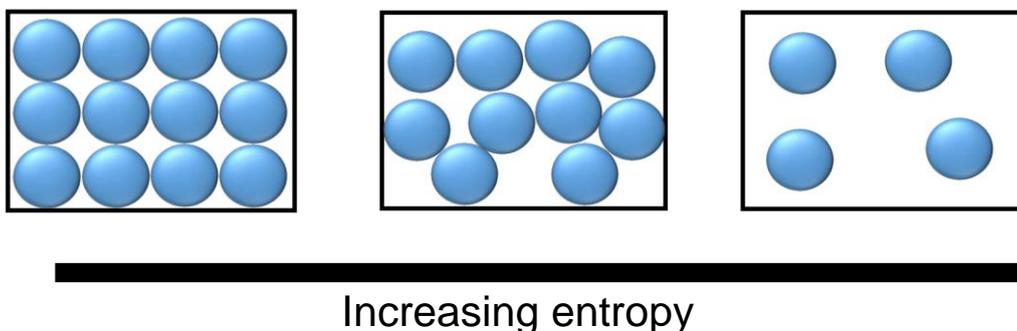
- A spontaneous process is a process that occurs without adding energy (other than the energy required to overcome the energy barrier).



- Spontaneous processes can be either fast or slow; both combustion and rusting are spontaneous processes but occur at very different rates.

Entropy (S)

- Entropy (S) refers to the distribution of available energy among the particles in a system.
- The more ways the energy can be distributed, the greater the entropy.
- Gases have a higher entropy than liquids which have a higher entropy than solids.
- Entropy increases as temperature increases.



- The table below has absolute entropy values for ice, liquid water and steam.
- The entropy increases from $\text{H}_2\text{O}_{(s)}$ to $\text{H}_2\text{O}_{(g)}$.

State of matter	Absolute entropy (S^\ominus) $\text{J K}^{-1} \text{mol}^{-1}$
$\text{H}_2\text{O}_{(s)}$	41.3
$\text{H}_2\text{O}_{(l)}$	70.0
$\text{H}_2\text{O}_{(g)}$	188

Predicting entropy changes

Factors that can change the entropy of a system include:

- changes in temperature
- changes of state (freezing, evaporating)
- dissolving (or crystallisation)
- changes in amounts of gaseous reactants or products

Factors that increase entropy (positive entropy change, + ΔS)

Dissolving	$\text{NaCl}_{(s)} \rightarrow \text{Na}^+_{(aq)} \text{Cl}^-_{(aq)}$
Increase in mol of gas	$\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ $\text{C}_3\text{H}_{8(g)} + 5\text{O}_{2(g)} \rightarrow 3\text{CO}_{2(g)} + 4\text{H}_2\text{O}_{(g)}$ $\text{CH}_4(g) + \text{H}_2\text{O}_{(g)} \rightarrow 3\text{H}_2(g) + \text{CO}_{(g)}$
Changes of state (melting, evaporation / boiling / vaporisation, sublimation)	$\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$

Factors that decrease entropy (negative entropy change, - ΔS)

Crystallisation	$\text{Na}^+_{(aq)} \text{Cl}^-_{(aq)} \rightarrow \text{NaCl}_{(s)}$
Decrease in mol of gas	$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$ $\text{C}_2\text{H}_{4(g)} + \text{H}_{2(g)} \rightarrow \text{C}_2\text{H}_{6(g)}$ $2\text{Mg}_{(s)} + \text{O}_{2(g)} \rightarrow 2\text{MgO}_{(s)}$
Changes of state (freezing, condensation, deposition)	$\text{H}_2\text{O}_{(g)} \rightarrow \text{H}_2\text{O}_{(l)}$

Exercises: Predict the entropy change in the following examples, giving a reason for your choice.

1. $\text{Br}_{2(l)} \rightarrow \text{Br}_{2(g)}$
2. $\text{Na}_2\text{CO}_{3(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{CO}_{2(g)} + 2\text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$
3. $\text{AgNO}_{3(aq)} + \text{NaCl}_{(aq)} \rightarrow \text{AgCl}_{(s)} + \text{NaNO}_{3(aq)}$
4. $2\text{S}_2\text{O}_3^{2-}_{(aq)} + \text{I}_{2(aq)} \rightarrow \text{S}_4\text{O}_6^{2-}_{(aq)} + 2\text{I}^-_{(aq)}$
5. $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$

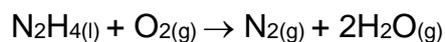
Standard entropy change (ΔS°)

- The standard entropy change of reaction (ΔS°) can be calculated using the equation:

$$\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

- A perfectly ordered crystal at zero kelvin has an entropy of zero.
- Absolute entropy values are always positive.

Example: Calculate the entropy change for this reaction:



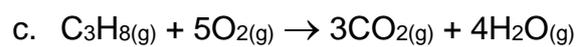
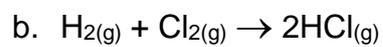
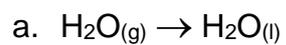
Substance	S° ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{H}_2\text{O}(\text{g})$	188
$\text{O}_2(\text{g})$	205
$\text{N}_2(\text{g})$	192
$\text{N}_2\text{H}_4(\text{l})$	121

Exercises: Use the data in the table to answer the following questions.

Substance	S° ($\text{J K}^{-1} \text{mol}^{-1}$)	Substance	S° ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{H}_2\text{O}(\text{g})$	189	$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	70	$\text{C}_3\text{H}_8(\text{g})$	270
$\text{H}_2(\text{g})$	131	$\text{O}_2(\text{g})$	205
$\text{Cl}_2(\text{g})$	223		
$\text{HCl}(\text{g})$	187		

- Predict the sign of ΔS° for the following reactions and explain your reasoning.
 - $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
 - $\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$

2. Calculate ΔS° for the above reactions.



Gibbs free energy

- The energy associated with a chemical reaction that can be used to do work.
- ΔG must be negative for a spontaneous process.

$$\Delta G = \Delta H - T\Delta S$$

ΔG – Gibbs free energy change (kJ mol^{-1})

ΔH – change in enthalpy (kJ mol^{-1})

T – temperature in kelvin, K

ΔS – change in entropy ($\text{J K}^{-1} \text{mol}^{-1}$)

Example: Calculate ΔG for this reaction at 500 K, using the data in the table. State and explain if the reaction is spontaneous at this temperature.



Compound	ΔH_f° (kJ mol^{-1})	S° ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{CaCO}_{3(\text{s})}$	-1207	92.9
$\text{CaO}_{(\text{s})}$	-635	39.7
$\text{CO}_{2(\text{g})}$	-394	214

Determine the temperature at which the reaction will be spontaneous.

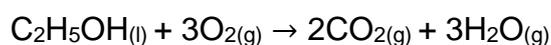
Standard change in Gibbs free energy (ΔG^\ominus)

- The standard change in Gibbs free energy (ΔG^\ominus) is the change in Gibbs free energy measured under standard conditions (298 K and 100 kPa).

$$\Delta G^\ominus = \sum \Delta G_f^\ominus \text{ products} - \sum \Delta G_f^\ominus \text{ reactants}$$

- ΔG_f^\ominus – the standard Gibbs free energy of formation is the change in Gibbs free energy when one mole of a compound is formed from its elements in their standard states under standard conditions (100 kPa and 298 K).

Example: Calculate the ΔG^\ominus for the following reaction. State and explain if the reaction is spontaneous at 298 K.



Compound	ΔG_f^\ominus (kJ mol ⁻¹)
C ₂ H ₅ OH(l)	-175
CO ₂ (g)	-394
H ₂ O(g)	-229

The effect of ΔH , ΔS and T on the spontaneity of a chemical reaction

Exothermic reactions

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	positive > 0	any temperature		

- ΔH is negative and ΔS is positive, therefore ΔG will be negative at any temperature.
- An exothermic reaction with an increase in entropy will be spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	high		

ΔH	ΔS	T	ΔG	spontaneity
negative < 0	negative < 0	low		

- ΔG will be negative only at low temperatures; at high T, ($T\Delta S$) makes ΔG positive.

Endothermic reactions

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	negative < 0	any temperature		

- ΔH is positive and ΔS is negative, therefore ΔG will be positive at any temperature.
- An endothermic reaction with a decrease in entropy will be non-spontaneous at any temperature.

ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	high		

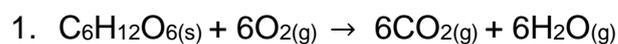
ΔH	ΔS	T	ΔG	spontaneity
positive > 0	positive > 0	low		

- ΔG will be negative only at high temperatures ($T\Delta S > \Delta H$); at low temperatures $\Delta H > T\Delta S$ ($+\Delta G$).

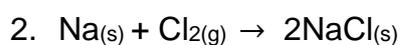
Summary

ΔS		
$\Delta H < 0 \quad \Delta S > 0$ Spontaneous at any temperature		$\Delta H > 0 \quad \Delta S > 0$ Spontaneous at high temperatures
		ΔH
$\Delta H < 0 \quad \Delta S < 0$ Spontaneous at low temperatures		$\Delta H > 0 \quad \Delta S < 0$ Non-spontaneous at any temperature

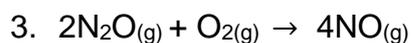
Exercises: Determine the spontaneity of the following reactions, giving a reason for your answer.



$$\Delta H < 0 \quad \Delta S > 0$$



$$\Delta H < 0 \quad \Delta S < 0$$



$$\Delta H > 0 \quad \Delta S > 0$$