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Junior College 1

The Ultimate Exam Revision Notes

Syllabus 9476

H2 Chemistry

Chemical Energetics

Many students tend to mix up or forget key definitions such as enthalpy change of reaction, formation, combustion, neutralisation, and atomisation. They also often struggle to rearrange equations and apply Hess' Law accurately when calculating unknown enthalpy changes.

Use this revision notes to help you decide whether you need to reinforce your basics or move ahead with more challenging questions.

Attempt all questions before checking the answers — practice makes progress.

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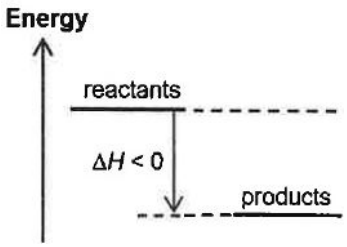
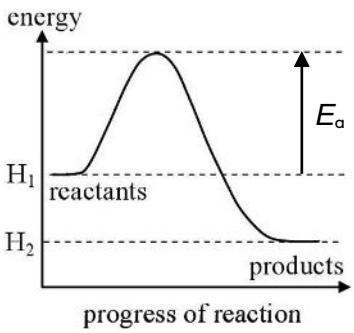
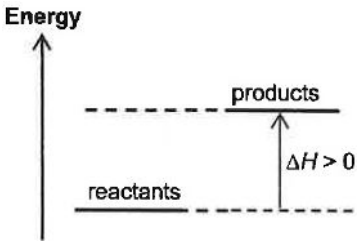
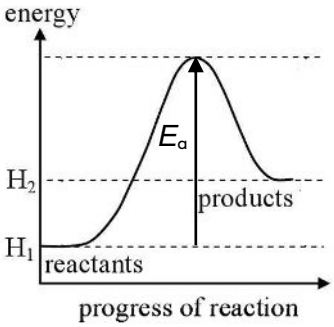
Chapter 10. Chemical Energetics

Enthalpy Changes

- **Enthalpy** (*H*) is a measure of energy content in a system. The higher the enthalpy, the less thermodynamically stable the substance.
- **Enthalpy change** (ΔH) of a reaction is the change in the amount of heat energy in the system due to the chemical reaction.

Exothermic Reactions	Endothermic Reactions
• Heat is released from the reacting system. • Temperature of surroundings increases.	• Heat is absorbed into the reacting system. • Temperature of surroundings decreases.
Energy Level Diagram  *Energy Profile Diagram*  	*Energy Level Diagram*  *Energy Profile Diagram* 
• As energy level of products is lower than that of reactants, $\Delta H < 0$. • Products are more stable than reactants.	• As energy level of products is higher than that of reactants, $\Delta H > 0$. • Products are less stable than reactants.
• Bond formation is exothermic process.	• Bond breaking is endothermic process.

- Elements in their standard state (e.g. $S_8(s)$, $Br_2(l)$, $H_2(g)$) are usually defined to have zero enthalpy.

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Definitions of Enthalpy Change

Standard conditions

- Temperature: 25 °C (or 298 K)
- Pressure: 1 bar (or 10^5 Pa)

standard enthalpy change of	symbol and type	definition, notes and example
formation	$\Delta H_f^\ominus$ endo or exo	energy change when <u>one mole of a species is formed</u> from its <u>constituent elements in standard states</u> at 298 K and 1 bar • $\Delta H_f^\ominus$(elements) = 0 kJ mol^{-1} • e.g. $H_2(g) + S(s) + 2\ O_2(g) \rightarrow H_2SO_4(l)$ $H_2(g) + P(s) + 2\ O_2(g) + e^- \rightarrow H_2PO_4^-(aq)$ Some schools prefer $S_8(s)$ and $P_4(s)$ • The more negative the $\Delta H_f^\ominus$ of a compound, the more stable the compound is relative to its constituent elements.
combustion	$\Delta H_c^\ominus$ exo	energy <u>released</u> when <u>one mole of a substance is completely burned in excess oxygen at 298 K</u> and 1 bar • $\Delta H_c^\ominus(CO_2)$ = 0 kJ mol^{-1}, $\Delta H_c^\ominus(H_2O)$ = 0 kJ mol^{-1} • e.g. $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$
neutralisation	$\Delta H_{neut}^\ominus$ exo	energy <u>released</u> when <u>one mole of water is formed</u> from the <u>neutralisation of an acid and an alkali</u> at 298 K and 1 bar • Typically exothermic because of (covalent) <u>bond formed</u> between H^+ and OH^- to form H_2O (in the ionic equation). • Weak acids/alkalis will have <u>less exothermic</u> $\Delta H_{neut}^\ominus$ as energy is required to fully ionise the weak acids/alkalis. • e.g. ½ $Ba(OH)_2(aq) + HCl(aq) \rightarrow$ ½ $BaCl_2(aq) + H_2O(l)$ • $\Delta H_{neut}^\ominus$ between strong bases and strong acids ≈ −57 kJ mol^{-1} • $\Delta H_{neut}^\ominus$ <u>can be endothermic</u> if the acid and base used are <u>very weak</u>. However, this is <u>very rare</u>.
lattice energy	$\Delta H_{latt}^\ominus$ exo	energy <u>released</u> when <u>one mole of a solid ionic compound is formed from its constituent gaseous ions</u> at 298 K and 1 bar • ionic bond strength $\propto \lvert\Delta H_{latt}^\ominus\rvert \propto \left\lvert \frac{q_+ \times q_-}{r_+ + r_-} \right\rvert$ • since ionic bonds are formed, $\Delta H_{latt}^\ominus < 0$. • e.g. $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$ • theoretical LE deviation from experimental LE arises when ionic bond has covalent character

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standard enthalpy change of	symbol and type	definition, notes and example

solution	$\Delta H_{sol}^{\ominus}$
	endo or exo
		energy change when one mole of solute is completely dissolved in a solvent to form an infinitely dilute solution at 298 K and 1 bar
		• the dissolution of an ionic salt involves:
		  ○ breaking ionic bonds in the ionic solute
		  ○ forming ion-dipole interactions between ions and water
		• more exothermic $\Delta H_{sol}^{\ominus} \Longrightarrow$ more soluble ionic salt.
		• e.g. $CaBr_2(s) \rightarrow Ca^{2+}(aq) + 2\ Br^-(aq)$

hydration	$\Delta H_{hyd}^{\ominus}$ exo	energy released when one mole of a gaseous ion is dissolved in a large amount of water at 298 K and 1 bar • strength of ion-dipole interaction $\propto \Delta H_{hyd}^{\ominus} \propto \left\lvert\frac{q_+}{r_+}\right\rvert$ or $\left\lvert\frac{q_-}{r_-}\right\rvert$ • Since ion-dipole interactions are formed, $\Delta H_{hyd}^{\ominus} < 0$. • e.g. $Na^+(g) \rightarrow Na^+(aq)$
bond dissociation energy	BDE endo	exact energy absorbed to break one mole of a particular gaseous covalent bond to give gaseous atoms • All species in the reaction must be in the gaseous state. • Since covalent bonds are broken, BDE is endothermic. • e.g. $H—Br(g) \rightarrow H(g) + Br(g)$
bond energy	BE endo	average energy absorbed to break one mole of gaseous covalent bonds to give gaseous atoms • average value of different X-Y bond energies obtained from different compounds containing the X-Y bond • Since covalent bonds are broken, BE is endothermic. • All species in the reaction must be in the gaseous state. • e.g. $H—Br(g) \rightarrow H(g) + Br(g)$
atomisation	$\Delta H_{at}^{\ominus}$ endo	energy absorbed when one mole of gaseous atoms is formed from its element at 298 K and 1 bar • $\Delta H_{at}^{\ominus}$(noble gases) = 0 kJ mol^{-1} • For diatomic gases $\mathbf{X}_2$, BE($\mathbf{X}$–$\mathbf{X}$) = $2\Delta H_{at}^{\ominus}[\mathbf{X}_2(g)]$. • Since bonds/intermolecular forces are broken, $\Delta H_{at}^{\ominus} < 0$. • e.g. $\frac{1}{2} Br_2(l) \rightarrow Br(g)$

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standard enthalpy change of	symbol and type	definition, notes and example
ionisation energy	IE_1 endo	**First ionisation energy (1st IE)** energy absorbed to remove one mole of electrons from one mole of gaseous atoms of the element to form one mole of a singly positively charged gaseous cations • Since electrostatic attraction between nucleus and valence electrons are overcome, IE > 0. • e.g. $Mg(g) \rightarrow Mg^+(g) + e^-$
	IE_2 endo	**Second ionisation energy (2nd IE)** energy absorbed to remove one mole of electrons from one mole of gaseous singly charged gaseous cations to form one mole of doubly charged gaseous cations • 2nd IE is more endo than 1st IE due to stronger electrostatic attractions between the cation and the electron. • e.g., $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$
electron affinity	EA 1st EA exo	**First electron affinity (1st EA)** energy released when one mole of electrons is added to one mole of gaseous atoms to form one mole of singly negatively charged gaseous ions • 1st EA is exothermic as electrostatic attraction between nucleus and incoming electrons are formed. • e.g. $Br(g) + e^- \rightarrow Br^-(g)$
	2nd EA endo	**Second electron affinity (2nd EA)** energy absorbed when one mole of electrons is added to one mole of singly negatively charged gaseous ions to form one mole of doubly negatively charged gaseous ions • 2nd EA (and subsequent EAs) are endothermic as additional energy is required to overcome electrostatic repulsion between anion and incoming electron. • e.g. $Br^-(g) + e^- \rightarrow Br^{2-}(g)$

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Hess' Law

Hess' law states that the enthalpy change accompanying a chemical reaction is the same regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.

General steps to construct an energy cycle and calculate Δ*H* of a reaction:

Step 1. Write the balanced equations (including state symbols) for all the reactions.

Step 2. Start the energy cycle by writing down the most 'complicated' reaction (usually the reaction with the greatest number of atoms).

Step 3. Complete the cycle by adding in equations which correspond to the data given, ensuring that all stages are balanced.

Step 4. Write the corresponding Δ*H* values next to the arrows, taking particular care of the sign and multiplier.

Step 5. Apply Hess' law to calculate the enthalpy change required.

sum of clockwise arrows = sum of anti-clockwise arrows

Worked Example

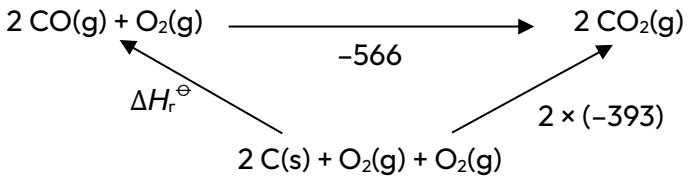
You are provided with the following information.

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^{\ominus} = -393\ kJ\ mol^{-1}$

$2\ CO(g) + O_2(g) \rightarrow 2\ CO_2(g)$ $\quad \Delta H^{\ominus} = -566\ kJ\ mol^{-1}$

Using Hess' law, calculate $\Delta H_r^{\ominus}$ for the reaction: $2\ C(s) + O_2(g) \rightarrow 2\ CO(g)$.

Solution



By Hess' law,

$$2 \times (-393) = \Delta H_r^{\ominus} + (-566)$$

$$\Delta H_r^{\ominus} = \underline{-220\ kJ\ mol^{-1}}$$

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Quick Formulae

Calculation Type	Quick Formula
Formation	$\Delta H_r^\ominus = \sum \Delta H_f^\ominus$(products) – $\sum \Delta H_f^\ominus$(reactants)
Combustion	$\Delta H_r^\ominus = \sum \Delta H_c^\ominus$(reactants) – $\sum \Delta H_c^\ominus$(products)
Bond energies	$\Delta H_r^\ominus = \sum$ BE(bonds broken in reactants) – $\sum$ BE(bonds formed in products)

Worked Example

You are given the following data.

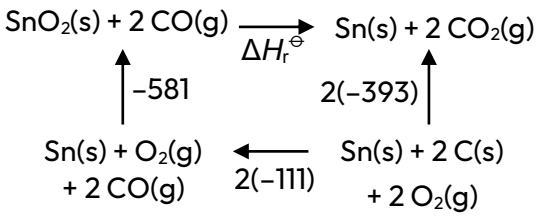
Substance	$SnO_2(s)$	$CO_2(g)$	$CO(g)$
$\Delta H_f^\ominus$ / kJ mol^{-1}	–581	–393	–111

Calculate the standard enthalpy change accompanying the following reaction.

$$SnO_2(s) + 2\,CO(g) \rightarrow Sn(s) + 2\,CO_2(g)$$

Solution

Method 1: By Energy Cycle



By Hess' Law,

$$\Delta H_r^\ominus + (-581) + 2(-111) = 2(-393)$$

$$\Delta H_r^\ominus = \underline{+17.0 \text{ kJ mol}^{-1}}$$

Method 2: By Formula

$\Delta H_r^\ominus = \sum \Delta H_f^\ominus$(products) – $\sum \Delta H_f^\ominus$(reactants)

$\Delta H_r^\ominus = 2(-393) + 0 - [(-581) + 2(-111)]$

$\Delta H_r^\ominus = \underline{+17.0 \text{ kJ mol}^{-1}}$

$\Delta H_f^\ominus$ (elements) = 0

Worked Example (involving ΔH_c°)

Calculate standard enthalpy change of formation of methane given following information.

Substance	C(s)	$H_2(g)$	$CH_4(g)$
$\Delta H_c^\ominus$ / kJ mol^{-1}	–393	–286	–887

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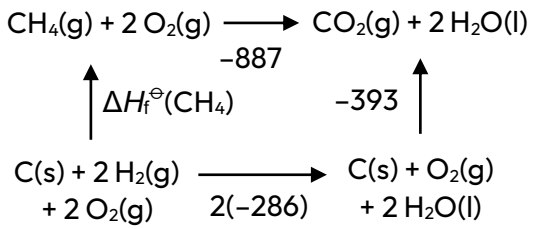
Solution

$$C(s) + 2\,H_2(g) \rightarrow CH_4(g) \qquad \Delta H_r^{\ominus}(CH_4)$$

Method 1: By Energy Cycle



By Hess' law,

$\Delta H_f^{\ominus}(CH_4) + (-887) = 2(-286) + (-393)$

$\Delta H_f^{\ominus}(CH_4) = 2(-286) + (-393) - (-887)$

$\Delta H_f^{\ominus}(CH_4) = \underline{-78.0\ kJ\ mol^{-1}}$

Method 2: By Formula

$\Delta H_r^{\ominus} = \sum \Delta H_c^{\ominus}(\text{reactants}) - \sum \Delta H_c^{\ominus}(\text{products})$

$\Delta H_f^{\ominus}(CH_4) = 2(-286) + (-393) - (-887)$

$\Delta H_f^{\ominus}(CH_4) = \underline{-78.0\ kJ\ mol^{-1}}$

Remember to consider the stoichiometry.

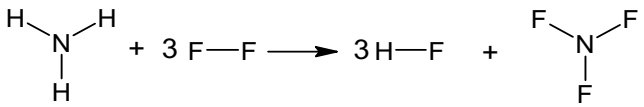
Worked Example (Involving bond energy)

Given the bond energies in the table below, find the enthalpy change for the reaction

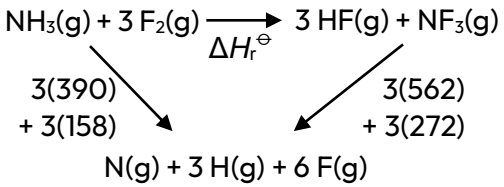
$$NH_3(g) + 3\,F_2(g) \rightarrow 3\,HF(g) + NF_3(g),$$

bond	N–H	F–F	H–F	N–F
bond energy / kJ mol^{-1}	390	158	562	272

Solution



Method 1: By Energy Cycle



By Hess' law,

$\Delta H_r^{\ominus} + 3(562) + 3(272) = 3(390) + 3(158)$

$\Delta H_r^{\ominus} = \underline{-858\ kJ\ mol^{-1}}$

Method 2: By Formula

$\Delta H_r^{\ominus} = \sum \text{BE(bonds broken in reactant)} - \sum \text{BE(bonds formed in product)}$

$\Delta H_r^{\ominus} = 3(390) + 3(158) - 3(562) - 3(272)$

$= \underline{-858\ kJ\ mol^{-1}}$

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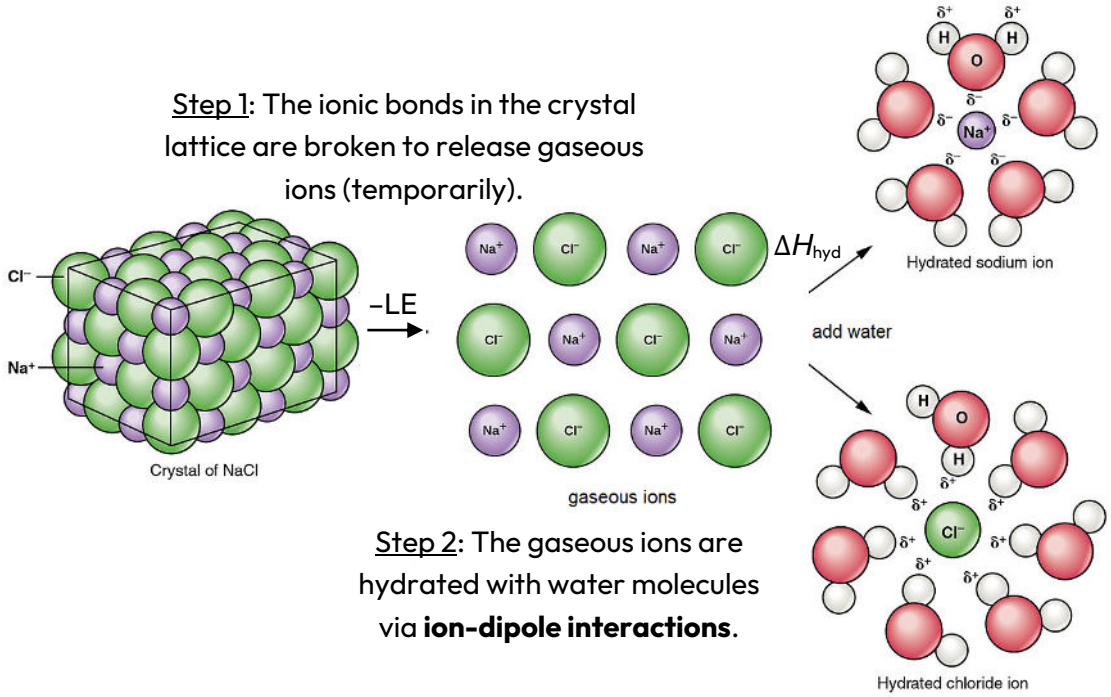
Bond Energies from *Data Booklet*

- Bond energies in polyatomic molecules can be found in the *Data Booklet*. They only represent average values of all molecules containing that bond.
- All species must be in gaseous state.

Dissolution of Ionic Salts



$$\Delta H_{sol}^{\ominus} = \sum \Delta H_{hyd}^{\ominus} - \Delta H_{LE}^{\ominus}$$

ΔH_{soln} can either be exothermic or endothermic. The more exothermic ΔH_{soln} is, the more soluble the ionic compound.	ΔH_{hyd} is exothermic due to the formation of ion-dipole interactions. The magnitude of ΔH_{hyd} is a measure of the strength of ion-dipole interactions. $\Delta H_{hyd} \propto \left\lvert \frac{q^+}{r^+} \right\rvert$ or $\left\lvert \frac{q^-}{r^-} \right\rvert$	ΔH_{LE} is exothermic due to the formation of ionic bonds. The magnitude of lattice energy is a measure of the ionic bond strength. $\Delta H_{LE} \propto \left\lvert \frac{q^+ \times q^-}{r^+ + r^-} \right\rvert$

- Note that ionic charge usually plays a more significant role compared to ionic radius.

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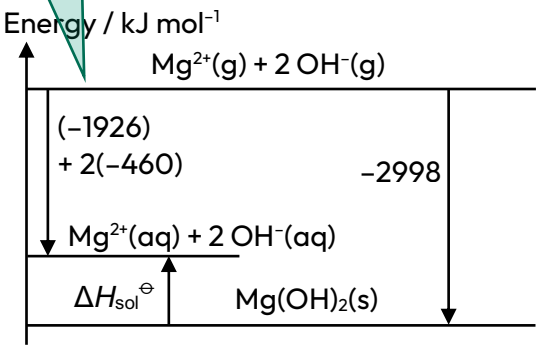
Worked Example (Energetics of dissolution of ionic solids)

Use the enthalpy changes below to calculate the enthalpy change of solution for $Mg(OH)_2$.

enthalpy changes	$\Delta H^{\ominus}$ / kJ mol^{-1}
hydration of Mg^{2+}	–1926
hydration of OH^-	–460
lattice energy of $Mg(OH)_2$	–2998

Tip: Begin with gaseous ions at the highest energy level.

Method 1: By Energy Level or Cycle



By Hess' law,

$(-2998) + \Delta H_{sol}^{\ominus} = (-1926) + 2(-460)$

$\Delta H_{sol}^{\ominus} = \underline{+152 \text{ kJ mol}^{-1}}$

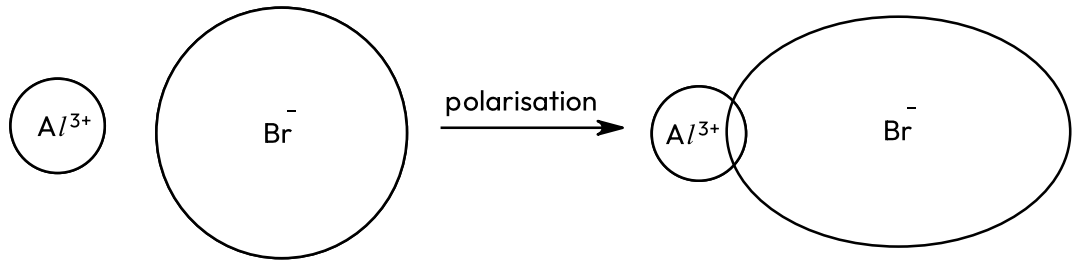
Method 2: By Formula

$\Delta H_{sol}^{\ominus} = \sum \Delta H_{hyd}^{\ominus} - \Delta H_{latt}^{\ominus}$

$\Delta H_{sol}^{\ominus} = (-1926) + 2(-460) - (-2998)$

$\Delta H_{sol}^{\ominus} = \underline{+152 \text{ kJ mol}^{-1}}$

Theoretical and Experimental Lattice Energy



theoretical LE
assumes a **pure ionic model**

experimental LE accounts
for **covalent character in the ionic compound**

- An ionic compound with <u>high charge density in cation (high polarising power)</u> and <u>large electron cloud of anion</u> experiences <u>large polarisation</u>, giving its <u>ionic bond some covalent character</u>. Hence, its experimental lattice energy (LE) deviates from theoretical LE.

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Worked Example

(a) State and explain how the hydration energies of Be^{2+} and Ca^{2+} differ from each other.

Solution

$$\Delta H_{hyd} \propto \left|\frac{q^+}{r^+}\right|$$

Since Be^{2+} and Ca^{2+} have the same ionic charge but Be^{2+} has a smaller ionic radius than Ca^{2+}, Be^{2+} has a higher charge density and polarising power. As such, ion-dipole interactions formed between Be^{2+} and water molecules are stronger, resulting in more exothermic hydration energy.

(b) Explain why beryllium oxide has a more exothermic lattice energy than beryllium carbonate.

Solution

$$\Delta H_{LE} \propto \left|\frac{q^+ \times q^-}{r^+ + r^-}\right|$$

Since oxide ion has a smaller anionic radius than carbonate ion, the ionic bonds formed in beryllium oxide is stronger, resulting in more exothermic lattice energy than beryllium carbonate.

(c) Beryllium oxide has a theoretical and experimental lattice energy of –4430 kJ mol^{-1} and –4500 kJ mol^{-1} respectively. Suggest why there is a discrepancy in the values.

Solution

Be^{2+} has high charge density (high ionic charge and small ionic radius), polarising the anionic cloud of oxide, giving the ionic bond some degree of covalency and leading to a discrepancy between theoretical and experimental lattice energies.

(d) Explain why there is a greater deviation between experimental lattice energy and theoretical lattice energy for $AlCl_3$ than MgF_2.

Solution

- Al^{3+} has a larger charge density and hence, larger polarising power than Mg^{2+} and Cl^- has a larger electron cloud size and is hence more polarisable than F^-.
- $AlCl_3$ has more covalent character than MgF_2 and experiences greater deviation.

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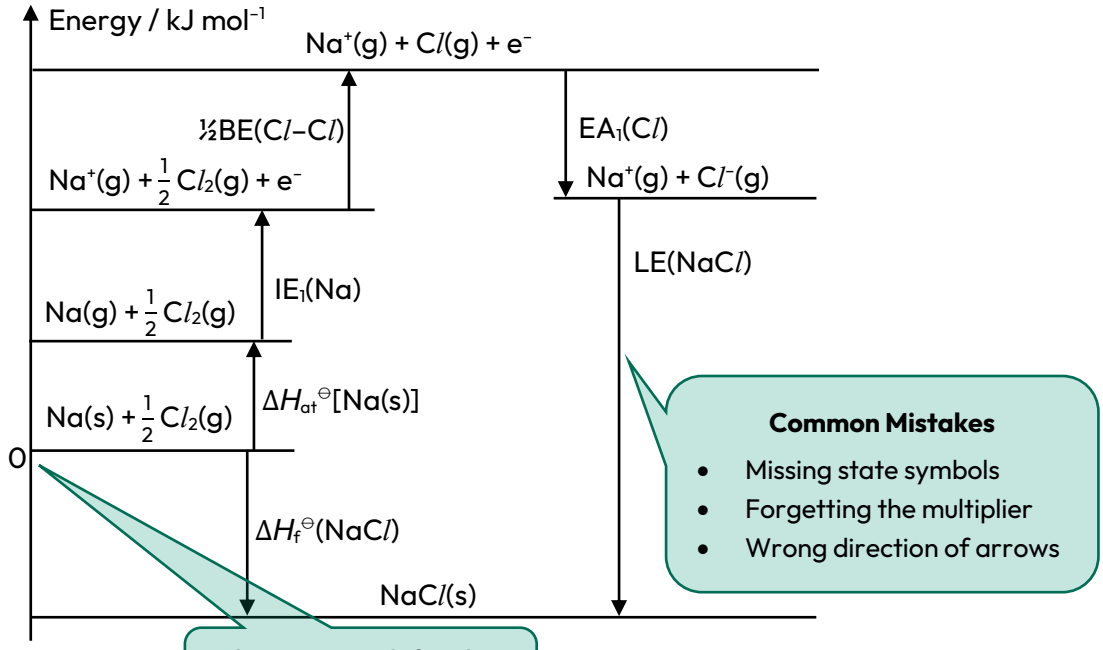
Born-Haber Cycle

➢ The Born-Haber cycle connects the enthalpy change of formation and lattice energy of an ionic solid through an energy level diagram (or energy cycle).



Applying Hess' law,

$$\Delta H_{at}^{\ominus}[Na(s)] + IE_1(Na) + \tfrac{1}{2}BE(Cl–Cl) + EA_1(Cl) + LE(NaCl) = \Delta H_f^{\ominus}(NaCl)$$

Notes:

Elements in their standard state refer to the most stable form of an element at standard conditions, which are 25°C (298 K) and 1 bar pressure.

F

Formation

- ΔH_f is energy change to form 1 mol of the ionic solid from their constituent elements at standard state.
- Elements in standard state are defined to have zero enthalpy.
- ΔH_f of ionic solids are *usually* exothermic.

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

A

Atomisation

- ΔH_{at} is energy absorbed to form 1 mol of gaseous atom from its element at standard state.
- ΔH_{at} is endothermic as energy is required to overcome metallic bonds in metals.

$$Na(s) \rightarrow Na(g)$$

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I

Ionisation Energy

- First ionisation energy is energy absorbed to ionise 1 mol of gaseous metal atoms into its 1 mol of its gaseous cations by removing 1 mol of electrons.
- The values of ionisation energy are found in the *Data Booklet*.
- Ionisation energy is endothermic as energy is required to overcome attractive forces between nucleus of the species and the leaving electron.

$$Na(g) \rightarrow Na^{+}(g) + e^{-}$$

B

Bond Energy

- Bond energy is the energy required to break 1 mol of gaseous covalent bond in non-metals to release gaseous atoms.
- The values of bond energy are found in the *Data Booklet*.
- Bond energy is endothermic as energy is required to break strong covalent bonds in molecules of non-metals.
- For elements that exist as diatomic gaseous molecules at standard conditions, $2\Delta H_{at}$ = BE.

$$Cl\text{–}Cl(g) \rightarrow 2\ Cl(g)$$

E

Electron Affinity

- First electron affinity is the energy released to ionise 1 mol of non-metal gaseous atoms into 1 mol of gaseous anions.
- First electron affinity is exothermic as attractive forces are formed between nucleus and incoming electron.

$$Cl(g) + e^{-} \rightarrow Cl^{-}(g)$$

- Second and subsequent electron affinities will be endothermic as energy is absorbed to overcome the repulsion between anions and the incoming electron (like charges).

$$\text{e.g. } O^{-}(g) + e^{-} \rightarrow O^{2-}(g)$$

L

Lattice Energy

- Lattice energy is energy released to form 1 mol of ionic solid from its gaseous ions.
- Lattice energy is exothermic as energy is released when ionic bonds are formed between gaseous ions.

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s)$$

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Calorimetry

- Heat is released/absorbed by reaction:

$$q_1 = -\Delta H \times n$$

where q_1 is energy change in J,

ΔH is the enthalpy change in J mol^{-1},

n refers to amount of reacted/produced species with a stoichiometric ratio of **1** in the chemical equation. For e.g.,

  - substance combusted if ΔH_c;
  - water produced if ΔH_{neut};
  - solute dissolved if ΔH_{soln}.

- By conservation of energy, all the heat generated will be transferred to either
  - water inside the calorimeter,
  - the calorimeter setup or
  - the surroundings.
- Heat absorbed/released by water:

$$q_2 = mc\Delta T$$

where

q_2 is energy change of water in J,

m is mass of water heated up in g,

c is specific heat capacity of water (4.18 J g^{-1} K^{-1})

$\Delta T = T_{final} - T_{initial}$ is temperature difference in K or °C.

- Heat may be transferred to the calorimetric setup:

$$q_3 = C\Delta T$$

where

C is heat capacity of calorimeter in J K^{-1},

$\Delta T = T_{final} - T_{initial}$ is the temperature difference in K or °C.

- Heat is released to the surroundings.

The process efficiency, E, is given by

$$0 < E < 1$$

If $E = 0$, the process is inefficient, i.e. all the heat produced by reaction is not transferred to the water.

If $E = 1$, the process is efficient, i.e. all the heat produced by reaction is transferred to the water.

$$E \times q_1 = q_2 + q_3$$

Assumptions Made

- If process efficiency is not given, one could assume there is negligible heat loss to the surroundings.
- The solution is dilute enough for its density and specific heat capacity to be the same as water (i.e. 1.0 g cm^{-3} and 4.18 J g^{-1} K^{-1} respectively).

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Worked Example

0.5 g of magnesium powder was added to 80.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid at 22.0°C. The temperature of the mixture rose to 34.5 °C.

If the heat efficiency is 75 %, calculate the enthalpy change of the following reaction. State the assumptions made.

$$Mg(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Solution

$$\text{Amount of Mg} = \frac{0.5}{24.3} = 0.02058 \text{ mol}$$

$$\text{Amount of HC}l = 1.0 \times \frac{80.0}{1000} = 0.0800 \text{ mol}$$

Thus, Mg is limiting reagent while HC*l* is in excess.

Assume that

(1) The specific heat capacity of the solution is 4.18 J g^{-1} K^{-1};

(2) The density of the solution is 1.0 g cm^{-3}.

$q_2 = mc\Delta T$

$q_2 = 80.0 \times 4.18 \times (34.5 - 22.0)$

$q_2 = +4180$ J

$E \times q_1 = q_2$

$0.75 \times q_1 = +4180$

$q_1 = +5573$ J

$q_1 = -\Delta H \times n$

$+5573 = -\Delta H \times 0.02058$

$\Delta H = -270813$ J mol^{-1}

$\Delta H = \underline{-271 \text{ kJ mol}^{-1}}$

After solid Mg has reacted with the acid, the volume of the resulting solution is still at 80.0 cm^3. Do not add mass of solid into volume!

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Worked Example (bomb calorimeter)

A 0.483 g sample of glycine (M_r = 75) was placed in a bomb calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.54°C.

In a separate experiment using the same calorimeter, the combustion of 0.986 g of benzoic acid (M_r = 122) gave a temperature rise of 2.14°C. The enthalpy change of combustion of benzoic acid is −3054 kJ mol^{-1}.

What is the enthalpy change of combustion, in kJ mol^{-1}, of glycine?

Solution

$$n(\text{benzoic acid}) \text{ used} = \frac{0.986}{122} = 0.00808 \text{ mol}$$

$q_1 = -\Delta H \times n$	$q_3 = C\Delta T$
$q_1 = -(-3054 \times 1000) \times 0.00808 = 24682$ J	$24682 = C(2.14)$
	$C = 11534$ J K^{-1}

Note that we have assumed that process efficiency is 100%, i.e. E = 1.

Note that C is the heat capacity of the calorimeter. Since the same calorimeter is used for glycine, the C value will be the same.

$$n(\text{glycine}) \text{ used} = \frac{0.483}{75} = 0.00644 \text{ mol}$$

$q = C\Delta T$	$q = -\Delta H \times n$
$q = (11534)(0.54)$	$6228 = -\Delta H \times 0.00644$
$q = 6228$ J	$\Delta H = -967120$ J mol^{-1} = <u>−967 kJ mol^{-1}</u>

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Entropy Change

Entropy (S) measures the degree of disorder in a system.

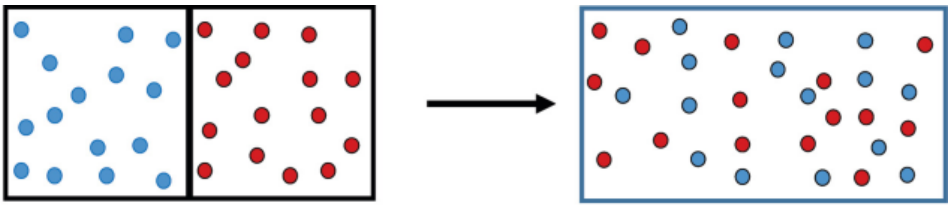
- It is related to the number of ways the particles in the system can be arranged, or the number of ways the energy in the system can be distributed among the particles in the system.
- An increase in disorder results in a larger S value, giving $\Delta S > 0$ (and vice versa).

Factors Affecting Entropy

1. Temperature
   - An increase in temperature increases the average kinetic energy of the particles and broadens the Boltzmann energy distribution of the particles.
   - There are more ways to distribute energy among the particles when the particles adopt a higher temperature, resulting in an increase in disorder and entropy.

2. Mixing of Particles

   Mixing of particles results in an increase in volume available for each gas, giving more ways to arrange the particles, resulting in an increase in disorder and entropy ($\Delta S > 0$).



3. Change in Phase
   - Gaseous particles are the most randomly arranged, followed by liquid particles then solid particles (which have the most ordered arrangement).

$$S_{gas} >> S_{liquid} > S_{solid}$$

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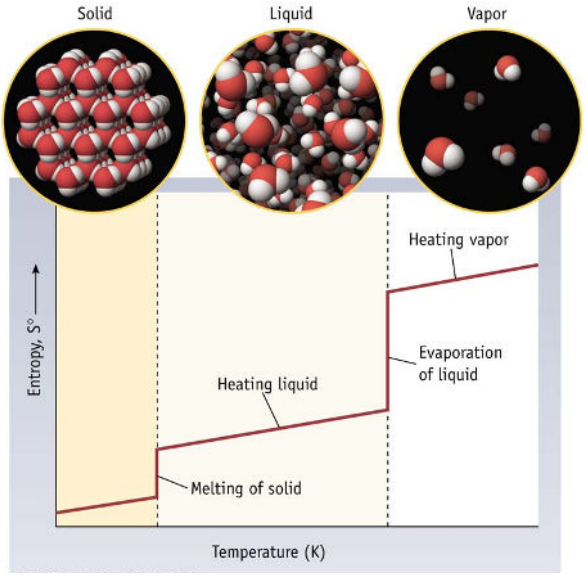
From solid to liquid phase

- When solid melts, the particles move more freely in the liquid state and become more disordered with more ways to distribute the particles and their energy in the liquid state.
- This results in a sudden increase in entropy.



From liquid to gaseous phase (or solid to gaseous phase)

- When a liquid converts to a gas, the particles can move **even more** freely.
- Hence there is a **larger** sudden increase in entropy ($\Delta S >> 0$) as there are **even more** ways to distribute the particles and their energy in the gaseous state.

4. Change in the number of particles (especially for gaseous systems)
   - Gaseous particles have the highest entropy since they are the most randomly arranged.
   - Aqueous species are also free to move about, and hence also have high entropy.
   - A reaction where the products have more gaseous/aqueous species than the reactants will have more ways to arrange the particles, and hence experience an increase in disorder and entropy.
   - Some examples:

chemical reaction	change in particles	change in entropy
$N_2O_4(g) \longrightarrow 2\ NO_2(g)$	no. of gaseous particles increased by 1 mol	$\Delta S > 0$
$C_4H_8(g) + 6\ O_2(g) \longrightarrow 4\ CO_2(g) + 4\ H_2O(l)$	no. of gaseous particles decreased by 3 mol	$\Delta S < 0$
$2\ Na(s) + 2\ HCl(aq) \longrightarrow 2\ NaCl(aq) + H_2(g)$	no. of gaseous particles increased by 1 mol	$\Delta S > 0$
$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$	no. of aqueous particles decreased by 2 mol	$\Delta S < 0$
$N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$	no. of gaseous particles did not change	$\Delta S \approx 0$

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Gibbs' Free Energy Change

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

where ΔG is the Gibbs' free energy change of reaction in kJ mol^{-1},

ΔH is the enthalpy change of reaction in kJ mol^{-1},

T is the absolute temperature in K,

ΔS is the entropy change of reaction in kJ mol^{-1} K^{-1}.

Sign of ΔG	Conclusion
$\Delta G < 0$	forward reaction is spontaneous
$\Delta G = 0$	at equilibrium (e.g. phase changes)
$\Delta G > 0$	forward reaction is not spontaneous

Gibbs free energy change		enthalpy change		entropy change	
indication of spontaneity of reaction		measures change in energy content of reactants and products		measures change in disorder in system	
$\Delta G^{\ominus} > 0$	non-spontaneous	$\Delta H^{\ominus} > 0$	endothermic	$\Delta S^{\ominus} > 0$	more disorder
$\Delta G^{\ominus} = 0$	equilibrium	$\Delta H^{\ominus} < 0$	exothermic	$\Delta S^{\ominus} < 0$	less disorder
$\Delta G^{\ominus} < 0$	spontaneous				

Worked Example (Gibbs free energy change of a phase transition)

52 kJ of energy is required to vaporise 1 mol of liquid butanoic acid ($C_4H_8O_2$) at its boiling point of 118 °C. Calculate the entropy change of vaporisation of butanoic acid at 118 °C.

Solution

Since $\Delta G = 0$ at 118 °C when there is a phase change, we have

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

$$0 = (+52.0) - (118 + 273)\Delta S_{vap}$$

$$\Delta S_{vap} = \underline{+0.133 \text{ kJ mol}^{-1} \text{ K}^{-1}}$$

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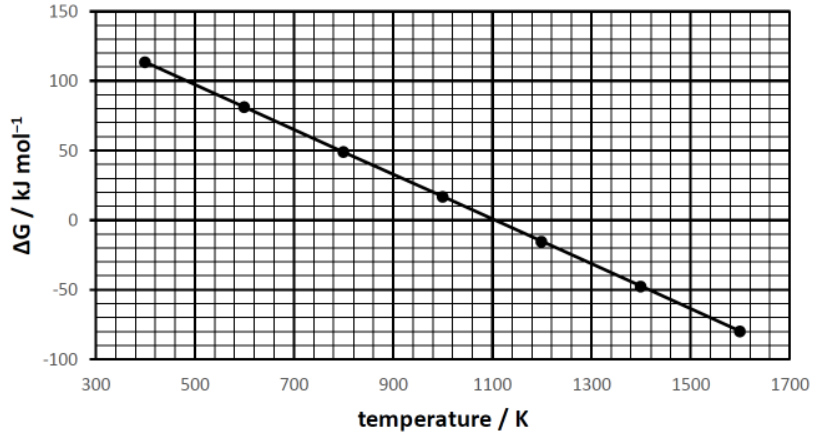
Worked Example (Interpreting an Ellingham diagram)



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

gradient of line = $-\Delta S$

y-intercept = ΔH

Impact of Temperature on $\Delta G^{\ominus}$

- At higher T, the contribution of ΔS to ΔG becomes more significant, thus ΔG will likely follow the sign of $-T\Delta S$.
- At lower T, the contribution of ΔH to ΔG becomes more significant, thus ΔG will likely follow the sign of ΔH.

Case	ΔH	ΔS	$-T\Delta S$	ΔG	Description	Examples	Dependence on temperature
1	–	+	–	–	spontaneous at all T	combustion	independent of temperature
2	+	–	+	+	non-spontaneous at all T	photosynthesis	
3	+	+	–	+ or –	spontaneous at higher T; non-spontaneous at lower T;	melting, boiling	dependent on temperature
4	–	–	+	+ or –	spontaneous at lower T; non-spontaneous at higher T;	condensation, freezing	

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Worked Example (Temperature dependent spontaneity)

Consider the Haber process:

$$N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g) \qquad \Delta H^\ominus = -92.4\ kJ\ mol^{-1}$$

Determine if the reaction is energetically spontaneous at low or high temperatures.

Solution

Since the number of gaseous particles decrease from 4 mol to 2 mol, there are less ways to arrange the particles, resulting in lower disorder and entropy. Thus, $\Delta S^\ominus < 0$.

$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ Note that $\Delta H^\ominus < 0$, $\Delta S^\ominus < 0$. Thus, $-T\Delta S^\ominus > 0$.

For $\Delta G^\ominus < 0$, $\Delta H^\ominus$ needs to be more significant than $-T\Delta S^\ominus$. Thus, temperature needs to be low.

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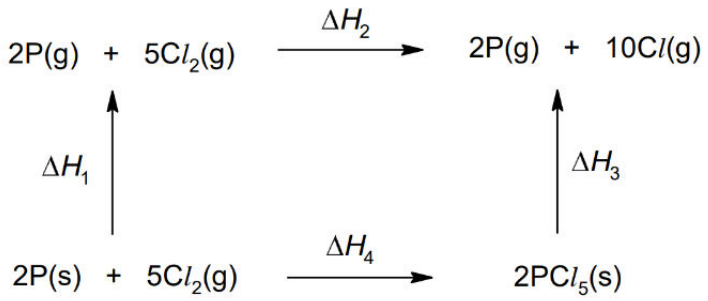
Question 1: Are You Familiar with the Different Enthalpy Changes?

Use of the Data Booklet is relevant to this question.

The following reactions at 298 K, form an energy cycle.



Which descriptions of the enthalpy changes are correct?

1 $\Delta H_1 + \Delta H_2 > +1220$ kJ mol^{-1}

2 ΔH_3 = 10 x P–C*l* bond energy

3 $\Delta H_4 = 2 \times \Delta H^{\ominus}_{formation}$ of $PCl_5(s)$

A 1 and 2 **B** 1 and 3 **C** 2 and 3 **D** 1,2 and 3

( )

Question 2: Constructing an Energy Level Diagram

Lead(II) carbonate thermally decomposes according to the equation.

$$PbCO_3(s) \longrightarrow PbO(s) + CO_2(g) \qquad \Delta H_{decomp} < 0$$

Some enthalpy changes are listed below.

Enthalpy change of formation of $PbCO_3(s)$	=	–532 kJ mol^{-1}
Enthalpy change of atomisation of lead	=	+195 kJ mol^{-1}
Enthalpy change of combustion of carbon	=	–394 kJ mol^{-1}
Lattice energy of lead(II) oxide	=	–3520 kJ mol^{-1}
First electron affinity of oxygen	=	–141 kJ mol^{-1}
Second electron affinity of oxygen	=	+798 kJ mol^{-1}

By using data in this question and relevant data in the *Data Booklet*, construct a fully-labelled energy level diagram to determine the enthalpy change of decomposition of lead(II) carbonate. [4]

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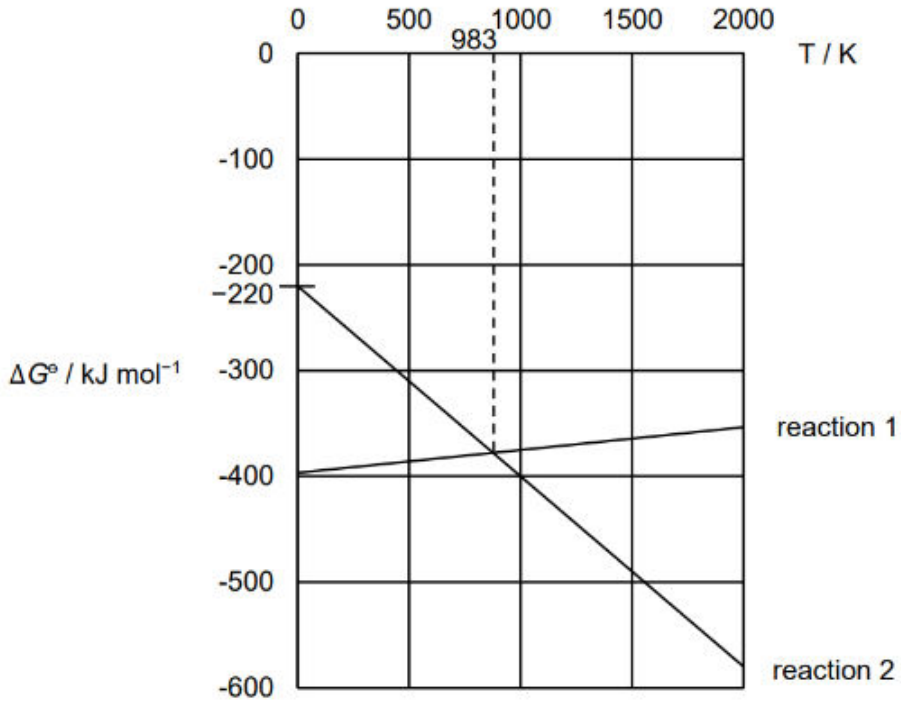
Question 3: Ellingham Diagram

An Ellingham diagram is a plot of ΔG versus temperature and it can be used to show the stability of compounds at various temperatures.

The following Ellingham diagram is for reactions 1 and 2.

reaction 1 **W** + **X** ⟶ **Y**

reaction 2 2 **W** + **X** ⟶ 2 **Z**



Which statement is incorrect?

A Reaction 1 is favoured at lower temperatures.

B The entropy change of reaction 2 is negative.

C The enthalpy change of reaction 2 is –220 kJ mol^{-1}.

D At 983 K, ΔG of reaction 2 **Z** ⟶ **W** + **Y** is zero.

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Question 1: Are You Familiar with the Different Enthalpy Changes?

Answer: **B**

1 **Correct**.

Recall that the definition of bond energy is breaking 1 mol of a covalent bond in the gaseous state. ΔH_2 is 5 Cl_2(g) ⟶ 10 Cl (g) and 5 mol of Cl–Cl bonds are broken in the gaseous state. ΔH_2 = 5 x BE(Cl–Cl) = 5 x (+244) = +1220 kJ mol^{-1}

ΔH_1 represents the reaction 2 P(s) ⟶ 2 P(g). P(s) to P(g) requires energy to overcome the intermolecular force of attractions (instantaneous dipole–induced dipole interactions; P atoms are non–polar) between the P(s) atoms to form P(g) atoms.

Hence, $\Delta H_1 + \Delta H_2 >$ + 1220 kJ mol^{-1}

2 **Incorrect**.

Since bond energy is breaking 1 mol of a covalent bond in the gaseous state, and PCl_5 is in the solid state, this does not represent bond energy.

10 BE(P–Cl) would be represented by: 2 PCl_5(g) ⟶ 2 P(g) + 10 Cl(g)

3 **Correct**.

2 mol of PCl_5(s) are formed from the constituent elements in their standard states.

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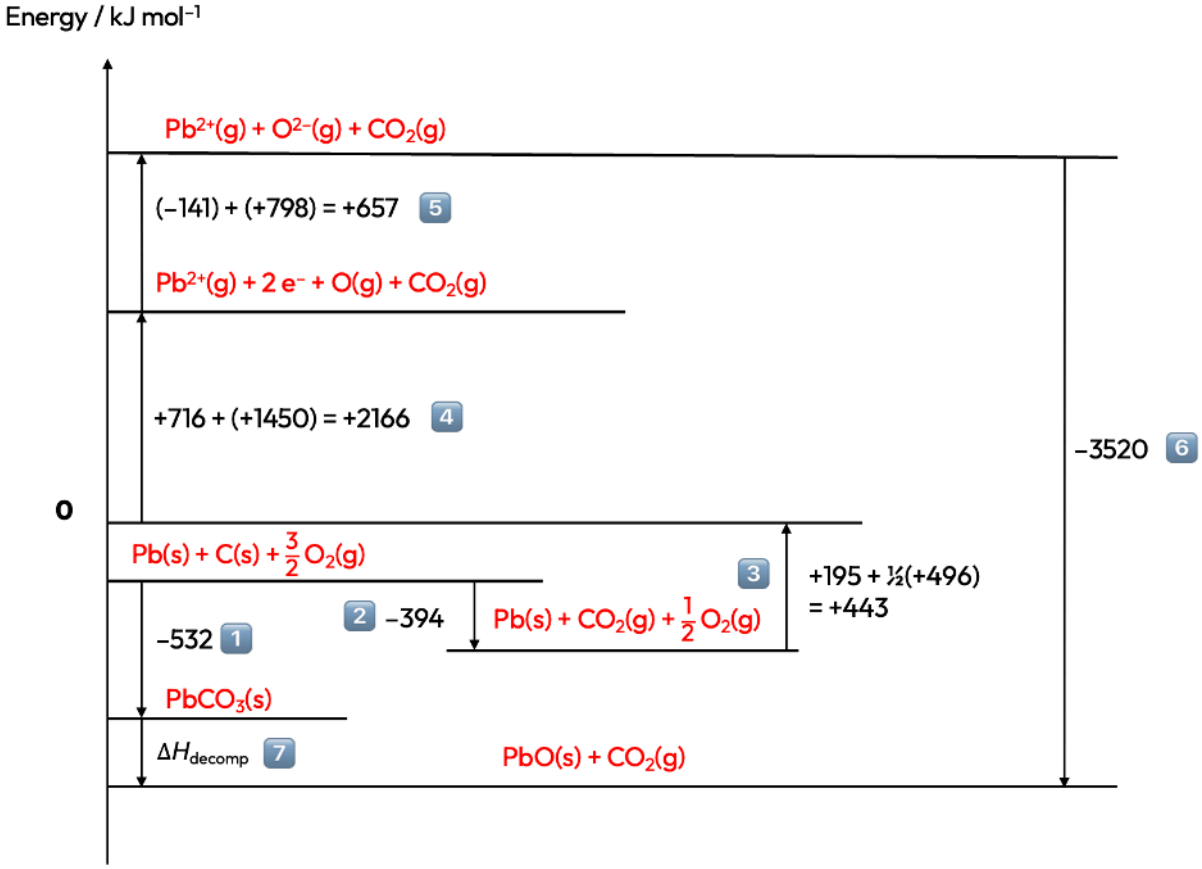
Question 2: Constructing an Energy Level Diagram



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Question 3: Ellingham Diagram

A is **correct**.

As temperature decreases, ΔG becomes more negative.

B is **incorrect**.

$\Delta G = \Delta H - T\Delta S$. Since the y–axis is ΔG and the x-axis is T, the equation represents Y = mX + C, where m, the gradient = $-\Delta S$. Since gradient of reaction 2 is negative, ΔS of reaction 2 is positive.

C is **incorrect**.

$\Delta G = \Delta H - T\Delta S$. Since the y–axis is ΔG and the x-axis is T, the equation represents Y = mX + C, where C, the y–intercept = $-\Delta H$, is –220 kJ mol^{-1}.

D is **incorrect**.

The lines for reaction 1 and 2 intersect at 983 K. The ΔG for both reactions have the same value, approximately –370 kJ mol^{-1}.

reaction 1 **W** + **X** ⟶ **Y** ΔG = –370 kJ mol^{-1}

reaction 2 2 **W** + **X** ⟶ 2 **Z** ΔG = –370 kJ mol^{-1}

The reaction: 2 **Z** ⟶ **W** + **Y** is simply the reverse of reaction 2 + reaction 1.

Hence, ΔG of that reaction is –(–370) + (–370) = 0 kJ mol^{-1}.

Note: ΔG can be treated similarly to ΔH.

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