

ENERGETICS

↳ Energy and changes in it

Enthalpy (H) is the "heat quantity" or the energy of a system

↳ Enthalpy itself cannot be measured directly, only change in enthalpy (ΔH) can be measured

• Two types of enthalpy changes are:

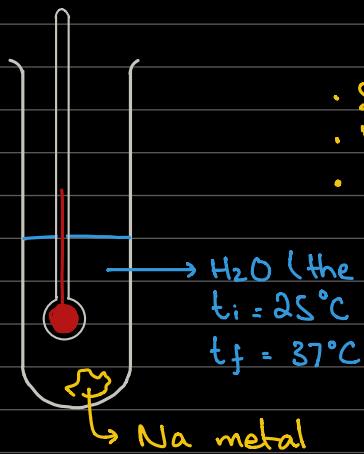
1. Exothermic

- ΔH is negative
- Heat energy is lost / released to the surroundings

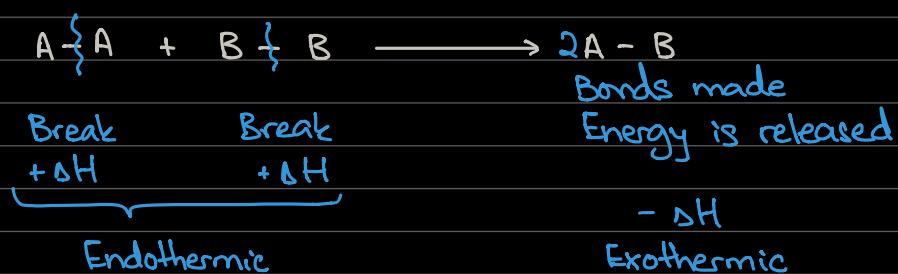
2. Endothermic

- ΔH is positive
- Heat energy is gained / absorbed from the surroundings

EXOTHERMIC REACTIONS



- Surroundings temperature increases
- In this case, the system is the Na being dissolved
- test tube feels warm to touch

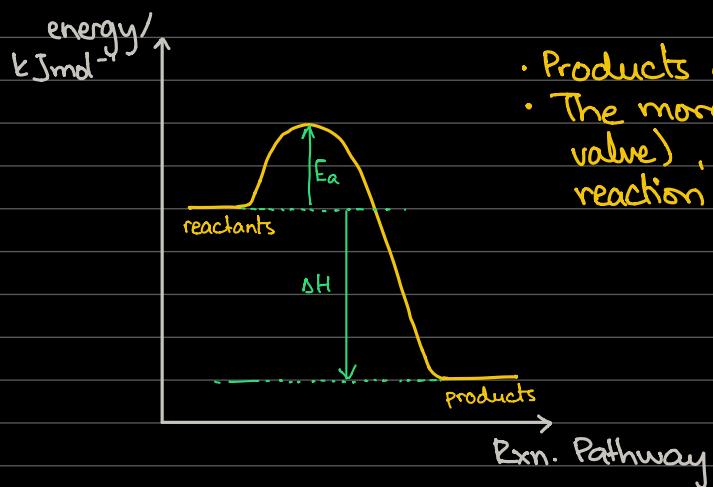


$$\Delta H = H_{\text{reactants}} - H_{\text{products}}$$

↓ ↓
total for total for
bond breaking bond making

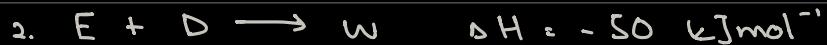
- In exothermic reactions, bond making releases more energy than the energy put in to break all the bonds in the reactants

ENERGY PROFILE DIAGRAMS



- Products are at a lower energy level
- The more exothermic the reaction (greater $-\Delta H$ value), the more stable the product of that reaction

Example :



- Reaction 1 is more likely to take place as ΔH is more exothermic and the product C is more stable (than the product W)

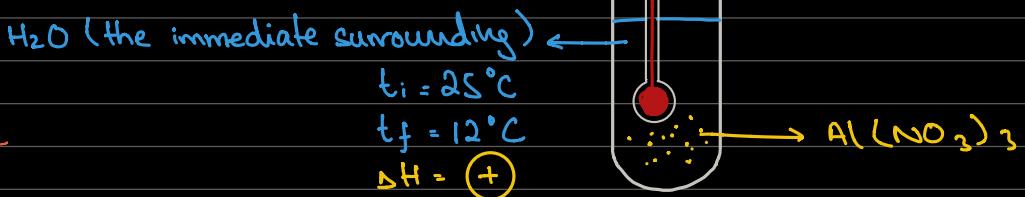
ENDOTHERMIC REACTIONS

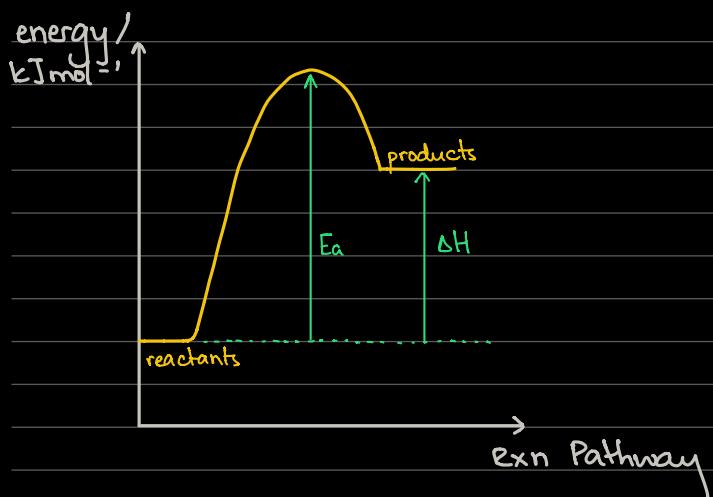
- Absorb heat from the surroundings so the surrounding temperature decreases and the thermometer records the decrease in the surrounding temperature.
- Test tube / container feels cooler to touch

$$|t_f - t_i| = \Delta t$$

$$\Delta T = \Delta t$$

Note: The change in temperature is always written as a positive value





- The more endothermic a reaction, the less stable the product

product A $\Delta H = +17 \text{ kJ/mol}^{-1}$

product B $\Delta H = +30 \text{ kJ/mol}^{-1}$

In this case, product A is more stable

LAB CALCULATION OF ΔH

Enthalpy change of solution ($\Delta H_{\text{solution}}$)

Energy change on dissolving

Example: NaOH(s) in water

Required:

1. Thermometer
2. Conical Flask
3. Distilled water \rightarrow known volume / mass
4. NaOH \rightarrow weigh using digital balance

STEPS :

Step 1: Transfer 50cm³ of distilled water into a conical flask using a burette

Step 2: Record the initial temperature (t_i) of water

Step 3: Weigh out NaOH(s), (ie. 4g)

Step 4: Transfer the NaOH (4g) to the conical flask and stir until it is dissolved.

Step 5: Record the maximum or minimum temperature attained on the thermometer (t_f)

$$t_i = 25^\circ\text{C}$$

$$t_f = 35^\circ\text{C}$$

$$\Delta t = 10^\circ\text{C}$$

$Q = mc\Delta t$ where $Q = \text{heat content (not necessarily per mole)}$

$$Q = (50)(4.18)(10)$$

$$Q = 2090\text{J}$$

$m = \text{mass of water only (50g)}$

$c = \text{specific heat capacity of water (J/molK) (4.18J/molK)}$

$$\Delta t = 10^\circ\text{C}$$

Note:

'c' is the energy in Joules required to raise the temperature of 1g of a substance by 1 Kelvin

$\Delta H = \text{energy change per mol}$

$$n(\text{NaOH}) = \frac{4.00\text{g}}{40} = 0.1\text{mol}$$

$$\text{Note: } \Delta H = \frac{Q}{n}$$

$n \times \frac{1000}{k\text{J}}$ because we converted to kJ

$$0.1\text{mol} \longrightarrow 2090\text{J}$$

$$1\text{mol} \longrightarrow 20900\text{J}$$

where $n = \text{no. of moles}$

$$\Delta H = -20.9\text{kJ/mol}$$

Exothermic

Note: ΔH is always expressed in kJ/mol

• Enthalpy changes are measured under standard conditions:

if applicable \longrightarrow 25°C temperature
 1 atm pressure
 1 mol/l dm^3 solution

• When writing thermochemical equations, state symbols must be given

Example of thermochemical equation:



$\Delta H^\ominus \rightarrow$ "naught" signifies standard conditions

DIFFERENT TYPES OF ENTHALPY CHANGES

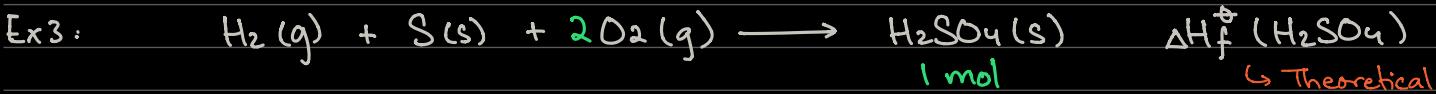
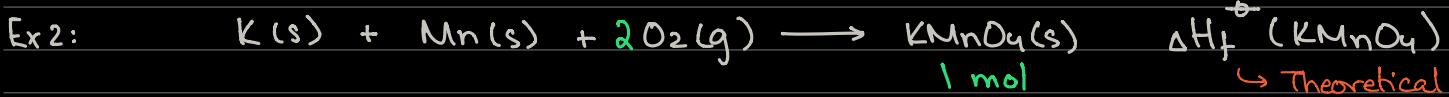
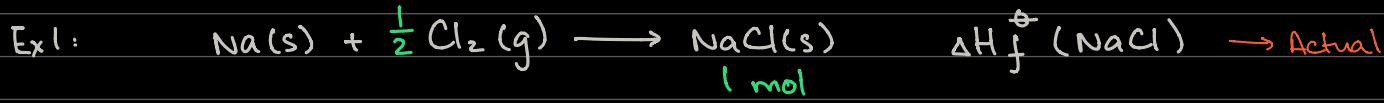
1. $\Delta H^\ominus_{\text{rxn}}$ or ΔH^\ominus_r : Standard enthalpy change of reaction

- is the enthalpy change that occurs when stoichiometric quantities / moles of reactants react together (as shown in the equation) to give products under standard conditions

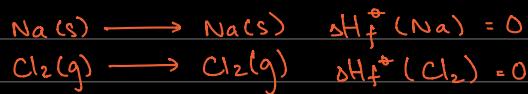
2. ΔH_f° : Standard enthalpy change of formation

The enthalpy change that occurs when 1 mol of a compound is formed from its elements in their standard states under standard conditions

Note: "Formation" can be actual (doable in lab) or theoretical



Note: ΔH_f° of elements is always zero

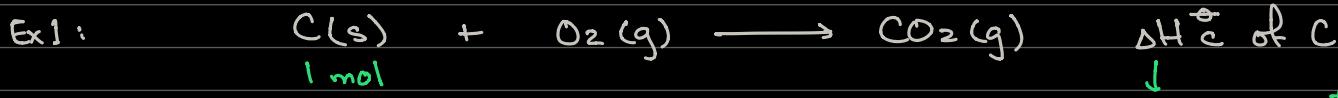


Theoretical values are also important as they're used in calculations

3. ΔH_c° : Standard enthalpy change of combustion

. is the enthalpy change that occurs when 1 mole of a substance is burnt completely in excess oxygen under standard conditions

Note: ΔH_c° is always exothermic
 and it always applies to complete combustion

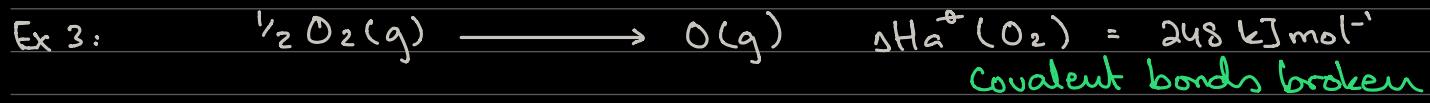
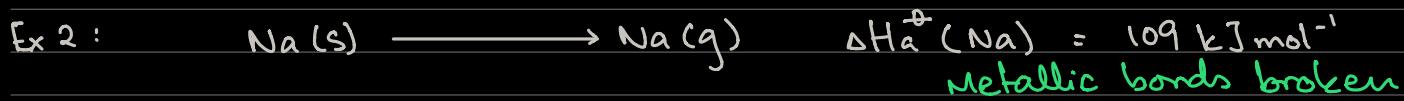
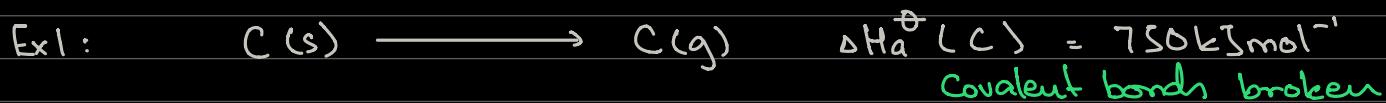


Also the ΔH_f° of CO_2
 as 1 mol of CO_2 is formed



4. ΔH_a^\ominus : Standard Enthalpy change of atomization

- is the enthalpy change that occurs when 1 mol of gaseous atoms is produced from the element in its standard state under standard conditions
- ΔH_a^\ominus is always endothermic



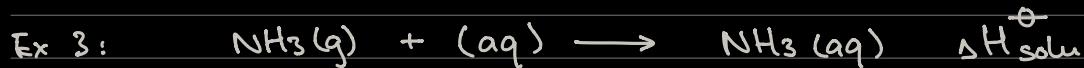
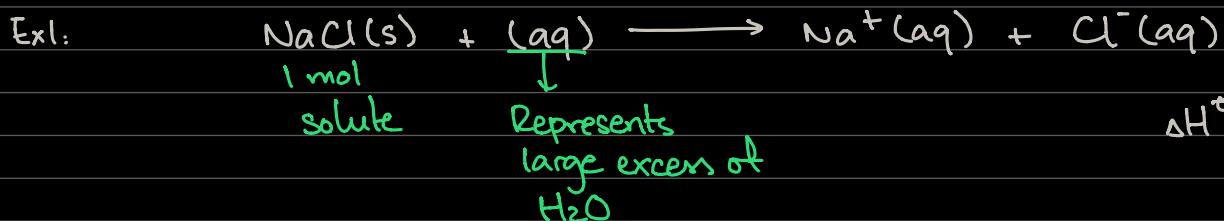
ΔH_a^\ominus is always positive as energy is put in to break the bonds

5. $\Delta H_{\text{soln}}^\ominus$: The standard enthalpy change of solution

is the enthalpy change that occurs when 1 mol of solute is dissolved in an infinite amount of water to form a dilute solution under standard conditions.

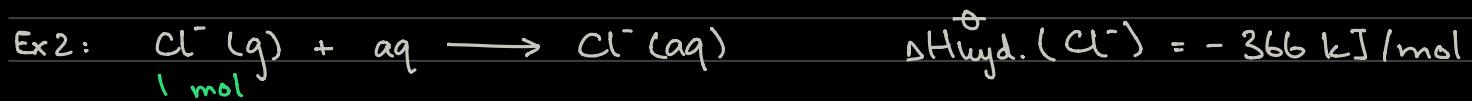
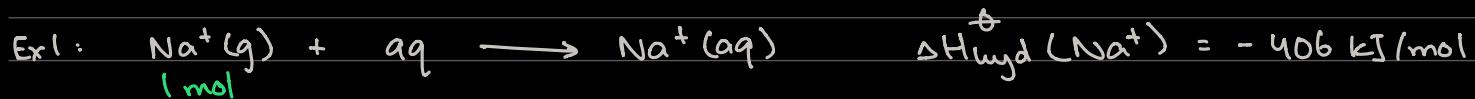
→ This just ensures that all of the solute is dissolved and also implies that if any more water was to be added, there would be no further heat change

- Can be either exo. or endo.



- If $\Delta H_{\text{soln}}^\ominus$ is highly endothermic, that means that the solute is not soluble in water
- If $\Delta H_{\text{soln}}^\ominus$ is highly exothermic, that means that the solute is highly soluble in water

6. $\Delta H_{\text{hyd.}}^\ominus$: The standard enthalpy change of hydration of an ion is the enthalpy change when 1 mol of gaseous ions is dissolved in a large excess of water under standard conditions



- $\Delta H_{\text{hyd.}}^\ominus$ will always be exothermic (-) because it is like bond-making
 ↳ Ion-dipole interactions are occurring (between H_2O polar molecules and ions)

Combining Ex1 and Ex2:



$$\begin{aligned}\Delta H_{\text{hyd.}}^\ominus(\text{total}) &= -406 + (-366) \\ &= -772 \text{ kJ/mol}\end{aligned}$$

- $\Delta H_{\text{hyd.}}^\ominus$ depends on the charge density of the ion
 - ↳ 1. charge of the ion
 - 2. ionic radius

- The higher the charge, the stronger the attraction with water, therefore more exothermic the reaction ($\Delta H_{\text{hyd.}}^\ominus$ is more -ive)
 - The smaller the radius of the ion, the more closely water is attracted and therefore, the more exothermic the reaction ($\Delta H_{\text{hyd.}}^\ominus$ is more -ive)
- ↳ The higher the charge density, the more exothermic $\Delta H_{\text{hyd.}}^\ominus$

| Cations | $\Delta H_{\text{hyd}}^\ominus (\text{kJ/mol})$ |
|--------------|---|
| H^+ | -1075 |

| | | | | | | | | |
|---------------|---|---|------|---|---------------|------|--------------|------|
| Group 1 | <table border="1"> <tr> <td>Li^+</td><td>-499</td><td rowspan="3">Radius increases Charge Density decreases Exothermic-ness decreases</td></tr> <tr> <td>Na^+</td><td>-390</td></tr> <tr> <td>K^+</td><td>-305</td></tr> </table> | Li^+ | -499 | Radius increases Charge Density decreases Exothermic-ness decreases | Na^+ | -390 | K^+ | -305 |
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| Na^+ | -390 | | | | | | | |
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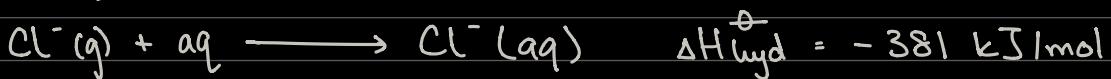
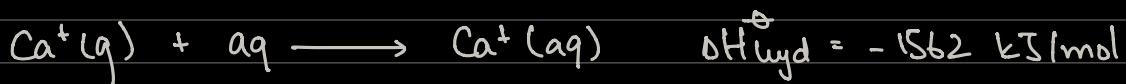
| | | | | | | |
|------------------|--|------------------|-------|------------------|------------------|-------|
| Group 2 | <table border="1"> <tr> <td>Mg^{2+}</td><td>-1891</td><td rowspan="2">Radius increases</td></tr> <tr> <td>Ca^{2+}</td><td>-1562</td></tr> </table> | Mg^{2+} | -1891 | Radius increases | Ca^{2+} | -1562 |
| Mg^{2+} | -1891 | Radius increases | | | | |
| Ca^{2+} | -1562 | | | | | |

Al^{3+} - 4163 → small ionic radius + high charge = high charge density

↓
highly exothermic
 $\Delta H_{\text{hyd}}^\ominus$

| | | |
|---------------|---|---------------------------------|
| Anion | $\Delta H_{\text{hyd}}^\ominus (\text{kJ/mol})$ | $\Delta H_{\text{hyd}}^\ominus$ |
| F^- | -457 | |
| Cl^- | -381 | |
| Br^- | -351 | |
| I^- | -307 | |

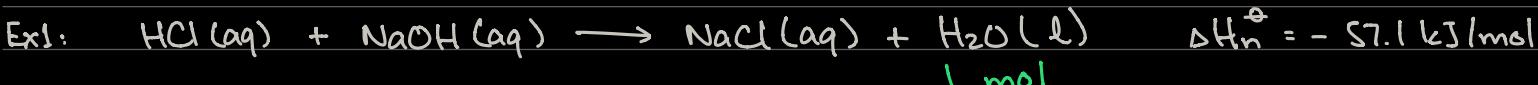
Example: $\Delta H_{\text{hyd}}^\ominus (\text{CaCl}_2)$



$$\begin{aligned} \Delta H_{\text{hyd}}^\ominus (\text{CaCl}_2) &= -1562 + 2(-381) \\ &= \underline{-2324 \text{ kJ/mol}} \\ &\quad \text{Am} \end{aligned}$$

7. ΔH_n^\ominus : Standard enthalpy change of neutralisation
is the enthalpy change when 1 mol of water is formed in a neutralisation reaction between an aqueous acid and an aqueous alkali under standard conditions

ΔH_n^\ominus is always exothermic (always -ive)



1 mol

Ionic equation: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l}) \rightarrow$ true for every neutralisation



2 mol



1 mol

$$\Delta H_n^\ominus = -58.2 \text{ kJ/mol}$$

- For all strong acids + strong alkalis, ΔH_n^\ominus is roughly the same, ie. close to -57 kJ/mol, as they ionise completely in water