

# 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 ( $\Delta H$ ) can be measured

• Two types of enthalpy changes are:

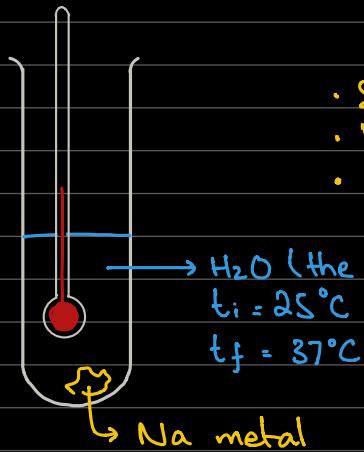
1. Exothermic

- $\Delta H$  is negative
- Heat energy is lost / released to the surroundings

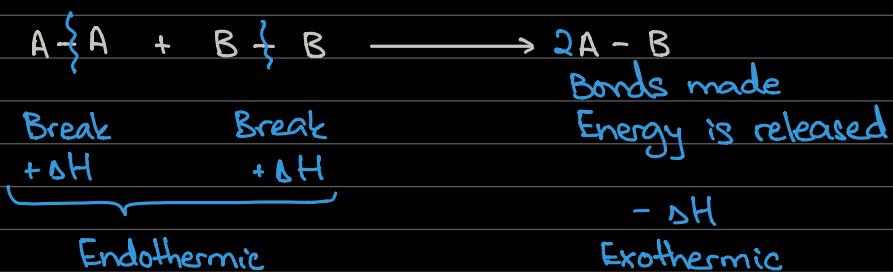
2. Endothermic

- $\Delta H$  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

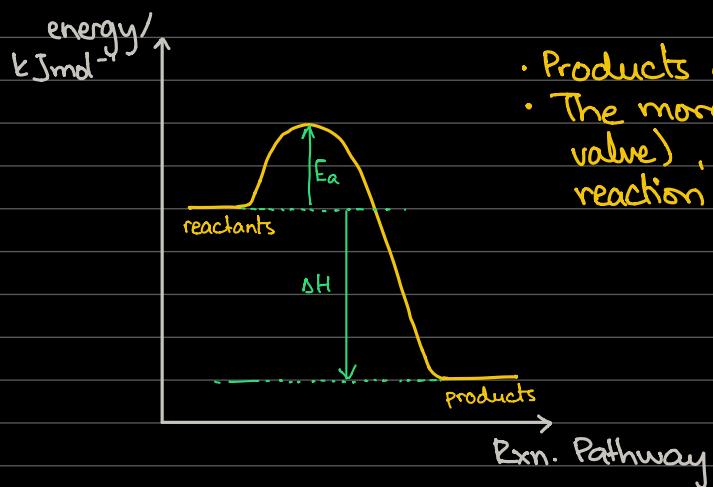


$$\Delta H = H_{\text{reactants}} - H_{\text{products}}$$

$\downarrow$  total for bond breaking       $\downarrow$  total for bond making

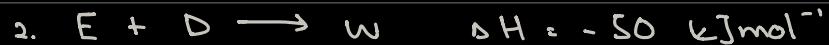
- In exothermic reactions, bond making releases more energy than the energy put in to break all the bonds in the reactants

## 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  $\Delta H$  is more exothermic and the product C is more stable (than the product W)

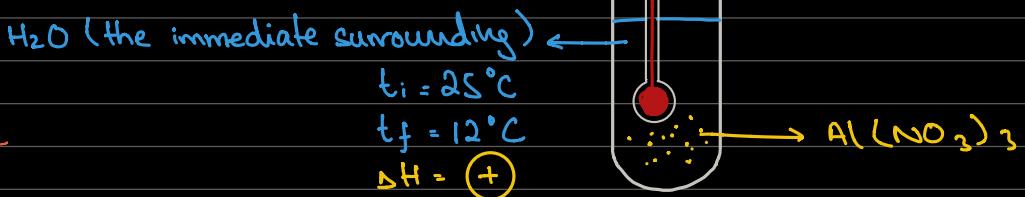
## ENDOTHERMIC REACTIONS

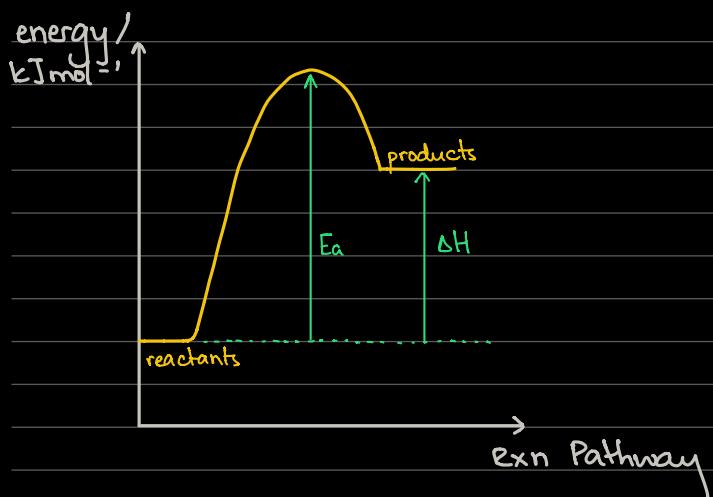
- Absorb heat from the surroundings so the surrounding temperature decreases and the thermometer records the decrease in the surrounding temperature.
- Test tube / container feels cooler to touch

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

$$\Delta T = \Delta t$$

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





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

product A  $\Delta H = +17 \text{ kJmol}^{-1}$

product B  $\Delta H = +30 \text{ kJmol}^{-1}$

↳ In this case, product A is more stable

## LAB CALCULATION OF $\Delta H$

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 → known volume / mass
4. NaOH → 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:  $\Delta H$  is always expressed in kJ/mol

• Enthalpy changes are measured under standard conditions:

if applicable  $\longrightarrow$   $25^\circ\text{C}$  temperature  
 $1\text{ atm}$  pressure  
 $1\text{ mol/l dm}^3$  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

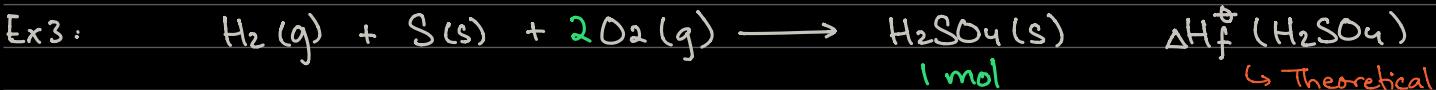
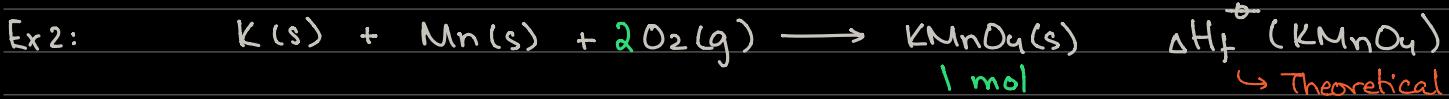
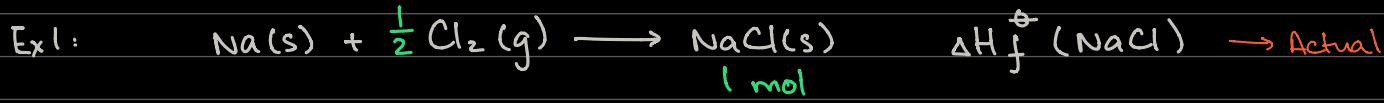
1.  $\Delta H^\ominus_{\text{rxn}}$  or  $\Delta H^\ominus_r$  : Standard enthalpy change of reaction

- 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

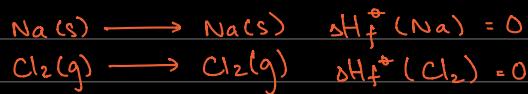
## 2. $\Delta H_f^\circ$ : Standard enthalpy change of formation

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:  $\Delta H_f^\circ$  of elements is always zero

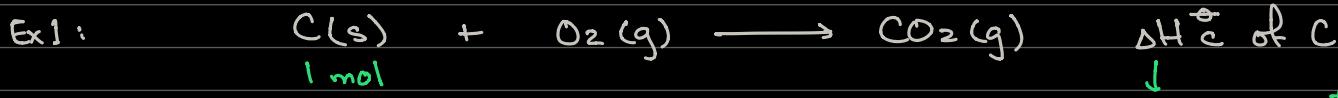


Theoretical values are also important as they're used in calculations

## 3. $\Delta H_c^\circ$ : 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:  $\Delta H_c^\circ$  is always exothermic  
 and it always applies to complete combustion

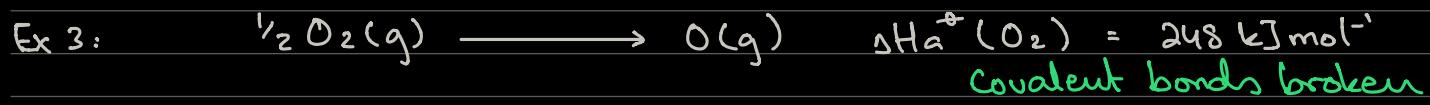
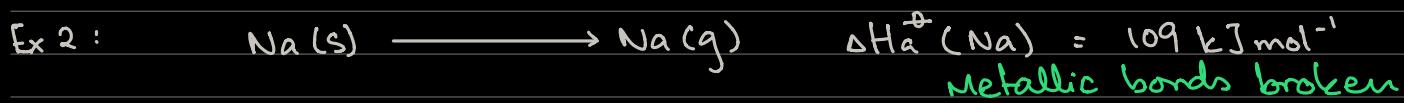
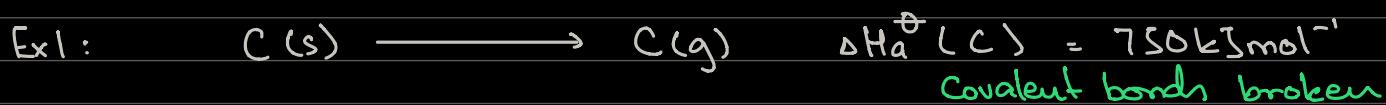


Also the  $\Delta H_f^\circ$  of  $\text{CO}_2$   
 as 1 mol of  $\text{CO}_2$  is formed



#### 4. $\Delta H_a^\ominus$ : 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
- $\Delta H_a^\ominus$  is always endothermic



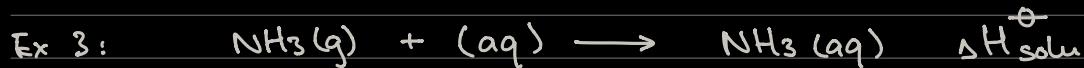
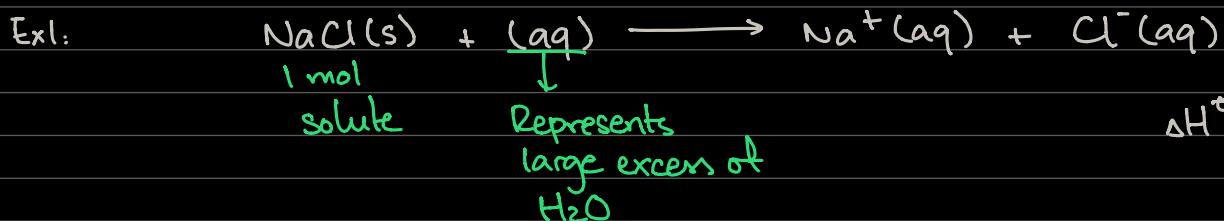
$\Delta H_a^\ominus$  is always positive as energy is put in to break the bonds

#### 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.

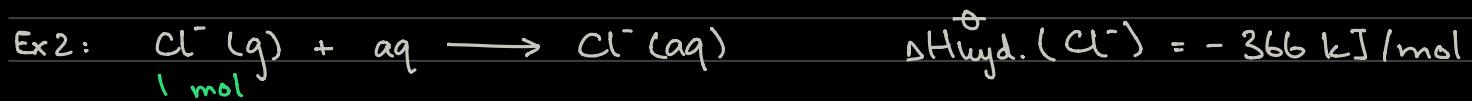
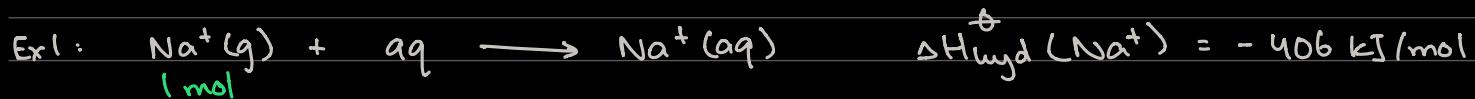
→ This just ensures that all of the solute is dissolved and also implies that if any more water was to be added, there would be no further heat change

- 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  $\text{H}_2\text{O}$  polar molecules and ions)

Combining Ex 1 and Ex 2:



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

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

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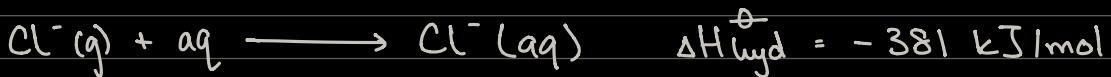
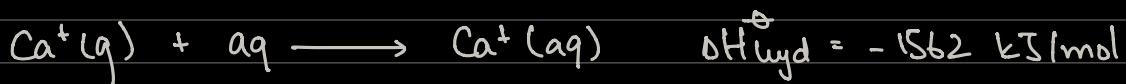
Group 2	<table border="1"> <tr> <td><math>\text{Mg}^{2+}</math></td><td>-1891</td><td rowspan="2">Radius increases</td></tr> <tr> <td><math>\text{Ca}^{2+}</math></td><td>-1562</td></tr> </table>	$\text{Mg}^{2+}$	-1891	Radius increases	$\text{Ca}^{2+}$	-1562
$\text{Mg}^{2+}$	-1891	Radius increases			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

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

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

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

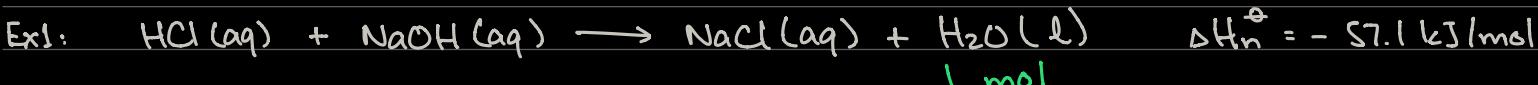
Example:  $\Delta H_{\text{hyd}}^\ominus (\text{CaCl}_2)$



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

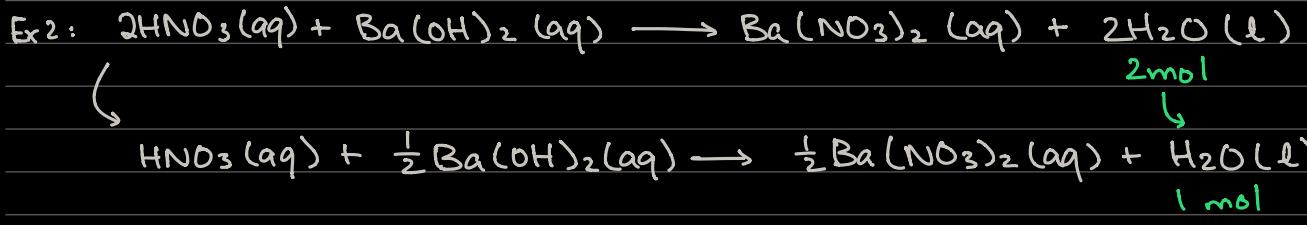
7.  $\Delta H_n^\ominus$ : Standard enthalpy change of neutralisation  
is the enthalpy change when 1 mol of water is formed in a neutralisation reaction between an aqueous acid and an aqueous alkali under standard conditions

$\Delta H_n^\ominus$  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



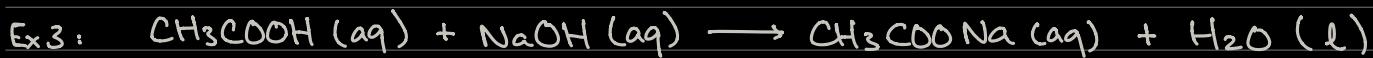
$$\Delta H_n^\ominus = -58.2 \text{ kJ/mol}$$

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

on the other hand...

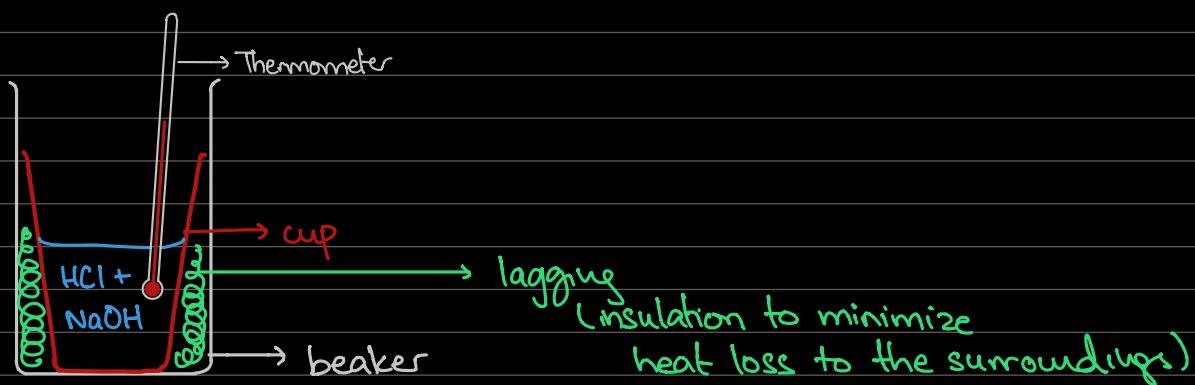
- Weak acids or weak bases do not ionise completely in water so the  $\Delta H_n^\circ$  for weak acids is less exothermic (or less -ive).

↳ But the ionic equation is the same



LAB :  $\Delta H_n^\circ$  by experimentation

- use a calorimeter  
An insulated piece of apparatus used to measure  $\Delta H$  by experimentation
  - However, in lab, we use a styrofoam or plastic cup as a calorimeter



HCl = 100cm<sup>3</sup>, 0.5 mol/dm<sup>3</sup>

NaOH = 100cm<sup>3</sup>, 0.5 mol/dm<sup>3</sup>

Volume is measured using a burette

1. Run out 100 cm<sup>3</sup> of HCl using a burette into the plastic cup
2. Record the initial temperature ( $t_i$ ) of HCl
3. Run out 100cm<sup>3</sup> of NaOH(aq) into a separate 100cm<sup>3</sup> beaker
4. Record it's initial temperature ( $t_i$ ) of NaOH
5. Add the NaOH(aq) to the HCl, stir with the thermometer and record the maximum temperature on the thermometer. This is the final temperature ( $t_f$ )

Example:

$$t_i \text{ HCl} = 25.5^\circ\text{C}$$

$$t_i \text{ NaOH} = 25.3^\circ\text{C}$$

$$t_f = 28.7^\circ\text{C}$$

$$\Delta t = 28.7 - 25.4 = 3.3^\circ\text{C}$$

$$\text{avg } t_i = \frac{25.5 + 25.3}{2}$$

$$= 25.4^\circ\text{C}$$

$$Q = \cancel{mc} \downarrow \overset{m \text{ is the mass of HCl + NaOH}}{\Delta t}$$

Note: HCl + NaOH → density is taken as same as that of water

$$\text{Vol HCl} = 100\text{cm}^3 \rightarrow \text{Mass HCl} = 100\text{g}$$

$$\text{Vol NaOH} = 100\text{cm}^3 \rightarrow \text{Mass NaOH} = 100\text{g}$$

$$Q = mc \Delta t$$

$$Q = (100 + 100)(4.18)(3.3)$$

$$Q = 2758.8 \text{ J}$$

$$n(\text{HCl}) = 0.05 \text{ mol}$$

$$n(\text{NaOH}) = 0.05 \text{ mol}$$

$$c = 0.5 \text{ mol/dm}^3$$

$$V = 100\text{cm}^3$$

$$n = 0.05 \text{ mol}$$



$$2758.8 \text{ J} / 0.05 \text{ mol}$$

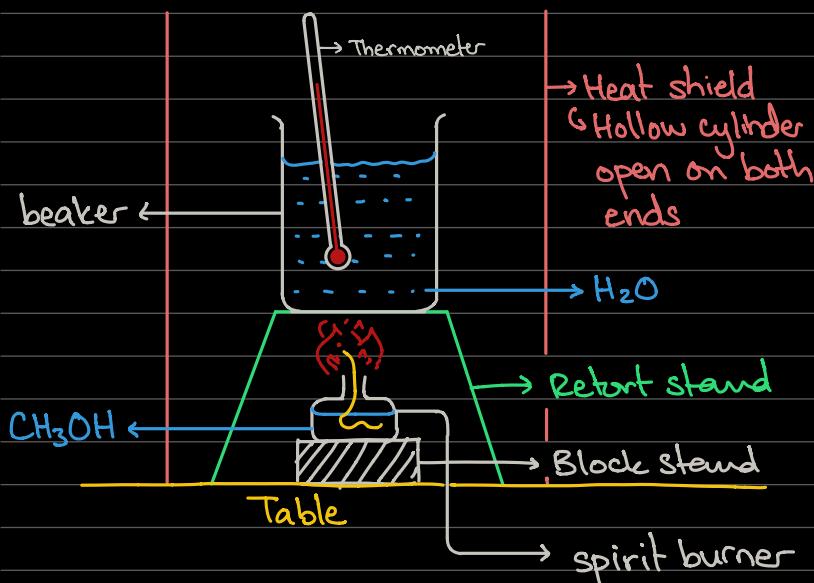
$$\Delta H_n^\ominus = -55176 \text{ J/mol}$$

$$\Delta H_n^\ominus = -55.2 \text{ kJ/mol}$$

$$\text{Note} \rightarrow \Delta H = \frac{Q}{n \times 1000}$$

Note: If either the acid or the alkali is in excess or limiting, then use the moles of the limiting reagent

### $\Delta H_c^\ominus$ by experiment:

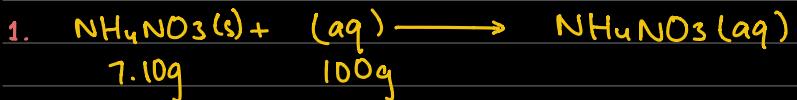


Assumption: The heat energy evolved on burning methanol is being transferred to the water, and the water temperature rises.

But realistically, a lot of heat is lost to the surroundings

As such, a heat shield is used to minimize heat loss to the surroundings

Questions from Energy Changes Booklet on Google Classroom



$$\begin{aligned} c &= 4.18 \text{ J/gK} \\ t_i &= 18.2^\circ\text{C} \\ t_f &= 12.8^\circ\text{C} \end{aligned}$$

Calculate  $\Delta H_{\text{soln}}^\ominus$

$$\begin{aligned} \Delta t &= |t_f - t_i| \\ &= |12.8 - 18.2| \end{aligned}$$

$$\Delta = 5.4^\circ\text{C}$$

$$\begin{aligned} Q &= mc\Delta t \\ &= (100)(4.18)(5.4) \end{aligned}$$

$$Q = 2257.2 \text{ J} / 0.08875 \text{ mol}$$

n(NH<sub>4</sub>NO<sub>3</sub>):

$$\begin{aligned} \text{Mr of NH}_4\text{NO}_3 &= 14 + 4 + 14 + 3(16) \\ &= 80 \text{ g} \end{aligned}$$

$$\begin{aligned} 1 \text{ mol} &\rightarrow 80 \text{ g} \\ x \text{ mol} &\rightarrow 7.1 \text{ g} \end{aligned}$$

$$\frac{80}{1} = \frac{7.1}{x}$$

$$x = \frac{7.1}{80}$$

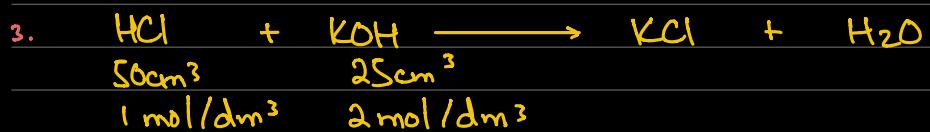
$$x = 0.08875 \text{ moles of NH}_4\text{NO}_3$$

$$\frac{2257.2}{0.08875} = 25433 \text{ J/mol}$$

$$\left[ \Delta H_{\text{soln}}^\ominus = +25.4 \text{ kJ/mol} \right] \rightarrow \text{Am}$$

↳ endothermic reaction

## 2. leave out



$$t_i = 15.3^\circ\text{C}$$

$$t_f = 24.3^\circ\text{C}$$

Calculate  $\Delta H_n^\ominus$ .

$$n(\text{HCl}) :$$

$$n = cv$$

$$n = 1 \times 0.05$$

$$n = 0.05 \text{ mol}$$

$$n(\text{KOH}) :$$

$$n = cv$$

$$n = 2 \times 0.025$$

$$n = 0.05 \text{ mol}$$

↑ neither reagent is in  
excess or limiting

$$\Delta t = t_f - t_i$$

$$= 24.3 - 15.3$$

$$= 9^\circ\text{C}$$

$$Q = mc\Delta t$$

$$Q = (50 + 25)(4.18)(9)$$

$$Q = 2821.5 \text{ J} / 0.05 \text{ mol}$$

$$\frac{2821.5}{0.05} = 56430 \text{ J/mol}$$

$$[\Delta H_n^\ominus = -56.4 \text{ kJ/mol}] \rightarrow \text{Ans}$$

↳ exothermic reaction



↳ Assume in excess

if concentration not given

$$t_i = 20^\circ\text{C}$$

$$t_f = 35.2^\circ\text{C}$$

$$\Delta t = 15.2^\circ\text{C}$$

Calculate  $\Delta H_r^\ominus$

↳ mass of liquid (HCl)

$$Q = mc\Delta t$$

$$= (200)(4.18)(15.2)$$

$$= 12707.2 \text{ J} / 0.0197 \text{ mol}$$

$$\frac{12707.2}{0.0197 \times 1000} = 643.3 \text{ kJ/mol}$$

$$n(\text{Mg}) :$$

$$\text{Mr Mg} : 24.3$$

$$\therefore \Delta H_r^\ominus = 643.3 \text{ kJ/mol} \rightarrow \text{Ans}$$

$$24.3\text{g} \rightarrow 1 \text{ mol}$$

$$0.48\text{g} \rightarrow x \text{ mol}$$

$$n(\text{Mg}) = 0.0197$$



$$\text{mass}(\text{H}_2\text{O}) = 200\text{g}$$

$$\text{mass}(\text{CH}_3\text{OH} + \text{burner}) \text{ at start} = 532.68\text{g}$$

$$\text{mass}(\text{CH}_3\text{OH} + \text{burner}) \text{ at end} = 531.72\text{g}$$

Mass of burned ethanol

$$532.68 - 531.72$$

$$= 0.96\text{g ethanol burnt}$$

$$t_i \text{ H}_2\text{O} = 18.3^\circ\text{C}$$

$$\Delta t = 29.6 - 18.3$$

$$t_f \text{ H}_2\text{O} = 29.6^\circ\text{C}$$

$$= 11.3^\circ\text{C}$$

$$c = 4.18 \text{ J/gK}$$

$$n(\text{CH}_3\text{OH}):$$

$$\text{Mr : 32}$$

$$\frac{0.96}{32} = 0.03 \text{ mol}$$

$$Q = mc\Delta t$$

$$Q = (200)(4.18)(11.3)$$

$$Q = 9446.8 \text{ J / 0.03 mol}$$

$$\frac{9446.8}{0.03 \times 1000} = 314.9 \text{ kJ/mol}$$

$$\therefore \Delta H_c^\theta = -314.9 \text{ kJ/mol} \rightarrow \underline{\text{Ans}}$$

## FREQUENTLY ASKED QUESTIONS

Q. What is "m" in  $Q = mc\Delta t$

Case 1 : Dissolving /  $\Delta H_{\text{soln}}^\theta$

solute +  $\text{H}_2\text{O}$

mass vol  $100\text{cm}^3$

↓ ↓

moles mass  $100\text{g}$

↓ ↓

use to find use this mass as

$\Delta H$  "m" in  $Q = mc\Delta t$

Case 2 : Neutralization /  $\Delta H_n^\theta$

Acid + Alkali

vol [  $100\text{cm}^3$  +  $100\text{cm}^3$  ] → 200g (assume same density as water)

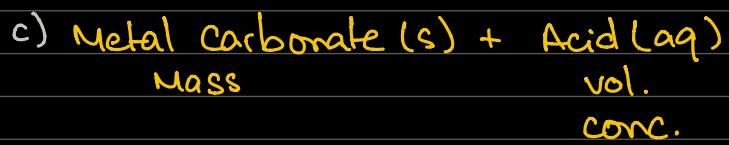
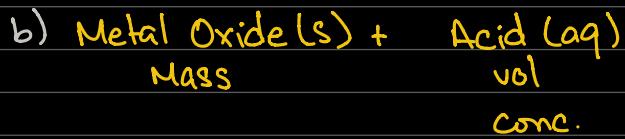
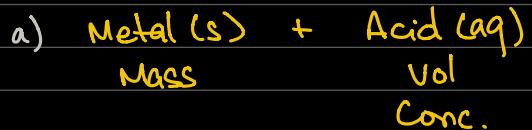
conc [  $2 \text{ mol/dm}^3$   $2 \text{ mol/dm}^3$  ]

→ use as "m" in  $Q = mc\Delta t$

→ use to calculate moles and determine which reagent is in excess / limiting

→ use limiting moles to find  $\Delta H_n^\theta$

### Case 3: $\Delta H_r^\ominus$



m in meat is the mass of the liquid component, ie the acid  
assuming density to be that of water

### Case 4: Combustion / $\Delta H_c^\ominus$

- known volume or mass of water heated when a fuel combusts

m in meat is the mass of  $H_2O$  being heated in meat

use fuel's moles to  
calculate  $\Delta H_c^\ominus$