07 Chemical Energetics I

1 Enthalpy Changes

DEFINITION **Enthalpy, H**: the measure of the energy content of a substance. A substance with lower enthalpy has greater _____.

Bond breaking _____ energy, bond forming _____ energy. ΔH is the heat change at constant pressure (kJ mol^{-1}).

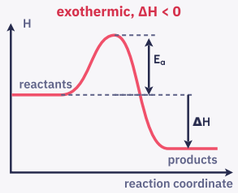
	Exothermic	Endothermic
ΔH	negative	positive
Heat	released to surroundings	absorbed from surroundings
Surroundings	temperature ↑	temperature ↓
Products	more stable	less stable

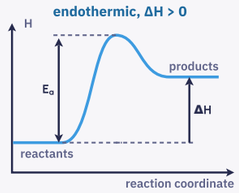
1.1 Energy profile diagrams

DEFINITION **Activation energy, E_a**: the minimum amount of energy reacting particles must possess for an _____ to take place.

- **Standard conditions**: _____, 1 bar (10^5 Pa), 1 mol dm^{-3} for solutions. $\Delta H^{\ominus}$(element in standard state) = 0
- Thermochemical equations need **state symbols**, ΔH scales with the amounts: doubling the equation doubles ΔH

NOTE Standard conditions (298 K, 1 bar) are **not** s.t.p. (273 K, 1 bar).





2 Standard Enthalpy Changes

Term	DEFINITION	Example equation	Sign
Reaction, $\Delta H_r^{\ominus}$	the enthalpy change when molar quantities of reactants, as specified by the balanced equation, react to form products under _____	$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	exo / endo
Formation, $\Delta H_f^{\ominus}$	the enthalpy change when one mole of the substance is formed from its _____ in their standard states under standard conditions ↳ $\Delta H_f^{\ominus}$ measures stability relative to the elements: negative → compound _____ than its elements	$2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$	exo / endo
Combustion, $\Delta H_c^{\ominus}$	the enthalpy change when one mole of the substance is _____ in oxygen under standard conditions	$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$	exo
Neutralisation, $\Delta H_{neut}^{\ominus}$	the enthalpy change when one mole of _____ is formed from the reaction of an acid and an alkali under standard conditions ↳ Strong acid + strong base: always −57.0 kJ mol^{-1}, as both fully dissociate → the reaction is just $H^+ + OH^- \rightarrow H_2O$. **Weak acid or base**: ΔH_{neut} is less exothermic than −57.0 (e.g. CH_3CO_2H, −55.2): (1) weak acid is only _____, (2) energy is absorbed to dissociate the undissociated acid → less energy released overall	$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	exo

2 Standard Enthalpy Changes (continued)

Term	DEFINITION	Example equation	Sign
Bond energy, BE	the _____ enthalpy change when one mole of covalent bonds between atoms in gaseous molecules is broken	$Cl–Cl(g) \rightarrow 2Cl(g)$	endo
Atomisation, $\Delta H_{at}^{\ominus}$	the enthalpy change when one mole of _____ is formed from the element in its standard state under standard conditions	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ (= ½BE)	endo
1st / 2nd IE	the enthalpy change when one mole of electrons is removed from one mole of gaseous atoms / _____	$Mg(g) \rightarrow Mg^+(g) + e^-$	endo
1st / 2nd EA	the enthalpy change when one mole of gaseous atoms / singly charged anions _____ one mole of electrons ↳ **Why is 1st EA negative but 2nd EA positive?** (1) 1st EA: energy is given off when electrostatic _____ forms between the positive nucleus and the electron added. (2) 2nd EA: energy is needed to overcome the _____ between the electron added and the singly charged anion, both negatively charged	$O(g) + e^- \rightarrow O^-(g)$	1st exo, 2nd endo
Lattice energy, LE	the energy released when one mole of the solid ionic compound is formed from its constituent _____ under standard conditions	$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	exo
Hydration, $\Delta H_{hyd}^{\ominus}$	the enthalpy change when one mole of _____ is hydrated under standard conditions ↳ Hydration is always exothermic: _____ interactions form between the ions and water molecules	$Na^+(g) + aq \rightarrow Na^+(aq)$	exo
Solution, $\Delta H_{sol}^{\ominus}$	the enthalpy change when one mole of the substance is completely dissolved to give an _____ solution under standard conditions, so that no further enthalpy change takes place on adding more solvent	$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$	exo / endo

IE, EA and LE values are per mole: e.g. IE(Mg) +736, $EA_1(O)$ −141, $EA_2(O)$ +844, LE(NaCl) −776 kJ mol^{-1}.

EXAM TIP **Read the definition off the term itself.** The term names what there is **one mole** of: **formation** → per mole of compound formed, **combustion** → per mole of substance burnt, **neutralisation** → per mole of water formed, **atomisation** → per mole of gaseous atoms formed, **hydration** → per mole of gaseous ions hydrated.

ANSWER STRUCTURE The enthalpy change when _____ of *(what the term names)* is *(formed / burnt / hydrated ...)* under _____.

Equation: give that species a coefficient of 1, then balance the rest, using fractions if needed, e.g. formation: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow \mathbf{1}\ C_2H_5OH(l)$.

3 Calorimetry

$q = -mc\Delta T$

m	mass of **solution** / g
c	specific heat capacity, 4.18 J g^{-1} K^{-1}
ΔT	$T_{final} - T_{initial}$

$\Delta H = q / n$

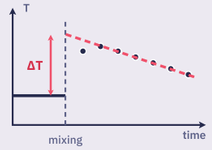
n	amount of **limiting** reagent (or the specified substance) / mol

Assumptions

- Negligible heat loss to the _____
- Negligible heat absorbed by the calorimeter
- Density of solution = _____, c of solution = c of water

Temperature correction

For slow reactions, plot T against time and **extrapolate** back to the time of mixing to account for heat loss.



WORKED EXAMPLE: NEUTRALISATION A student mixes 40.0 cm³ of 2.0 mol dm^{-3} HCl at 22.3 °C with 50.0 cm³ of 2.0 mol dm^{-3} NaOH at 22.5 °C. The highest temperature reached is 34.6 °C. Find ΔH_{neut}.

1. Initial T = $\frac{40.0(22.3) + 50.0(22.5)}{90.0}$
   = 22.41 °C (weighted average)
2. q = −(90.0)(4.18)(34.6 − 22.41)
   = _____
3. n_{HCl} = 0.08000 mol (limiting) = n_{H_2O} formed
4. ΔH_{neut} =
   −4586 ÷ 0.08000 = _____

WORKED EXAMPLE: COMBUSTION Burning 0.530 g of ethanol in a spirit burner heats 250 g of water by 10.4 °C. Find ΔH_c of ethanol.

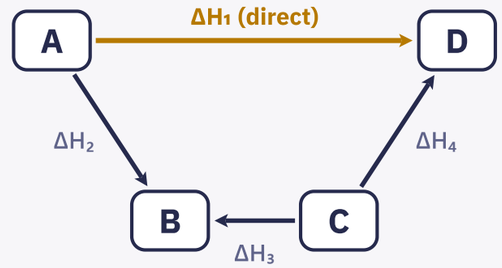
1. q = −250 × 4.18 × 10.4 = −10 870 J
   = −10.87 kJ
2. $n_{ethanol}$ = 0.530 ÷ 46.0 = 0.01152 mol
3. ΔH_c = −10.87 ÷ 0.01152 = _____

Less exothermic than the data value (−1368) because of heat loss to surroundings, heat absorbed by the calorimeter, or _____ _____. Efficiency: q′ = (x / 100) q.

4 Hess' Law

DEFINITION **Hess' Law**: the enthalpy change of a chemical reaction depends only on the _____ _____ of the system and is independent of the _____ taken.

From ΔH_c	$\Delta H_r = \Sigma\Delta H_c$(reactants) − $\Sigma\Delta H_c$(products)
From ΔH_f	$\Delta H_r = \Sigma\Delta H_f$(products) − $\Sigma\Delta H_f$(reactants)
From BE	$\Delta H_r = \Sigma$BE(bonds broken) − ΣBE(bonds formed)



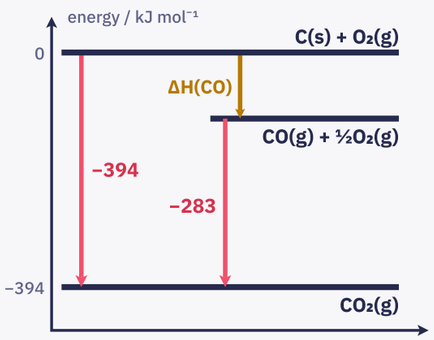
$\Delta H_1 = \Delta H_2 - \Delta H_3 + \Delta H_4$: going against an arrow changes its sign

4.1 Energy level diagram: ΔH_f(CO)

$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H_c(C) = -394$
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$	$\Delta H_c(CO) = -283$

$\Delta H_f(CO) = -394 - (-283) =$ _____

Check: arrows down for exothermic, elements at 0, state symbols.



4.2 Using combustion and bond energies

WORKED EXAMPLE: FROM ΔH_c Propane cannot be made directly from its elements. Find $\Delta H_f(C_3H_8)$ given ΔH_c / kJ mol^{-1}: C −394, H_2 −286, C_3H_8 −2220.

$3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$
$\Delta H_f = 3(-394) + 4(-286) - (-2220)$
= _____

WORKED EXAMPLE: FROM BE Estimate ΔH for the Haber process, $N_2 + 3H_2 \rightarrow 2NH_3$, given BE / kJ mol^{-1}: N≡N 944, H–H 436, N–H 390.

$\Delta H = [944 + 3(436)] - [6(390)]$
= _____

BE values are **averages** over many molecules, so ΔH from bond energies differs from values found by other methods.

5 Lattice Energy and the Born–Haber Cycle

5.1 Factors affecting lattice energy

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-}$$

Compound	LE / kJ mol⁻¹
NaCl	**−776**
NaBr	**−742**
$MgCl_2$	**−2375**

- Br^- has the same charge but a _____ than Cl^- → LE(NaBr) less exothermic than LE(NaCl)
- Mg^{2+}: higher charge, smaller radius than Na^+ → LE($MgCl_2$) _____

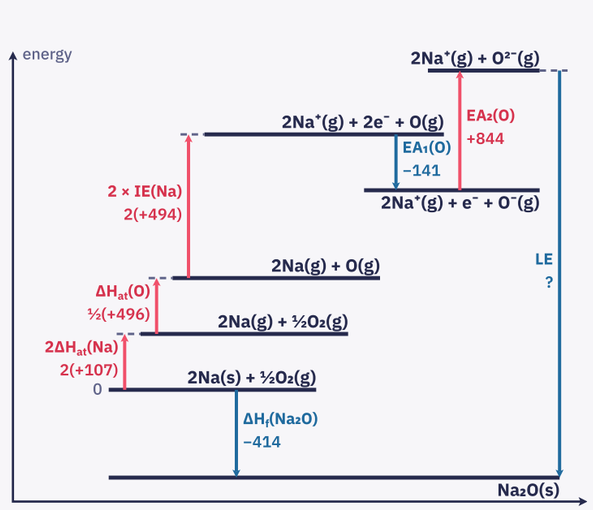
EXAM TIP Compare lattice energies as "more / less exothermic", never "larger / smaller".

NOTE Experimental LE more exothermic than theoretical (e.g. AgI, $MgCl_2$) → _____ from polarisation of the anion.

5.2 Born–Haber cycle for Na_2O

How to build a Born–Haber cycle (not to scale)

1. Draw the **elements** in their standard states at 0
2. **Atomise** each element (up): ΔH_{at}, times the number of atoms
3. **Ionise** the metal atoms (up): sum of IEs
4. **Add electrons** to the non-metal: EA_1 down, EA_2 up
5. Gaseous ions → solid: **LE** (down), ΔH_f joins elements to solid



Calculating LE:
ΔH_f = sum of the other steps

$-414 = 2(107) + ½(496) + 2(494) - 141 + 844 + LE$

LE = _____

6 Hydration and Solution

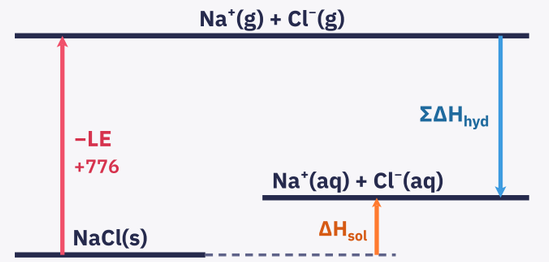
6.1 Using hydration and lattice energies

$\Delta H_{hyd} \propto q / r$

Small, highly charged ions attract water molecules more strongly → more exothermic hydration.

$\Delta H_{sol} = -LE + \Sigma\Delta H_{hyd}$

Dissolving happens in two steps: **(1)** break the lattice into gaseous ions, which **takes in** energy (−LE), then **(2)** surround the gaseous ions with water, which **gives out** energy ($\Sigma\Delta H_{hyd}$).



not to scale

WORKED EXAMPLE The enthalpy change of solution of NaCl is +5 kJ mol⁻¹. The lattice energy of NaCl is −776 kJ mol⁻¹ and the enthalpy change of hydration of Na^+ is −390 kJ mol⁻¹.
(a) Calculate the enthalpy change of hydration of Cl^-.
(b) $\Delta H_{hyd}(I^-)$ is −308 kJ mol⁻¹. Explain why it is less exothermic than $\Delta H_{hyd}(Cl^-)$.

(a)

1. $\Delta H_{sol} = -LE + \Delta H_{hyd}(Na^+) + \Delta H_{hyd}(Cl^-)$
2. $+5 = -(-776) + (-390) + \Delta H_{hyd}(Cl^-)$
3. $\Delta H_{hyd}(Cl^-) = 5 - 776 + 390 =$ _____

(b)

1. I^- has the same charge but a _____ _____ than Cl^-
2. → lower charge density
3. → _____ ion–dipole interactions with water molecules → less energy released