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CHEMICAL ENERGETICS

Enthalpy change (ΔH) : Amount of heat energy transferred during a chemical reaction, at a constant pressure.

Lattice energy ($\Delta H^{\ominus}_{latt}$) : Enthalpy change when 1 mole of ionic compound is formed from its gaseous ions, under standard conditions.

- always exothermic ∵ energy released when gaseous ions combine to form solid ionic lattice ⇒ -ve value
- large -ve value ∵ huge release in energy when gaseous ions combine.
- large -ve value ⇒ ionic compound much more stable than gaseous ions
  - → strong electrostatic forces of attraction btwn opp. charge ions in solid lattice vs. no electrostatic attraction btwn ions in gas state.
  - → more exothermic value ⇒ stronger ionic bonds in lattice.

eg. $Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s)$

Standard Enthalpy change of atomisation ($\Delta H^{\ominus}_{at}$) : Enthalpy change when 1 mole of gaseous atoms is formed from its element in standard state, under standard conditions.

- always endothermic : energy required to break bonds btwn atoms of element to gaseous atoms ⇒ +ve value

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

Standard conditions
- 298K
- 1atm / 101 kPa

Electron Affinity

EA_1: Enthalpy change when 1 mole of e^- is added to 1 mole of gaseous atoms to form 1 mole of gaseous ions, ~~under Standard conditions~~ each with a single -ve charge, under standard conditions.

$$X(g) + e^- \rightarrow X^-(g)$$

EA_1 : exothermic ⇒ -ve value

↳ energy released when adding e^-

EA_2, EA_3: successive electron affinities; represent formation of 1 mole of gaseous ions w/ 2- & 3- charges

$$X^-(g) + e^- \rightarrow X^{2-}(g)$$
$$X^{2-}(g) + e^- \rightarrow X^{3-}(g)$$

EA_2 & EA_3 : endothermic ⇒ +ve value

↓

incoming e^- added to already -ve ion ∴ energy needed to overcome repulsion

Factors affecting EA

- EA depends on how strongly nucleus attracts incoming e^-.
- stronger nuclear attraction ⇒ more energy released ⇒ EA more exothermic (more -ve)

① Nuclear charge ↑ ⇒ Nuclear attraction ↑ ⇒ More exo
② Atomic radius ↑ ⇒ Nuclear attraction ↓ ⇒ Less exo
③ Shielding ↑ ⇒ Nuclear attraction ↓ ⇒ Less exo

Trends in EA

→ Across period:

- EA of non-metals more exo w/ max at Group 17.
- nuclear charge ↑ ⇒ nuclear attraction ↑
- more energy released ∴ EA, more exothermic.

→ Down group 16 & 17

- EA less exo down grp; exception: O & F (1st member)
- atomic radius ↑, shielding ↑ ⇒ nuclear attraction ↓
- less energy released ∴ EA, less exothermic

exceptions:

- O & F have vs small atomic radius ∴ high e^- density surrounding nucleus.
- Inc. repulsion btwn incoming e^- & existing e^-.
- Repulsion weakens nuclear attraction.
- ~~Thus~~ ∴ EA, less exo than expected.

Born-Haber Cycle

↳ to calc. lattice enthalpy, which cannot be found by exp.

↑ endothermic; energy ↑
↓ exothermic; energy ↓

Steps

① Start w/ elements in standard state

$Na(s) + \frac{1}{2}Cl_2(g)$

② Atomisation of metal

$Na(s) \rightarrow Na(g)$ • ΔH_{at}° of Na

③ Atomisation of non-metal

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ • ΔH_{at}° of Cl

④ Ionisation of metal

$Na(g) \rightarrow Na^+(g) + e^-$ • IE_1 of Na

⑤ Electron affinity of non-metal

$Cl(g) + e^- \rightarrow Cl^-(g)$ • EA_1 of Cl

⑥ Lattice formation

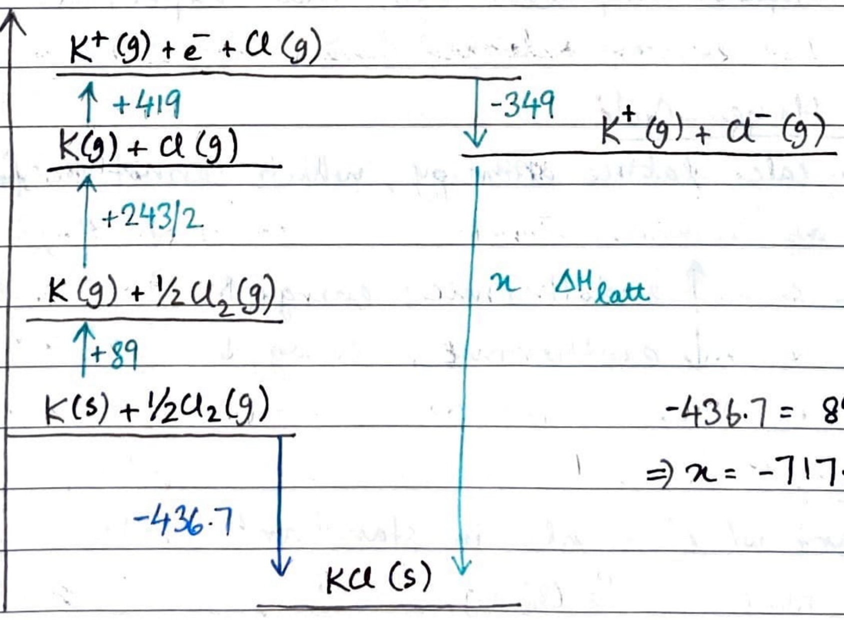
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ • ΔH_{latt}

⑦ Link to enthalpy of formation

$\Delta H_f = \Delta H_{at}^\ominus(Na) + \Delta H_{at}^\ominus(Cl) + \cancel{\Delta H}\ IE_1(Na) + EA_1(Cl) + \Delta H_{latt}^\ominus$

eg: ~~[illegible]~~ KCl

$\Delta H_{at}^\ominus(K)$	89 kJ mol⁻¹	$K(s) \rightarrow K(g)$
$IE_1(K)$	~~418~~ 419 kJ mol⁻¹	$K(g) \rightarrow K^+(g) + e^-$
$\Delta H_{at}^\ominus(Cl)$	243 kJ mol⁻¹	$\cancel{\tfrac{1}{2}} Cl_2(g) \rightarrow 2Cl(g)$
$EA_1(Cl)$	-349 kJ mol⁻¹	$Cl(g) + e^- \rightarrow Cl^-(g)$



$-436.7 = 89 + 121.5 + 419 - 349 + x$

$\Rightarrow x = -717.2$

$\Delta H_f = \Delta H_{at}^\ominus + \Delta H_{at}^\ominus + IE + EA + \Delta H_{latt}^\ominus$

$$\boxed{\Delta H_f = \Delta H_1^\ominus + \Delta H_{latt}^\ominus}$$

$$\boxed{\Delta H_{latt}^\ominus = \Delta H_f - \Delta H_1^\ominus}$$

$\Delta H_1^\ominus$ = sum of enthalpy changes to convert the elements in standard states → gaseous ions.

Factors affecting lattice energy

① charge of ion } of ions in crystalline lattice
② ionic radius

→ Ionic charge ↑ ⇒ more exothermic lattice energy
- Ionic charge ↑ ⇒ charge density ↑
- stronger electrostatic forces of attraction btwn opp. charged ions.
- ∴ more energy released when lattice formed.

→ Ionic radius ↑ ⇒ less exothermic lattice energy
- Ionic radius ↑ ⇒ charge density ↓ (charge spread over greater volume).
- Distance btwn centres of ions ↑
- weaker electrostatic forces of attraction btwn opp. charged ions.
- ∴ less energy released when lattice formed.

Standard Enthalpy change of solution ($\Delta H_{sol}^{\ominus}$): Enthalpy change when 1 mole of an ionic substance dissolves in sufficient water to form a very dilute solution, under standard conditions.

→ aq is used to show that solid is dissolved in water.

eg $KCl (s) + aq \rightarrow KCl (aq)$ OR $KCl (s) + aq \rightarrow K^{+} (aq) + Cl^{-} (aq)$

→ $\Delta H_{sol}^{\ominus}$ can be exothermic OR endothermic

Standard Enthalpy change of hydration ($\Delta H_{hyd}^{\ominus}$): Enthalpy change when 1 mole of a specified gaseous ion dissolves in sufficient water to form a very dilute solution, under standard conditions.

eg. $Mg^{2+} (g) + aq \rightarrow Mg^{2+} (aq)$

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* Hydration enthalpy = measure of energy released when there is an attraction formed btwn the ions & water molecules - when hydrated ion forms.

- when ionic solid dissolves, splits into cations & anions
- water is polar : $\underbrace{\delta^- O}_{\text{attracted to cations}}$ & $\underbrace{\delta^+ H}_{\text{attracted to anions}}$
- these interactions form ion-dipole bonds btwn. ions & water molecules.

→ ΔH°_{hyd} is exothermic.

Energy cycles

- Route 1 : solid ionic lattice → ions in aq. solution
  ΔH°_{sol} (enthalpy change of solution)

- Route 2 : solid ionic lattice → gaseous ions → ions in aq. solution
  $-\Delta H^{\circ}_{latt} + \Delta H^{\circ}_{hyd}$ (reverse lattice enthalpy + hydration enthalpies of each ion)

* ΔH°_{latt} = lattice formation enthalpy (bond forming)
$-\Delta H^{\circ}_{latt}$ = lattice dissociation enthalpy (bond breaking)

$$\boxed{\Delta H^{\circ}_{sol} = -\Delta H^{\circ}_{latt} + \Delta H^{\circ}_{hyd}}$$

$$\boxed{\Delta H^{\circ}_{hyd} = \Delta H^{\circ}_{sol} + \Delta H^{\circ}_{latt}}$$

eg. Energy cycle & energy level diagram to calculate $\Delta H_{hyd}^{\ominus}$ of Cl^- ion in KCl.

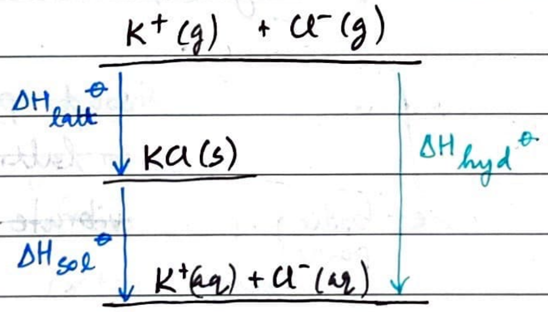
$\Delta H_{latt}^{\ominus}(KCl) = -711\ kJ\ mol^{-1}$
$\Delta H_{sol}^{\ominus}(KCl) = 26\ kJ\ mol^{-1}$
$\Delta H_{hyd}^{\ominus}(K^+) = -322\ kJ\ mol^{-1}$

$$\begin{tikzcd}
K^+(g) + Cl^-(g) \arrow[rr, "\Delta H_{hyd}^{\ominus}"] \arrow[dr, "\Delta H_{latt}^{\ominus}"'] & & K^+(aq) + Cl^-(aq) \\
& KCl(s) \arrow[ur, "\Delta H_{sol}^{\ominus}"'] &
\end{tikzcd}$$

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

$\Rightarrow -322 + x = -711 + 26 = -685$

$x = -685 + 322 = -363\ kJ\ mol^{-1}$



factors affecting enthalpy of hydration

① Ionic charge
② Ionic Radius

→ Ionic charge ↑ ⇒ more exothermic hydration enthalpy
- ionic charge ↑ ⇒ charge density ↑
- stronger ion-dipole interactions
- ∴ more energy released during hydration

→ Ionic radius ↑ ⇒ less exothermic hydration enthalpy
- Ionic radius ↑ ⇒ charge density ↓
- weaker ion-dipole interactions
- less energy released during hydration

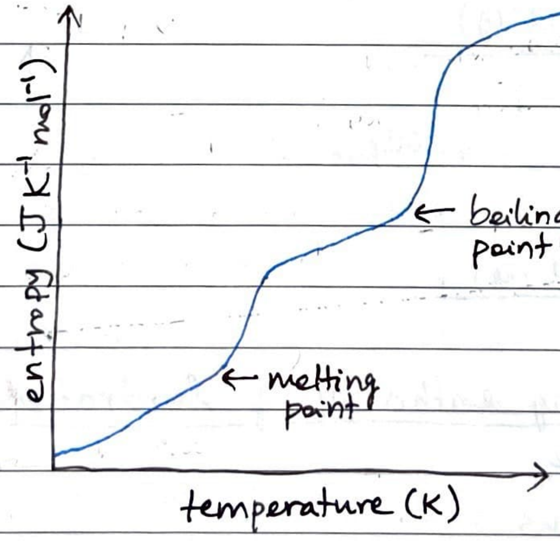
Entropy (S): Entropy of a given system = no. of possible arrangements of the particles and their ~~energies~~ energy in the system; measure of how disordered a system is.

↳ higher disorder ⇒ higher entropy ⇒ system more energetically stable (∵ energy more spread out)

→ **Entropy btwn physical states**

order of entropy: gas > liquid > solid

*some exceptions: eg. $CaCO_3$ (solid) has higher entropy than mercury (liquid).



~~solid: particles fixed in lattice & can only vibrate~~

~~solid → liquid (melting):~~

entropy ↑ ∵ more movement of particles, particles more spread out, particles less ordered / more disorder, more ways of arranging energy.

→ **Entropy and dissolving**

→ Dissolving solid in solvent: entropy ↑

- particles less ordered, more spread out, ~~less ordered~~, more ways of arranging energy.

→ Crystallisation of salt from solution: entropy ↓

- particles more ordered, close tgthr in lattice, fewer ways of arranging energy.

→ **Factors affecting entropy**

- complexity of substance: complex substances w/ more atoms have higher entropy than simple substances w/ fewer atoms. eg. $CaCO_3 > CaO$
- hardness: harder substances have lower entropy than softer/less rigid substances of same type.
  eg. diamond < graphite

→ **Entropy change in reactions**

- gas molecules most disordered ∴ dominate entropy changes. if no. of gaseous molecules in reaction changes, entropy changes.
- no. of gas molecules ↑, no. of ways of arranging them ↑, entropy ↑

eg. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ Decomposition of $CaCO_3$
formation of gas increases disorder ∴ entropy ↑

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ Haber process
no. of gaseous molecules decreases from 4 to 2
∴ less disorder due to fewer ways of arranging energy ∴ entropy ↓
↳ N_2 & H_2 are energetically more stable than NH_3.

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$$\boxed{\Delta S_{system}^{\theta} = \Sigma S_{products}^{\theta} - \Sigma S_{reactants}^{\theta}}$$

(standard ~~enthalpy~~ entropy change of system.

eg. $2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$

$S^{\theta}[Mg(s)] = 32.60\ J\ K^{-1}\ mol^{-1}$

$S^{\theta}[O_2(g)] = 205.0\ J\ K^{-1}\ mol^{-1}$

$S^{\theta}[MgO(s)] = 38.20\ J\ K^{-1}\ mol^{-1}$

$$\Delta S_{system}^{\theta} = 2 \times 38.2 - (2 \times 32.6 + 205)$$
$$= -193.8\ J\ K^{-1}\ mol^{-1}$$

Gibbs Free Energy (G): energy change ~~&~~ that takes into account both entropy change & enthalpy change of reaction.

~~$\Delta G^{\theta} = \Delta H_{reaction}^{\theta} - \Delta S_{system}^{\theta}$~~

$$\boxed{\Delta G^{\theta} = \Delta H_{reaction}^{\theta} - T\Delta S_{system}^{\theta}}$$

units:

- $\Delta G^{\theta} = kJ\ mol^{-1}$
- $\Delta H = kJ\ mol^{-1}$
- $T = K$
- $\Delta S = J\ K^{-1}\ mol^{-1}$ REMEMBER to convert to $kJ\ K^{-1}\ mol^{-1}$ $\div 1000$!

eg. calc. Gibbs free energy for the following reaction at 298 K :

$$CH_3OH(l) + HBr(g) \longrightarrow CH_3Br(g) + H_2O(l)$$

$\Delta H_r^{\theta} = -47\ kJ\ mol^{-1}$

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$\Delta S^\ominus [CH_3OH(l)] = +240\ J\ K^{-1}\ mol^{-1}$

$\Delta S^\ominus [HBr(g)] = +99\ J\ K^{-1}\ mol^{-1}$

$\Delta S^\ominus [H_2O(l)] = +70\ J\ K^{-1}\ mol^{-1}$

$\Delta S^\ominus [CH_3Br(g)] = +246\ J\ K^{-1}\ mol^{-1}$

$$\Delta S_{system}^\ominus = \Sigma S_{products}^\ominus - \Sigma S_{reactants}^\ominus$$
$$= \cancel{246+}\ 246 + \overset{70}{\cancel{99}} - 240 - \cancel{99}\ 99 \approx -23\ J\ K^{-1}\ mol^{-1}$$
$$= -0.023\ kJ\ K^{-1}\ mol^{-1}$$

$$\Delta G^\ominus = \Delta H_{reaction}^\ominus - T\Delta S_{system}^\ominus$$
$$= -47 - 298(-0.023) = -40.1\ kJ\ mol^{-1}$$

Reaction feasibility

- when $\Delta G^\ominus$ is -ve, reaction is feasible & likely to occur.
- when $\Delta G^\ominus$ is +ve, reaction is not feasible & unlikely to occur.

Reaction feasibility & Temperature changes

↳ feasibility is affected by temperature.

	ΔH	ΔS	ΔG	Spontaneous?	Explanation
(i)	-ve	+ve	always -ve	always	both terms -ve
(ii) exothermic	-ve	-ve	-ve at low T, +ve at high T	only at low T	1st term -ve & 2nd term +ve. At high T, second term becomes large +ve & outweighs 1st
(iii)	+ve	-ve ~~+ve~~	always +ve	never	both terms +ve
(iv) endothermic	+ve	+ve	+ve at low T, -ve at high T	only at high T.	1st term +ve & 2nd -ve. At high T, 2nd becomes large negative & outweighs first.

$$\Delta G = \underbrace{\Delta H_{reaction}}_{\text{first term}} \underbrace{- T\Delta S_{system}}_{\text{second term}}$$

This corresponds to Le Chatelier's Principle:

- → for exothermic reactions, T↑ causes eq. position to shift in favour of reactants (in endothermic direction)
  - for exo, products not formed at high temp.
  - not feasible at high temp.
- → for endothermic reactions, T ↑ causes eq. position to shift in favour of products.
  - for endo, products formed at high temp.
  - feasible at high temp.