

Energetics - Chapter 5

Characteristics of Reactions

Exothermic → making bonds, rise in external temp, $-\Delta H$
→ energy released by product bond formation > energy used to break reactant bonds

Endothermic → breaking bonds, decrease in external temp, $+\Delta H$
→ energy released by forming prod bonds < energy used to break reactant bonds

Calor

Calorimeter problem

→ incomplete combustion
 → heat supplied to calorimeter itself / some heat lost to environment

Systems

Open: Chemicals + energy can be transferred between systems and surroundings

Closed: Only energy transferred between system + surroundings

To improve calorimeter, better insulation, abundant O_2 and etc

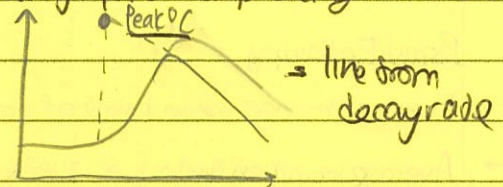
Calculating enthalpy change (kJ/mol)

$$q = \frac{\text{mass} \times \text{SHC} \times \Delta \text{temp}}{\text{moles of limiting reagent}}$$

$$q = \frac{m \cdot c \cdot \Delta T}{\text{moles}}$$

mass of the water or medium through which T change is observed

If shown graph of temp change do the following



Definitions + Things to know

ΔH_r ← reaction type
← standard conditions [100kPa, 1 mol/dm³, all substances in standard state]

- 1) ΔH_r^\ominus → enthalpy change when a reaction occurs in stated molar quantities, under standard conditions
- 2) ΔH_f^\ominus → standard enthalpy change when 1 mole of substance is formed from atoms of element
- 3) ΔH_c^\ominus → standard enthalpy change when 1 mol of fuel is combusted completely in excess oxygen
- 4) ΔH_{latt}^\ominus → standard enthalpy change when 1 mol of solid ionic crystal lattice is broken into gaseous ions
- 5) $\Delta H_{atomisation}^\ominus$ → When 1 mol of atoms in gas state are formed from ^{element} standard state
- 6) $\Delta H_{dissociation}^\ominus$ → when atoms ^{are} formed in gas state from 1 mole of the element in standard state
- 7) $\Delta H_{ionisation}^\ominus$ → enthalpy change when 1 mol of gas atoms lose 1 mol of electrons to form 1 mol + ions gas
- 8) $\Delta H_{electron\ affinity}^\ominus$ → enthalpy change when one mole of atoms in gas state gain 1 mole of electrons to form 1 mol of gaseous anions
- 9) $\Delta H_{hydration}^\ominus$ → energy change when 1 mole of gaseous ions dissolves in sufficient H_2O to give an infinitely dilute solution

Note, if you reverse a reaction, sign on ΔH changes

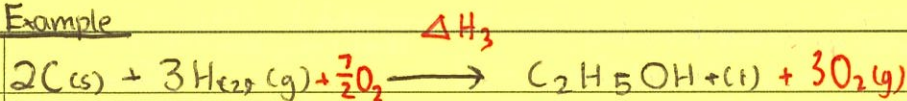
Hess' Law

- total enthalpy change of reaction is independent of route taken
- necessary if slow reaction, high activation energy, temp changes make reaction non standard

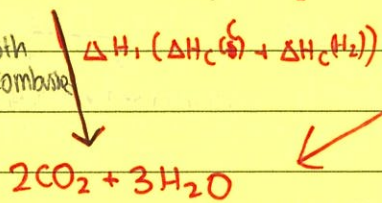
Example

Date

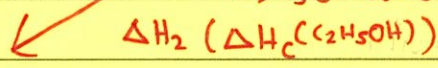
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if both are combusted



if C₂H₅OH combusts



Using vectors = $\Delta H_3 = \Delta H_1 - \Delta H_2$

$$= 2\Delta H_c(C) + 3\Delta H_c(H_2) - \Delta H_c(C_2H_5OH)$$

$$= \underline{\underline{-273kJ/mol}}$$

Bond Enthalpy

- Energy change when 1 mole of covalent bond in gas is ~~can~~ broken / formed
- Average bond enthalpy → average energy change when one mole of covalent bonds in gas state are broken under θ conditions.
- Bond breaking = endo, forming = exo

If the products have more energy than reactants, the reaction is endothermic

$$\sum \text{bond enthalpies in products} - \sum \text{bond enthalpies in reactants} = \Delta H_r$$

→ If you have an equation like this = $C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(g)$
 the use of average bond enthalpies ^(ABE) are not suitable as 2 of the chemicals involved are in liquid form, and ABE refers to gas forms. If the latent heat of vaporisation is subtracted from the ΔH_r calculated by ABE

→ Average → no account of neighbouring atoms → why different from experiment

Energy Cycles

Lattice Enthalpy → measure of strength of electrostatic forces of attraction between ions in an ionic solid

Factors affecting $\Delta H_{latt,diss}$

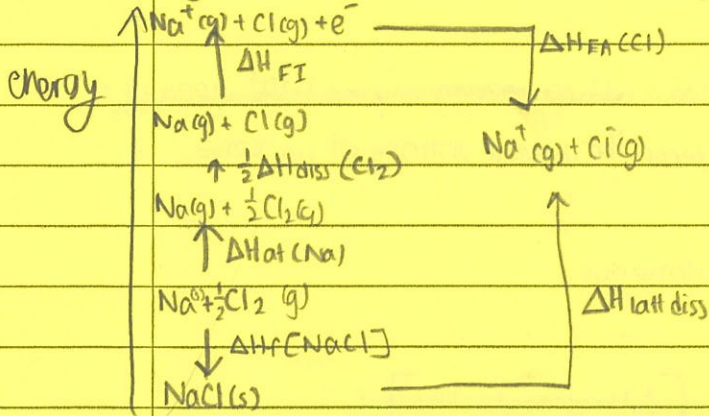
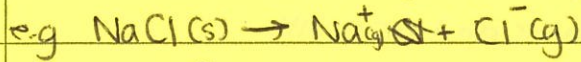
- 1) Ionic charge - The higher the charge on ^{ions} atoms involved, the stronger the electrostatic force of attraction between ions in the ionic solid. Hence, more energy is needed to break these forces of attraction ∴ $\Delta H_{latt,diss}$ rise
- 2) Ionic radius - The larger the ionic radius, the further the outer shells are from the positively charged nucleus ~~therefore~~, hence the electrostatic forces of attraction between ions are weaker, therefore ↓ ΔH_{latt}

Theoretical calculations assume molecules/ions are perfectly spherical with only 1 type of attraction [e.g. electrostatic for ΔH_{LE}]

Born-Haber Cycles → [when y axis = energy]

Date

No.



$$\Delta H_{latt\,diss} = \Delta H_{FEA}(Cl) + \Delta H_{FI}(Na) + \frac{1}{2}\Delta H_{diss}(Cl_2) + \Delta H_{at}(Na) - \Delta H_f(NaCl)$$

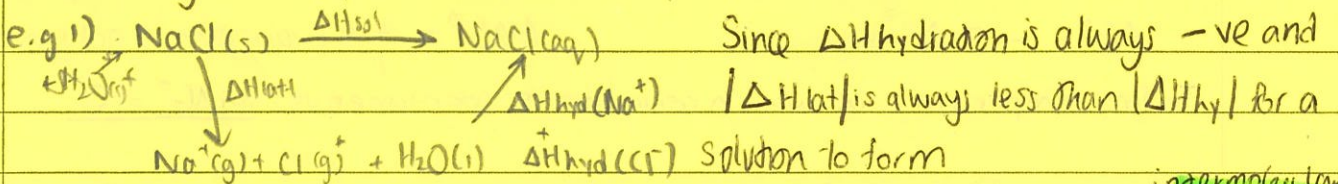
Solubility Reactions

$\Delta H_{latt\,diss} + \Delta H_{hyd} = \Delta H_{sol}$

$\Delta H_{solution}$ = enthalpy change when 1 mole of solute dissolves in an infinitely dilute solution of water under standard conditions.

Why infinitely dilute? → if small volume of water used, ions would just stick together

For something to dissolve, the overall ΔH_{sol} should be exothermic



The higher the ionic charge on ions, $\uparrow |\Delta H_{hyd}|$ since for stronger favourable ~~intermolecular~~ ^{intermolecular} forces formed between solute + solvent. The smaller the ion radius, the stronger the forces, therefore, $\uparrow |\Delta H|$.

Entropy Change

Entropy (S) → distribution of available energy amongst particles

[$S < I < aq < g$] - states ordered in increasing entropy, as movement of particles increase as you go across hence more ways to distribute energy, \uparrow entropy

The more particles there are (e.g. more moles of products than reactants), the more ways there are to distribute energy, as there are more possible configurations for atoms. \uparrow entropy

The more complex a molecule is, the higher its entropy because molecules with more bonds can move around in 3D space → more ways to distribute entropy $\therefore \uparrow$ entropy

Bear in mind that spontaneity is a yes no, not continuous

ΔS^\ominus_r Entropy Change \rightarrow Difference in entropies of products and reactants

$\frac{J}{K \cdot mol}$
remember to change to kJ

Spontaneous Reactions: reactions that occur without adding energy beyond that needed to overcome activation energy barrier. They increase the overall entropy of universe

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$

if ΔS_{total} is positive, the reaction is spontaneous

$\Delta S_{surr} = \frac{-\Delta H_{system}}{T}$

$\therefore \Delta S_{total} = \Delta S_{system \text{ or } reaction} - \left[\frac{\Delta H_{reaction/system}}{T} \right]$
convert to kJ/mol K

ΔH	ΔS	ΔS_{total}
-	+	+ve
-	-	+ve at low temperatures [$\uparrow \Delta S_{surr}$]
+	+	+ve at high temperatures [$\downarrow \Delta S_{surr}$]
+	-	Never +ve

ΔG takes into account direct entropy change from chemical reaction and the indirect energy change of the surroundings because of heat loss/gain

Gibbs Free Energy change

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

At $\Delta G^\ominus = -ve$, reaction is spontaneous

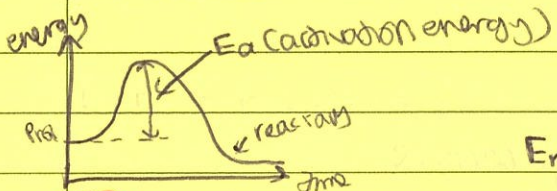
$\Delta G^\ominus = -T \Delta S^\ominus_{system}$

At $\Delta G^\ominus = +ve$, reaction is not spontaneous

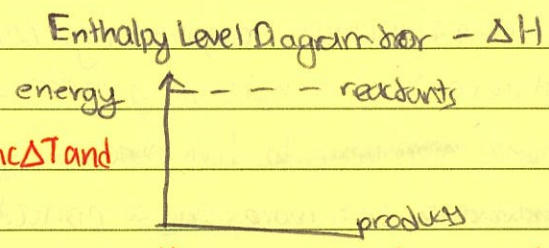
To find temperature at which reaction is spontaneous, set $\Delta G^\ominus = 0$

Ozone + Oxygen If a reaction requires extra energy to start, could be high activation energy or insufficient energy to react at stated temperature.

For exo/endo



Activation energy - energy needed to break the bonds in reactants



Tips

- \rightarrow if asked for heat evolved, use $q = mc\Delta T$ and give in J/kJ
- \rightarrow "Explain ΔS sign," \rightarrow state and compare with reaction, e.g. $2NH_3 \rightleftharpoons N_2 + 3H_2$, $+\Delta S$ because more moles of gas in prod than reactants
- \rightarrow Remember to divide if you have to multiply!