

REVISION NOTES: ENERGETICS

5.1 measuring energy changes

heat is a form of energy - there are energy changes in reactions.

↳ total energy is ALWAYS CONSERVED.

↳ energy changes can be EXOTHERMIC or ENDOTHERMIC in chem. reactions.

exothermic = increase in °C of surroundings [$\Delta H = -ve$]

endothermic = decrease in °C of surroundings [$\Delta H = +ve$]

enthalpy change (ΔH), in kJ mol^{-1} , is the change in the energy stored in reactants / products / chemicals.

↳ standard enthalpy change of reaction MUST occur @ 100 kPa, 298 K.

↳ to calculate ANY enthalpy change ...

$$Q = m \times c \times \Delta T$$

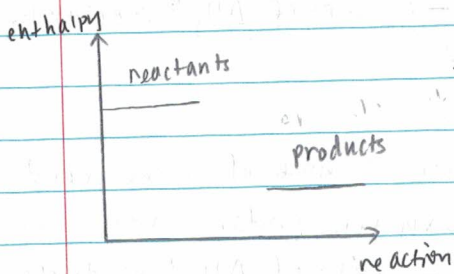
\swarrow mass (g) \downarrow heat capacity ($4.18 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1}$) \searrow °C change

Q/mol = must be moles of LIMITING REAGENT.

assuming...
 I. solution has same heat capacity as water
 II. solution has the same density as water (1 g/cm^3)
 ↳ mass = volume of solution.

enthalpy level diagrams

exothermic = energy IN reactants is greater than energy in products
 ie. enthalpy in reactants > products.



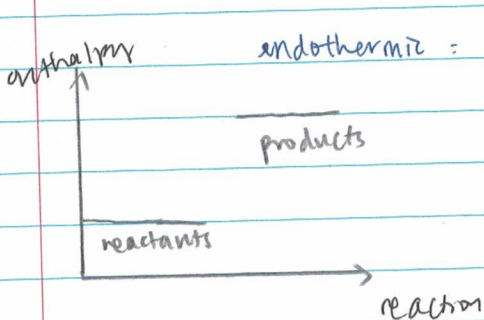
∴ you RELEASE energy.

∴ products are MORE stable than reactants because they are at LOWER energy levels.

E.g. combustion

& neutralization

because you make strong DH bonds
 bond making = exothermic.



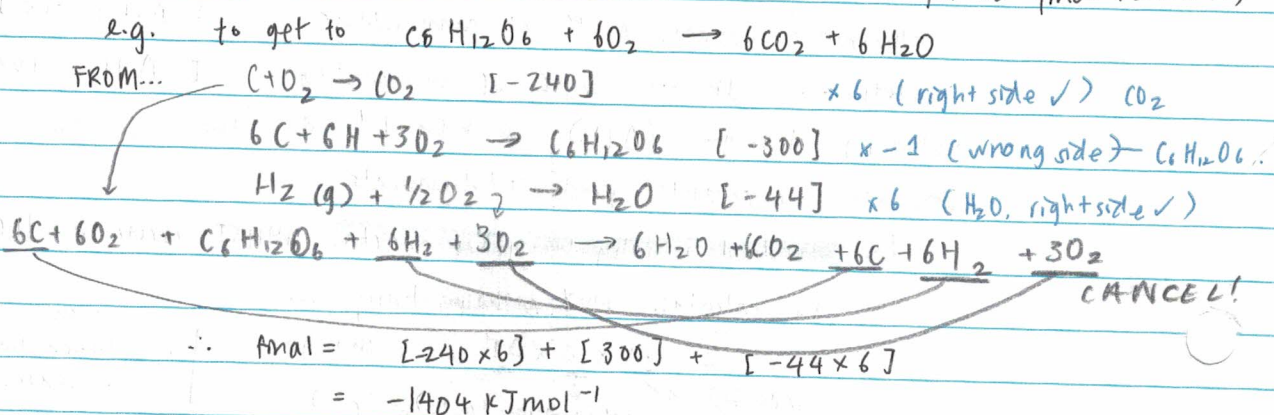
endothermic = energy in products is greater than in reactants

∴ take IN energy to get to products.

∴ products are less stable than reactants as they are at HIGHER energy / enthalpy (bonds broken in reactants are stronger than the ones formed in the products)

5.2 Hess' Law

Hess' law suggests that the enthalpy change for a reaction carried out in several steps is equal to the sum of enthalpy changes for individual steps (doesn't matter which route occurs to get to final reaction)



THE shortcut method (standard enthalpy change of formation)

(ΔH_f^\ominus is the enthalpy change required to make one mole of a compound from its elements in their standard state)

$$\Delta H_f^\ominus = \text{sum of } \Delta H_f^\ominus \text{ products} - \text{sum of } \Delta H_f^\ominus \text{ reactants.}$$

↳ values can be found @ table 12, pg 12

for the standard enthalpy change of combustion

(ΔH_c^\ominus is the enthalpy change when 1 mole of a compound is completely burned in excess oxygen under standard conditions)

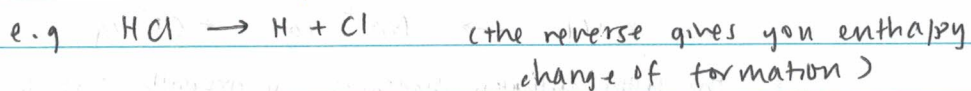
$$\Delta H_c^\ominus = \text{sum of } \Delta H_c^\ominus \text{ reactants} - \text{sum of } \Delta H_c^\ominus \text{ products.}$$

↳ values can be found @ table 13, pg 13

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5.3 Bond enthalpies

Average bond enthalpy is the amount of energy required to break ONE MOLE of a covalent bond in a gaseous molecule, averaged over several similar compounds



HOWEVER the average bond enthalpy does not take into account intermolecular forces (of a solid or liquid)

AND they are an average of same bond, different molecules

[different atoms in molecule = inaccurate]

$\therefore \Delta H_f^\ominus$ values are more acc. e.g. C-H_4 and C_6H_6 and CH_2

• bond making releases energy

• bond breaking requires energy

\therefore in exothermic reactions, bond breaking < bond making suggesting that bonds in REACTANTS were weaker than those in a product (easier to break)

\therefore in endothermic reaction (products less stable than reactants)

• to calculate enthalpy change with bond enthalpies...

$$\Delta H = \text{bonds broken} - \text{bonds formed}$$

[reactants] - [products]



$$[\text{C-H}] \times 4 + (\text{Cl-Cl}) \times 2, - [3(\text{C-H}), (\text{Cl-C}) + (\text{H-Cl})]$$

use data from table 11

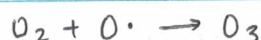
• Oxygen & ozone in the atmosphere

O_2 is :O=O: whilst O_3 is :O::O::O: $\therefore \text{O}_2$ bond stronger

O_2 broken by HIGHER energy, shorter wavelength — absorb high energy UV

\rightarrow formation of O_3 / O_2

O_3 — absorb low energy UV



] energy released as HEAT.

15-1 Energy cycles

Hess' law can be applied to other things, e.g. reactions involving ionic compounds!

- lattice enthalpy is the amount of energy required to separate one mole of a crystalline compound (lattice) into its constituent gaseous ions



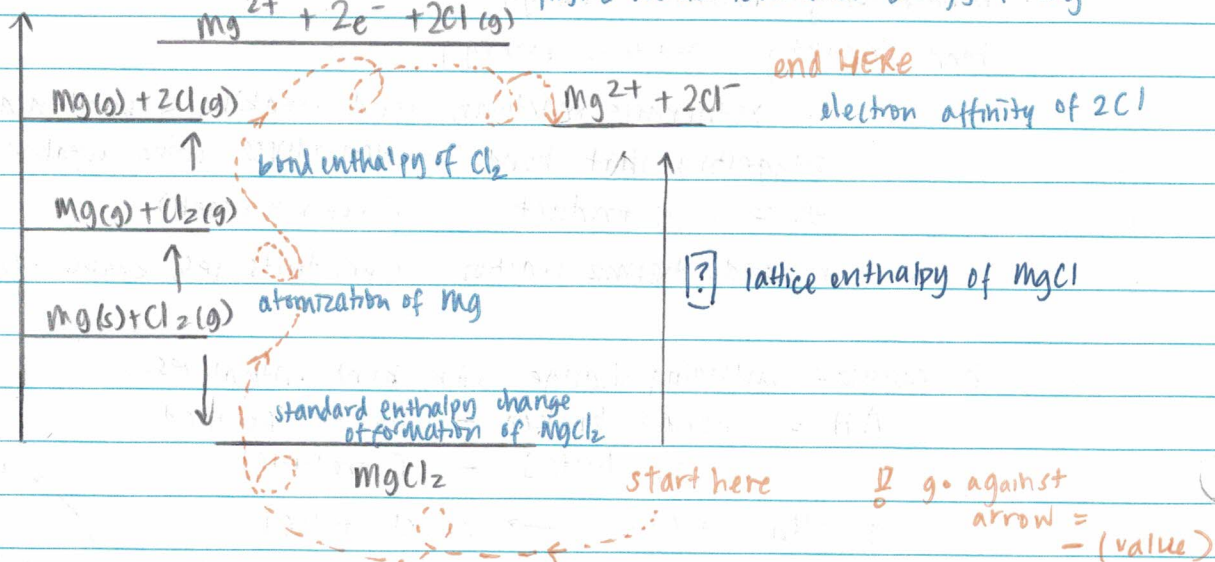
i.e. the lattice enthalpy measures the strength of an ionic bond

THIS CHANGES
depending on...

- size of ion (smaller ion = greater charge density = ↑ Δ)
- charge on ion (↑ charge ↑ attractive force)

the Born-Haber cycle shows individual steps in the enthalpy change of formation of a compound (ionic) OR lattice enthalpy.

e.g. magnesium chloride (lattice enthalpy)



important definitions...

enthalpy of atomization - enthalpy required to form 1 mole of gas from the element in its standard state

ionization energy - energy required to remove 1 mole of electrons from 1 mole of gaseous atoms (2nd IE is 1 mole of $2+$ ion) to produce 1 mole of $2+$ ions

electron affinity - energy RELEASED when 1 mole of a gaseous atom gains 1 mole of electrons to produce 1 mole of $1-$ ions

enthalpy of formation - energy change when 1 mole of compd is produced from its elements in their standard state.

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15.1 energy cycles (cont'd)

enthalpy of solutions can also be found through an energy cycle
the **standard enthalpy of solution** is the enthalpy change when one mole of a **solute** is dissolved in a excess of **pure solvent**
↳ dissolve in water - watch temperature rise.

there are 2 steps to an enthalpy of solution

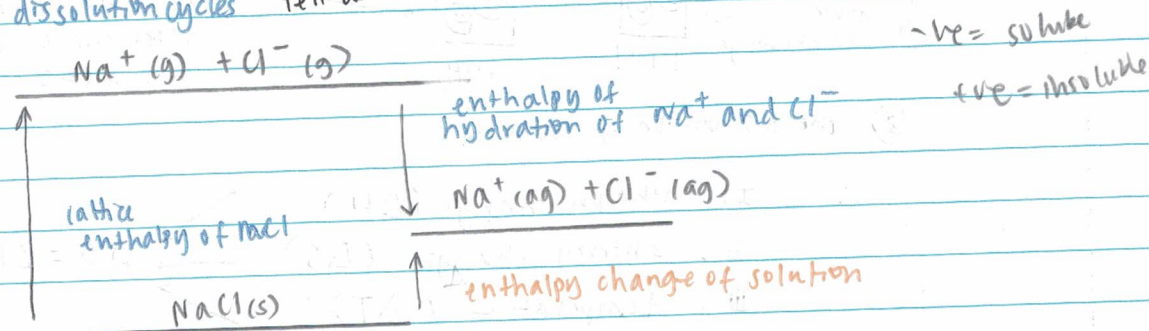
I: **separation** of ions from a lattice (same as lattice enthalpy)

II: **hydration** of ions (this **RELEASES** energy) = by water molecules

↳ this is hydration enthalpy when

1 MOLE of gaseous ions is added to water to form a dilute solution
 $(\text{Na}^+(\text{g}) \rightarrow \text{Na}^+(\text{aq}))$

so... is enthalpy of solution going to be +ve or -ve?
dissolution cycles tell us.



if $|\text{lattice enthalpy}| > |\text{enthalpy of hydration}|$, this will be more insoluble
i.e. endothermic [look @ position of products/reactants!]

if $|\text{lattice enthalpy}| < |\text{enthalpy of hydr.}|$, this is more soluble
i.e. exothermic

... what changes the enthalpy of hydration?

∴ ionic charge ↑ then it is easier to attract H^+ or OH^- ions

∴ value of hydration is greater, it releases more energy

∴ more exothermic (arrow larger)

BUT this is hard to predict as lattice enthalpy goes ↑ too when ionic charge increases ∴

(CHARGE DENSITY)
↑ ionic radius ↓

15.2 entropy and spontaneity

entropy is a measure of disorder in a system and how much energy is dispersed. If there are more ways to \leftrightarrow disperse energy = \uparrow entropy

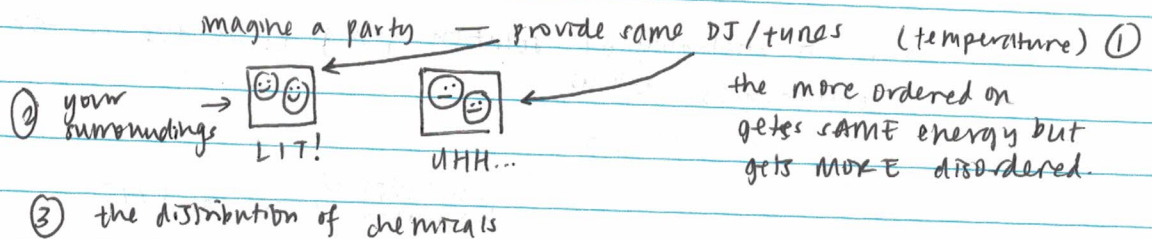
e.g. if a reaction \rightarrow disorder, entropy is +ve
 $(s) \rightarrow (g)$ or $(g) \rightarrow (g) + (g)$ [solid \rightarrow liquid evolution \rightarrow gas]

$$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

! beware of moles

spontaneity is when a reaction happens on its own w/o constant heating
 reactions are only spontaneous if they lead towards disorder
 (the universe tends towards disorder).

what affects spontaneity?



if ΔH is \rightarrow ^{sothermic} more energy \rightarrow likely \rightarrow spontaneous

$\Delta S > 0$ = entropy, the disorder

I. enthalpy change (ΔH)
 II. entropy change (ΔS)
 III. temperature (T)

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

spontaneous when $\Delta G = -ve$. ΔG measures the entropy change of a system AND surroundings.

if $\Delta G > 0$ (+ve) = not spontaneous

$\Delta G < 0$ (-ve) = spontaneous

ΔG ... when

\rightarrow rmb T is never -ve because K is never -ve

| ΔH | ΔS | spont? |
|------------|------------|--------|
| + | - | never |
| + | + | high T |
| - | - | low T |
| - | + | any |

you can also find Gibbs Free energy of Formation changes to figure out if a reaction is spontaneous or not.

$$\Delta G^\circ = \Delta G_f^\circ \text{ products} - \text{reactants } (\Delta G_f^\circ)$$

if ΔG_f° is -ve ... spontaneous!

if it's spontaneous, it favours the fwd reaction \rightarrow react prod.

248 - not

$$44 - 1.01x < 0$$

EFFECTS OF ENTHALPY & ENTROPY ON SPONTAN

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

(T: never negative bc Kelvin)

| ΔH | ΔS | Spontaneous |
|------------|------------|--------------------------------------|
| - | + | at all temp |
| - | - | low temps ($\Delta H > T\Delta S$) |
| + | + | high temperatures |
| + | - | never spontaneous! |

\therefore lower temperature = more spontaneous

(higher the temp, more spontaneous)

FREE ENERGY:

$$\Delta G = \Delta G_f \text{ products} - \Delta G_f \text{ reactants}$$

UNLESS they are combustion values.

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