RAFFLES INSTITUTION RAFFLES PROGRAMME - YEAR FOUR CHEMISTRY

EQUILIBRIA

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<u>Reversible Reactions</u>: Chemical reactions that can proceed in two directions: forwards and backward.

$$\text{Reactants} \rightleftharpoons \text{Products}$$

The left-to-right reaction is the forward reaction; the right-to-left reaction is the backward reaction. Reversible reactions tend not to go to completion; a mixture of reactants and products is always obtained. When the concentration of reactants and products are constant the system is at equilibrium.

At the start, because the concentration of reactants is greatest, the rate of forward reaction will be the greatest. As the reactants react, their concentration falls, causing the rate of forward reaction to decrease.
Meanwhile, the concentration of products is lowest at the start, so the rate of backward reaction is the lowest. As the rate of forward reaction is greater than the rate of backward reaction, the concentration of products starts to increase. This causes the rate of backward reaction to increase.
[For detailed explanation on rate of reaction and frequency of collisions see “REACTION KINETICS”]

<u>Dynamic Equilibrium</u>: Eventually, the **rate of forward reaction will be equal to the rate of backward reaction**. Note that both the forward and backward reactions are still occurring and have not stopped, but their rates are equal and hence there is **no net change in the concentration of either reactants or products**. Also note that the concentration for products and reactants do not need to be the same at 50%; it is just that the **rate** of forward and backward reactions are the same.

Also, equilibrium can be reached from different directions. The equilibrium state is independent of the direction from which it is approached, and the final mole ratio of the reactants and products is the same. (ie. Starting with reactants will give the same equilibrium as starting with products.)

<u>Le Chatelier's Principle</u>: If a system at equilibrium is subjected to a small change, the equilibrium's response is to counteract the change so as to minimise the effect of the change.

In general, when looking at an Equilibria question, always consider:
1. Enthalpy change ➔ Temperature
2. Mole ratio for gases ➔ Pressure
3. Products vs reactants ➔ Concentration

Consider an equilibrium mixture as follows:
$2A(g) + B(g) \rightleftharpoons 2C(g)$ ΔH = negative value   ➔ Note that ΔH refers to forward reaction most of the time. ie. This forward reaction is exothermic.

If temperature is **increased**, according to Le Chatelier's Principle,	the system counteracts this **increased** temperature by **removing** heat, thus favouring the **backward endothermic** reaction,	thus the position of equilibrium shifts to the **left**,	and the yield of C **decreases**.
If temperature is **decreased**, according to Le Chatelier's Principle,	the system counteracts this **decreased** temperature by **supplying** heat, thus favouring the **forward exothermic** reaction,	thus the position of equilibrium shifts to the **right**,	and the yield of C **increases**.
If concentration of A/B is **increased**, according to Le Chatelier's Principle,	the system counteracts this **increased** concentration by reacting the molecules of A/B away in order to **decrease the concentration**, thus favouring the **forward** reaction,	thus the position of equilibrium shifts to the **right**,	and the yield of C **increases**.
If concentration of A/B is **decreased**, according to Le Chatelier's Principle,	the system counteracts this **decreased** concentration by producing more molecules of A/B in order to **increase the concentration**, thus favouring the **backward** reaction,	thus the position of equilibrium shifts to the **left**,	and the yield of C **decreases**.
If pressure is **increased**, according to Le Chatelier's Principle,	the system counteracts this **increased** pressure by **decreasing** the total number of molecules, thus favouring the **forward** reaction,	thus the position of equilibrium shifts to the **right**,	and the yield of C **increases**.
If pressure is **decreased**, according to Le Chatelier's Principle,	the system counteracts this **decreased** pressure by **increasing** the total number of molecules, thus favouring the **backward** reaction,	thus the position of equilibrium shifts to the **left**,	and the yield of C **decreases**.

Note that increased temperature theoretically increases the rate of reactions according to ROR. However, the rate of forward and backward reactions will have different increases according to the enthalpy change. Hence, the overall ROR will be increase, but depending on the enthalpy change the yield of the desired product will vary. Vice versa for decreased temperature. Hence, it is necessary to strike a balance between rate and yield of reaction.

Note that a catalyst affects only the ROR and not the yield of the reaction.

Haber Process: Industrial synthesis of ammonia from its elements:
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92kJ/mol$

Nitrogen is obtained from the fractional distillation of air.
Hydrogen is obtained from the cracking of petroleum.

Conditions: 450°C, 200 atm, iron catalyst
Although decreasing the temperature would theoretically encourage the forward reaction and increase the yield of ammonia, it would also decrease the ROR. Hence, 450°C is the optimum temperature to balance between yield and rate of reaction.
Although increasing the pressure would theoretically encourage the forward reaction and increase the yield of ammonia, it would pose a safety hazard and also be very costly. Hence, 200 atm is the optimum pressure balance between yield, safety, and cost of reaction.

Ammonia from the Haber process is used to produce nitrogenous fertilisers for farmers such as ammonium nitrate.
Also recall that since these fertilisers are ammonium salts, they can react with bases to give water, a salt and ammonia.