Edexcel IAL Chemistry A-level

Topic 13: Chemical Equilibria

Detailed notes

Equilibrium Constant (Kc)

For reversible reactions, there is an equilibrium constant, **Kc**, that indicates the **position of equilibrium** for a reaction at a certain temperature. For a particular reaction, **Kc** always has the **same value,** unless the reaction conditions, and therefore the **position of equilibrium,** are changed.

In order to find the value of Kc, the **concentrations** of the substances in the reaction at the equilibrium position must be known. Kc is equal to the **concentration of the products divided by the concentration of the reactants**. The concentration terms are **raised to a power** of the same value as the number of moles of that substance.

Example:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Image courtesy of ScienceAid.net

The equilibrium constant has **varying units,** depending on the chemical reaction. The units can be calculated by **substituting the concentration units into the Kc expression**. Some of these units will then cancel, giving the overall units of Kc for that reaction.

Example:

$$2A + B \rightleftharpoons C$$

$$\frac{\mathrm{moldm^{-3}}}{(\mathrm{moldm^{-3}})^2(\mathrm{moldm^{-3}})} = \frac{1}{(\mathrm{moldm^{-3}})^2}$$

$$= \mathrm{mol^{-2}dm^{6}}$$

Image courtesy of ScienceAid.net

Homogeneous and Heterogeneous

The equilibrium constant, Kc, can be found for both **homogeneous** and **heterogeneous** reactions. Homogeneous reactions are reactions in which the reactants and products are in the same **phase**, whereas heterogeneous reactions are reactions in which some of the reactants and/or products are in different phases to each other.

For **homogeneous** reactions, Kc is calculated as shown **above**.

The **difference** when calculating Kc for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.

Example: $H_2O_{(g)} + C_{(s)} \rightarrow H_{2(g)} + CO_{(g)}$

The solid carbon is not included in the equation for Kc:

$$Kc = \frac{[H_2]\,[CO]}{[H_2O]}$$

Gaseous Equilibrium Constant (Kp)

Kp is the equilibrium constant used for **gaseous equilibria**. Kp is calculated from gaseous reactants and products. If all reactants and products are in the **gaseous state**, the system is said to be **homogeneous**.

Partial Pressure

Within a gaseous system, each gas has a **partial pressure**. The partial pressures add up to give the total system pressure. The partial pressure of a substance is found using the **molar fraction** of that substance and the **total pressure** of the system.

$$\text{Partial Pressure of A} = \frac{\text{Moles of A}}{\text{Total Moles}} \times \text{Total Pressure}$$

Partial pressure of A would be shown as **(P_A).**

Example:

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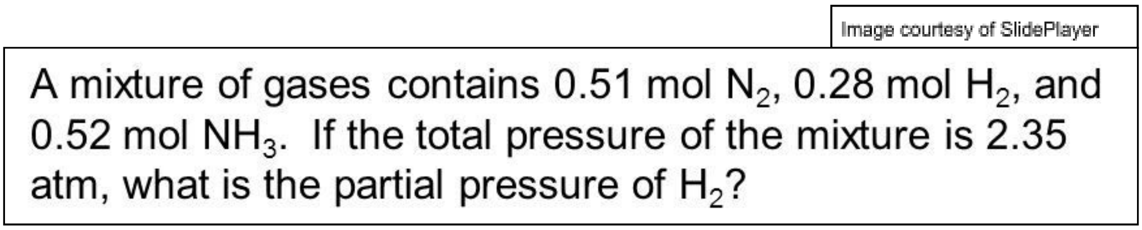

A mixture of gases contains 0.51 mol N_2, 0.28 mol H_2, and 0.52 mol NH_3. If the total pressure of the mixture is 2.35 atm, what is the partial pressure of H_2?

Total moles in the system = 0.51 + 0.28 + 0.52
= 1.31 moles

Molar fraction of H_2 = 0.28 / 1.31
= 0.21

$$(P_{H_2}) = 0.21 \times 2.35$$
$$= 0.50 \text{ atm}$$

Partial pressures are commonly measured in **Pascals** but can occasionally be measured in atmospheres.

Calculating Kp

Partial pressures allow the value of Kp for a gaseous equilibrium to be found. Kp is equal to the product of the **partial pressures of products** over the product of the **partial pressure of reactants**. It is similar to Kc in that any variation in moles **raises the partial pressure to a power** of equal quantity to the number of moles.

$$2A_{(g)} + 3B_{(g)} \longrightarrow Y_{(g)} + 2Z_{(g)}$$

$$Kp = \frac{(P_Y)(P_Z{}^2)}{(P_A{}^2)(P_B{}^3)}$$

The gaseous equilibrium constant has **varying units,** depending on the chemical reaction. The units can be calculated by **substituting the partial pressure units into the Kp expression**. Some of these units will then cancel, giving the overall units of Kp for that reaction.

Example:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$Kp = \frac{(kPa)^2}{(kPa)^2 \times kPa}$$

$$= kPa^{-1}$$

Homogeneous and Heterogeneous

Similarly to Kc, the gaseous equilibrium constant, Kp, can be found for both **homogeneous** and **heterogeneous** reactions.

For **homogeneous** reactions, Kp is calculated as shown **above**.

The **difference** when calculating Kp for **heterogeneous** reactions is that any terms representing a **solid** are **not included** in the calculation.

Example: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

The solid $CaCO_3$ and CaO are not included in the equation for Kp: $Kp = (P_{CO_2})$

Factors affecting Kc and Kp

The values of Kc and Kp are **not affected by concentration or pressure change** or by the use of a **catalyst**. However, they are affected by changing the reaction **temperature**.

Concentration and **pressure** changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

Temperature, on the other hand, does affect the position of the equilibrium, as this changes the **position** of the equilibrium, resulting in different concentrations of reactants and products. Therefore, the equilibrium constant changes with temperature.

If the forward reaction is **exothermic**, an increase in temperature will decrease the rate of the forward reaction because the equilibrium shifts to the **left** to oppose the change. This will decrease the concentrations of products and increase the concentrations of reactants, therefore the equilibrium constant (Kc or Kp) **decreases**.

If the forward reaction is **endothermic**, an increase in temperature will increase the rate of the forward reaction because the equilibrium shifts to the **right** to oppose the change. This will increase the concentrations of products and decrease the concentrations of reactants, therefore the equilibrium constant (Kc or Kp) **increases**.

Similar arguments can be made for the effect of **decreasing** the temperature.

Gibbs Free-Energy (ΔG)

ΔG is an **indicator of reaction feasibility.** ΔG (free energy change) is related to the equilibrium constant, K:

$$\boxed{\Delta G = -RT\ln(K)}$$

This shows that reactions are **feasible** (ΔG is less than or equal to zero) when the reaction has a **large value** for the equilibrium constant. It is therefore possible to predict the feasibility of a reaction at a known temperature if the equilibrium constant is known.

The following two equations can be used to see how the **equilibrium constant** and **temperature** change with **ΔS**:

The **entropy** of the surroundings is dependant on **enthalpy change** and **temperature**:

$$\boxed{\Delta S_{\text{surroundings}} = \frac{-\Delta H}{T}}$$

The total entropy is related to the **magnitude** of the equilibrium constant:

$$\boxed{\Delta S_{\text{total}} = R\ln(K)}$$