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7. Quantitative Equilibrium (II.6)

a) Equilibrium Expression

i) we can quantify (attach a numerical value) the equilibrium for most reactions by creating a **ratio** of **products to reactants**.

ii) Example: $A + B \rightleftharpoons C + D$

$$\frac{[C]\,[D]}{[A]\,[B]} \quad \text{or} \quad \frac{[\text{Products}]}{[\text{Reactants}]}$$

iii) Example: $2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$

$$\frac{[H_2][I_2]}{[HI][HI]} \quad \text{or} \quad \frac{[H_2][I_2]}{[HI]^2}$$

iv) The general expression for the equilibrium reaction is:

$$\mathbf{aA + bB \rightleftharpoons cC + dD} \qquad \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

b) Equilibrium Constant

i) the **ratio** obtained from the above equilibrium expression is a number unique to a particular reaction.

ii) This ratio is called the Equilibrium Constant or Keq

iii) Example: $2H_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2H_2O_{(g)}$

$$Keq = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

iv) Example: $BaSO_{4\,(s)} \rightleftharpoons Ba^{+2}{}_{(aq)} + SO_4{}^{-2}{}_{(aq)}$

$$Keq = [Ba^{+2}][SO_4{}^{-2}]$$

(Solids are omitted in the K_{eq} expression, because they do not affect the equilibrium. [solids] is not possible to change!! You ever hear of weak sugar? Strong sugar?!)

v) Example: $2NH_{3\,(l)} \rightleftharpoons N_{2\,(g)} + 3H_{2\,(g)}$

$$Keq = [N_2][H_2]^3$$

(Liquids are omitted in the K_{eq} expression, because they do not affect the equilibrium. Can water ever be strong or weak? No. Water is water. Its [ ] doesn't change.)

****vi) Example:** $CH_3COCH_{3\,(l)} + Cl_{2\,(g)} \rightleftharpoons CH_3COCH_2Cl_{(l)} + HCl_{(g)}$

$$Keq = \frac{[CH_3COCH_2Cl][HCl]}{[CH_3COCH_3][Cl_2]}$$

(<u>Exception</u>: if TWO liquids are in a reaction, they will dilute each other. This affects the concentration and thus the equilibrium. So they are included in the K_{eq} expression)*

vii) Write the K_{eq} for the following reactions:

$2Bi^{3+}{}_{(aq)} + 3H_2S_{(g)} \rightleftharpoons Bi_2S_{3(s)} + 6H^+{}_{(aq)}$ $\quad Keq = \dfrac{[H^+]^6}{[Bi^{+3}]^2[H_2S]^3}$

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ $\quad Keq = [CO_2]$

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c) What does the K_{eq} Value Mean?

Keq = [products] / [reactants]

- a Large K_{eq} = Large amount of products present at equilibrium Keq = [10] / [1] = large Keq
- a Small K_{eq} = Small amount of products present at equilibrium Keq = [1] / [10] = small Keq
  (large amounts of reactants present at equilibrium)

d) Factors that Affect K_{eq}

i) Pressure, concentration, surface area, catalyst

- The K_{eq} for every reaction is unique.
- If we change one of the above factors, the Keq is momentarily altered.
- But according to Le Chatelier's principle, the equilibrium will re-establish at the original K_{eq}!

- Changes in pressure, concentration, surface area and catalyst have no effect on Keq.

ii) Temperature.

- If we add a bunch of heat to the reaction and then stop, the equilibrium will re-establish at the original K_{eq} (just like above for pressure etc.)
- BUT if we heat to a certain temperature and hold that temperature indefinitely, the equilibrium will permanently shift (according to exo or endothermic)
- This permanent shift will change the K_{eq}

iii) Summary

- all factors, if changed, will momentarily shift an equilibrium, but the equilibrium will re-establish thus not affecting the K_{eq} value.
- temperature is the only factor that we can continually keep adding or removing, and if this is done we can affect the K_{eq} value.

iv) Example: $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) + 76kJ$

What happens to the K_{eq} in the above reaction if:

a) temperature is increased and held Keq decreases…rxn initially shifts left

b) heat is added for 5 seconds nothing to Keq…rxn initially shifts left

c) temperature is decreased and held Keq increases …..rxn initially shifts right

d) $NO_{(g)}$ is added nothing to Keg…rxn initially shifts right

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