Chemical Equilibrium

- When some types of chemical reactions occur in the gas or solution phases, these reaction attain “chemical equilibrium”, *i.e.*, the reaction does not go to completion, but the reaction vessel will contain both reactant species and product species mixed together.

Chemical Equilibrium

- This occurs when the concentrations of the reactants stop decreasing, and the concentrations of the products stop increasing.

  $2\ NO_2 \leftrightarrow N_2O_4$

  (I will use $\leftrightarrow$ to indicate an equilibrium process in my lecture notes)

Chemical Equilibrium

- NO_2 is a brown gas while N_2O_4 is colorless

  $2\ NO_2 \leftrightarrow N_2O_4$
- At any given time in a container of NO_2, some fraction of the gas will be in the form of NO_2, and some fraction will be in the form of N_2O_4.

Chemical Equilibrium

- Chemical equilibrium is a dynamic process—an individual molecule will repeatedly move from the NO_2 form to the N_2O_4 form, the overall concentrations of NO_2 and N_2O_4 do not change at a given temperature

  $2\ NO_2 \leftrightarrow N_2O_4$

Equilibrium Constant

- The "equilibrium constant", K_{eq}, for a chemical reaction indicates whether the reactants or the products will be favored in an equilibrium process
- The equilibrium constant in terms of concentrations is defined as:

$$aA + bB \leftrightarrow cC + dD$$

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

Equilibrium Constant

- For the $2\ NO_2 \leftrightarrow N_2O_4$ reaction, the equilibrium constant is given as:

$$K_C = \frac{[N_2O_4]}{[NO_2]^2}$$

Equilibrium Constant

- If the reaction involves a pure solid or pure liquid, these species do not appear in the equilibrium constant expression:

Example:

$CH_4(g) + H_2O(l) \leftrightarrow CO(g) + 3\ H_2(g)$

$$K_C = \frac{[CO(g)]\,[H_2(g)]^3}{[CH_4(g)]}$$

Note that $H_2O(l)$ does not appear in the denominator.

Equilibrium Constant

- If we have two or more equilibrium chemical reactions, we can combine their equilibrium constant expressions to get an overall equation for the net chemical reaction

Example

$H_2CO_3(aq) + H_2O(aq) \leftrightarrow HCO_3^-(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(aq) \leftrightarrow CO_3^{2-}(aq) + H_3O^+(aq)$

Equilibrium Constants

Example (con't.)

$H_2CO_3(aq) + H_2O(\ell) \leftrightarrow$

$HCO_3^-(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(\ell) \leftrightarrow$

$CO_3^{2-}(aq) + H_3O^+(aq)$

Net: $H_2CO_3(aq) + 2\ H_2O(\ell) \leftrightarrow$

$CO_3^{2-}(aq) + 2\ H_3O^+(aq)$

Equilibrium Constants

Example (con't.)

For the first reaction:

$H_2CO_3(aq) + H_2O(\ell) \leftrightarrow$

$HCO_3^-(aq) + H_3O^+(aq)$

$$K_{C_1} = \frac{[HCO_3^-(aq)][H_3O^+(aq)]}{[H_2CO_3(aq)]} = 4.2 \times 10^{-7}$$

Equilibrium Constants

Example (con't.)

For the second reaction:

$HCO_3^-(aq) + H_2O(l) \leftrightarrow$

$CO_3^{2-}(aq) + H_3O^+(aq)$

$$K_{C_2} = \frac{[CO_3^{2-}(aq)][H_3O^+(aq)]}{[HCO_3^-(aq)]} = 4.8 \times 10^{-11}$$

Equilibrium Constants

Example (con't.)

For the net reaction:

$H_2CO_3(aq) + 2\ H_2O(l) \leftrightarrow$

$CO_3^{2-}(aq) + 2\ H_3O^+(aq)$

$$K_C = \frac{[CO_3^{2-}(aq)][H_3O^+(aq)]^2}{[H_2CO_3(aq)]}$$

$$= K_{C_1} K_{C_2} = 2.0 \times 10^{-17}$$

Equilibrium Constant and Pressure

- How does the expression for the equilibrium constant change if pressure is used as the variable instead of concentration?
- Using the Ideal Gas Law:

$$P_A = \frac{nRT}{V} = [A]RT$$

$$\therefore [A] = \frac{P_A}{RT}$$

Equilibrium Constant and Pressure

- For the generic reaction

  $aA + bB \leftrightarrow cC + dD$

  we can write the equilibrium constant in terms of pressure

$$K_P = \frac{P_C^c \, P_D^d}{P_A^a \, P_B^b}$$

Equilibrium Constant and Pressure

- Substituting the relationship between pressure and concentration gives:

$$K_P = \frac{P_C^c \, P_D^d}{P_A^a \, P_B^b} = \frac{([C]RT)^c \, ([D]RT)^d}{([A]RT)^a \, ([B]RT)^b}$$

$$= \frac{[C]^c \, [D]^d}{[A]^a \, [B]^b} (RT)^{(c+d)-(a+b)} = K_C \, (RT)^{\Delta n}$$

where Δn is the change in the number of moles of gas phase molecules

Equilibrium Constant and Pressure

<u>Example:</u>

Determine K_P for the reaction

$N_2(g) + 3\ H_2(g) \leftrightarrow 2\ NH_3(g)$

$K_C = 3.5 \times 10^8$ at 25 °C

n(prod) = 2 n(react) = 4

$\Delta n = 2 - 4 = -2$

$$K_P = K_C \, (RT)^{\Delta n}$$

$$= 3.5 \times 10^8 \, \{(.0821)(298)\}^{-2}$$

$$= 5.8 \times 10^5$$

Using Equilibrium Constants

Example:

Determine $[SO_4^{2-}]$ when a solution of 1.00 M $H_2SO_4(aq)$ is prepared:

- Step 1—write a balance chemical equation
  $HSO_4^-(aq) + H_2O(\ell) \leftrightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
- Step 2—write an expression for the equilibrium constant

$$K_C = \frac{[SO_4^{2-}(aq)]\,[H_3O^+(aq)]}{[HSO_4^-(aq)]} = 1.2 \times 10^{-2}$$

Using Equilibrium Constants

Example:

Determine $[SO_4^{2-}]$ when a solution of 1.00 M $H_2SO_4(aq)$ is prepared:

- Step 3—determine the unknowns
  We can do this one of two ways: (1) let the reactants react, in which case we write:
  $HSO_4^-(aq) + H_2O(\ell) \leftrightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
  1.00 – x x 1.00 + x
  (2) let the reaction go to completion, and then let the some of the product go back to reactants:
  $HSO_4^-(aq) + H_2O(\ell) \leftrightarrow SO_4^{2-}(aq) + H_3O^+(aq)$
  x 1.00 – x 2.00 - x

Using Equilibrium Constants

Example:

Determine $[SO_4^{2-}]$ when a solution of 1.00 M $H_2SO_4(aq)$ is prepared:

- Step 4—solve equilibrium constant expression for unknowns

$$\frac{[SO_4^{2-}(aq)]\,[H_3O^+(aq)]}{[HSO_4^-(aq)]} = \frac{x(1.00+x)}{1.00 - x} = 1.2 \times 10^{-2}$$

$$x^2 + 1.012x - 0.012 = 0$$

Using the quadratic equation to solve for x, we get x = 0.012 M = $[SO_4^{2-}]$

Using Equilibrium Constants

Example:

H_2SO_3 is formed in an equilibrium reaction between SO_2 and H_2O

$$SO_2(g) + H_2O(g) \leftrightarrow H_2SO_3(aq)$$

SO_2 has an average concentration of .006 ppm, and H_2O has a vapor pressure of ~20 Torr

Determine the amount of H_2SO_3 in the troposphere

Step 1—write an expression for the equilibrium constant

$$K_P = \frac{P_{H_2SO_3}}{P_{SO_2}\,P_{H_2O}} = K_C\,(RT)^{\Delta n}$$

$$= \frac{8.47 \times 10^3}{(.0821)\,(298)} = 3.46 \times 10^2$$

Using Equilibrium Constants

Example:

Determine the amount of H_2SO_3 in the troposphere

$SO_2(g) + H_2O(g) \leftrightarrow H_2SO_3(aq)$

Step 2—determine pressures of reactants (pressures must be given in units of atm because the R used has atm units

H_2O: 20 Torr = .026 atm

SO_2: (.006 ppm)(1 atm) = 6 x 10^{-9} atm

Step 3—solve expression for P_{H2SO3}

$$P_{H_2SO_3} = (3.46 \times 10^2)\, P_{SO_2}\, P_{H_2O}$$

$$= (3.46 \times 10^2)(6 \times 10^{-9})(.026) = 5.4 \times 10^{-8}\ \text{atm}$$

Interpreting Equilibrium Constants

- If $K_C \gg 1$, then the reaction is strongly product-favored, *i.e.*, the mixture will contain more products than reactants
- If $K_C \ll 1$, then the reaction is strongly reactant-favored, *i.e.*, the mixture will contain more reactants than products
- If $K_C \approx 1$, the mixture will contain approximately equal amount of reactant and products

Interpreting Equilibrium Constants

Example:

Acetic acid, CH_3COOH, has a K_C of 1.8×10^{-5}

Determine the relative concentrations of CH_3COOH, CH_3COO^-, and H^+ in an aqueous solution

balanced equation: $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

$$K_C = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Interpreting Equilibrium Constants

Example (con't.):

build concentration table

	$[CH_3COOH]$	$[CH_3COO^-]$	$[H^+]$
initially	1.00	0.00	0.00
equilibrium	1.00 – x	x	x

solve equilibrium constant expression for unknown concentrations

$$\frac{x \cdot x}{1.00 - x} = 1.8 \times 10^{-5}$$

Interpreting Equilibrium Constants

Example (con't.):

assume x is small relative to the initial concentration of the acetic acid (reactant-favored condition because K_C << 1)

$$1.00 - x \approx 1.00$$

$$x^2 = 1.8 \times 10^{-5}$$

$$x = .0042 \text{ M}$$

check assumptions:
$1.00 - .0042 \approx 1.00$

the acetic acid in solution is .42% acetate ion (CH_3COO^-) with the remainder as acetic acid (CH_3COOH)

Interpreting Equilibrium Constants

Example (con't.):

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the acetic acid in solution is .42% acetate ion (CH_3COO^-) with the remainder as acetic acid (CH_3COOH)

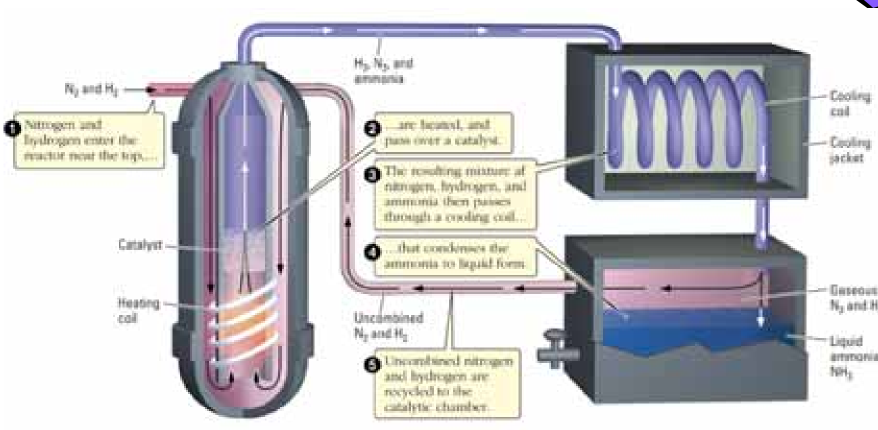
Le Chatelier's Principle

- If a stress, such as a change in concentration, pressure, temperature, etc., is applied to a system at equilibrium, the equilibrium will shift in such a way as to lessen the effect of the stress.

Production of Ammonia

$$N_{2(g)} + 3\,H_{2(g)} \xleftrightarrow[\text{high pressure and temperature}]{\text{catalysis}} 2\,NH_{3(g)} + \text{heat}$$

Haber-Bosch Process



Increase in Concentration or Partial Pressure

For the process:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$$

an increase in N_2 and/or H_2 concentration or pressure, will cause the equilibrium to shift towards the production of NH_3

Decrease in Concentration or Partial Pressure

For the process:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)}$$

likewise, a decrease in NH_3 concentration or pressure will cause more NH_3 to be produced

Changes in Temperature

For the process:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)} + \text{heat}$$

an increase in temperature will cause the reaction to shift back towards reactants because the reaction is exothermic

Increase in Volume

For the process:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)} + \text{heat}$$

an increase in volume, causes the equilibrium to shift to the left where there are more gaseous molecules

Decrease in Volume

For the process:

$$N_{2(g)} + 3\ H_{2(g)} \leftrightarrow 2\ NH_{3(g)} + \text{heat}$$

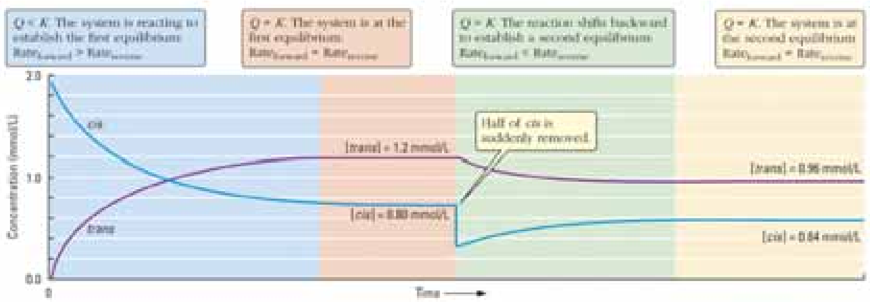
a decrease in volume, causes the equilibrium to shift to the right where there are fewer gaseous molecules

Stress on Equilibrium

Consider the reaction:

cis-2-butene ↔ *trans*-2-butene

$$K_C = \frac{[\text{trans}]}{[\text{cis}]} = 1.5 \quad (\text{at } 600\,\text{K})$$



Shifting of Equilibrium

For the reaction: $2\ NO_2(g) \leftrightarrow N_2O_4(g)$