Dr Kepert, Chem 1901

**Chemical Equilibrium I**

Silberberg 2nd Ed, Chapter 17

- Series of plots of concentration vs time
- Initial Rates
- Reaction Orders
- Rate Constant $k$ and actual rate law
- Integrated rate law (reaction order; half-life)
- Activation Energy $E_a$

**Rate Law:**

**Method**

**Reaction Mechanisms:**

- Determine Rate Law by Experiment
- Devise a mechanism
- Predict Rate Law for Mechanism
- If Predicted and Experimental Rate Laws do not agree
- Look for additional supporting evidence
- If Predicted and Experimental Rate Laws agree

**Kinetics: A Reminder**

**Chemical Equilibria:**

- The Extent Of Chemical Reactions

- Kinetics - the speed of reactions
- Equilibrium - the extent of reactions
  - No reaction goes to 100%.
  - All reactions are reversible.
  - Reactions incomplete because, at equilibrium:
    - rate of forward reaction = rate of reverse reaction
      (not because reaction stops!)

- Dynamic Equilibrium:
  - $aA + bB \rightarrow cC + dD$
  - forward (L to R) and reverse (R to L) reactions occur simultaneously.

- Example: $N_2O_4 \rightarrow 2 NO_2$
  - colourless
  - brown

- Concentration vs time

- Equilibrium concentration

- Equilibrium Constant

- $aA + bB \rightarrow cC + dD$

- * At equilibrium, concentrations are given by the Law of Mass Action:

  \[
  \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} = K
  \]

- $K = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$

- “Law” of Mass Action first deduced from experiment, then proved from laws of thermodynamics.
Magnitude Of Equilibrium Constants

At Equilibrium:
- if $K > 1$ ⇒
- if $K < 1$ ⇒
- if $K = 1$ ⇒

Relation between $K$ and Rate Constants

- Take system with elementary reactions, e.g.:
  \[ \text{Cl}_2 \leftrightarrow 2\text{Cl} \]
  \[ k_f \quad \text{and} \quad k_r \]
  For Elementary Reactions (usually unimolecular and bimolecular)

- at equilibrium, forward rate = reverse rate, so:

$K_c$ : Equilibrium Constant with respect to Concentration

- Reaction involving solutions:
  \[ aA + bB \rightarrow cC + dD \]
  \[ K_c = \frac{[cC][dD]}{[aA][bB]} \]
  \[ ] \text{units} = M (\text{mol} L^{-1}) \]
  • Units of $K_c$ depend on values of $a$, $b$, $c$ & $d$

$K_p$ : Equilibrium Constant with respect to Partial Pressure

- Reaction involving gases:
  \[ aA (g) + bB (g) \leftrightarrow cC (g) + dD (g) \]
  \[ K_p = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} \]
  \[ (p_A = \text{partial pressure of} \ A \ \text{at equilibrium}, \ etc.) \]
  • Units of $K_p$ = atm, etc.
  • Units of $K_p$ depend on values of $a$, $b$, $c$ & $d$

Example

Cl$_2$ is placed in a vessel and heated to 1400 K.
Cl$_2$(g) $\rightarrow$ 2Cl(g)
When equilibrium reached we find:
p$_{Cl_2}$ = 1 atm,  p$_{Cl}$ = 2.97 x 10^{-2} atm

- What is the value of $K_p$ at 1400 K?

Example from Kinetics II & III

Fast reversible reaction followed by a slow step:
(1) 2NO(g) + * $\leftrightarrow$ N$_2$O$_2$ (g) fast (equil. const. $K$)
(2) N$_2$O$_2$ (g) + O$_2$(g) $\rightarrow$ 2NO$_2$ slow (rate constant $k$)
2NO(g) + O$_2$(g) $\rightarrow$ 2NO$_2$(g) net reaction

Rate = rate of slow step = $k \ [N_2O_2][O_2]$

From (1), with equilibrium constant, \[ K = \frac{[N_2O_2]}{[NO][NO]} \]
\[ \Rightarrow [N_2O_3] = K[NO]^2 \]

So rate = $k \ [N_2O_2][O_2] = k \ K[NO]^2[O_2]$
\[ \Rightarrow \text{rate} = \text{constant} \times [NO]^2[O_2] \]
consistent with observed rate law

Relationship Between $K_p$ & $K_c$

- $pV = nRT$
  \[ [\text{concentration}] = \frac{n}{V} = \frac{P}{RT} \; \text{; (units} \ M \ \text{moles} \ L^{-1}) \]

Cl$_2$(g) $\rightarrow$ 2Cl(g)

\[ K_c = \frac{[Cl]^2}{[Cl_2]} = \frac{(p_{Cl}/RT)^2}{(p_{Cl_2}/RT)} \]

so $K_p$ = $K_c$($RT$)$^{-\Delta n}$

$\Delta n$ = (n$_{\text{gas products}}$ - n$_{\text{gas reactants}}$)

Catalysts and Equilibrium