Chemical Equilibrium I

Silberberg 2nd Ed, Chapter 17

www.chem.usyd.edu.au/hpage3.htm (login “chem”, passwd “chem@usyd”)

Any questions or requests - email to c.kepert@chem.usyd.edu.au
Kinetics: A Reminder
Kinetics: A Reminder
Rate Law: 
**Method**

- 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 $E_a$
Reaction Mechanisms: Method

- Determine Rate Law by Experiment
  - Devise a mechanism
  - Predict Rate Law for Mechanism
    - If Predicted and Experimental Rate Laws do not agree
      - START AGAIN!
    - If Predicted and Experimental Rate Laws agree
      - Look for additional supporting evidence
Kinetics: A Reminder

The diagram illustrates the concept of activated state in chemical kinetics. The activated state is the energy barrier that must be overcome for a reaction to proceed. The figure shows two temperature states, $T_1$ and $T_2$, with corresponding activation energies $E_{a\text{(fwd)}}$ and $E_{a\text{(rev)}}$ for the forward and reverse reactions, respectively. The fraction of collisions leading to reactants and products is also depicted.
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

\[ aA + bB \rightleftharpoons cC + dD \]
- forward (L to R) and reverse (R to L) reactions occur simultaneously.

Example: \( \text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2 \)
- colourless
- brown

* Equilibrium conc.s the same, whatever the starting composition.
Equilibrium Constant

\[ aA + bB \rightleftharpoons cC + dD \]

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

\[
\frac{[C_{eq}]^c[D_{eq}]^d}{[A_{eq}]^a[B_{eq}]^b} = K
\]

- \( K = \)

- “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.:

\[
\begin{align*}
&\text{Cl}_2 \rightleftharpoons 2\text{Cl} \\
&k_f \\
&k_r
\end{align*}
\]

For **Elementary Reactions** (usually unimolecular and bimolecular)

- at equilibrium, forward rate = reverse rate, so:
\[ K_c : \text{Equilibrium Constant with respect to Concentration} \]

- Reaction involving solutions:

\[
aA + bB \quad \rightleftharpoons \quad cC + dD
\]

\[
K_c = \frac{[C_{eq}]^c [D_{eq}]^d}{[A_{eq}]^a [B_{eq}]^b}
\]

[ ] units = M (mol L\(^{-1}\))

- Units of \( K_c \) depend on values of \( a, b, c \& d \)
$K_p : \text{Equilibrium Constant with respect to Partial Pressure}$

- Reaction involving gases:

$$aA \ (g) + bB \ (g) \ \rightleftharpoons \ cC \ (g) + dD \ (g)$$

$$K_p = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b}$$

($p_A = \text{partial pressure of } A \text{ at equilibrium, etc.}$)

units of $p_A = \text{atm, etc.}$

- 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.

\[
\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl(}g\text{)}
\]

When equilibrium reached we find:

\[p_{\text{Cl}_2} = 1 \text{ atm, } p_{\text{Cl}} = 2.97 \times 10^{-2} \text{ atm}\]

* What is the value of \(K_p\) at 1400 K?
Relationship Between $K_p$ & $K_c$

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

\[
\text{Cl}_2 (g) \rightleftharpoons 2\text{Cl} (g)
\]

\[
K_c = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} = \frac{(p_{\text{Cl}}/RT)^2}{(p_{\text{Cl}_2}/RT)} = \frac{(p_{\text{Cl}})^2}{p_{\text{Cl}_2}} \frac{1}{RT}
\]

so $K_c = K_p(RT)^{-1}$ for this particular reaction

- In general:
  \[
  K_p = K_c (RT)^{\Delta n}
  \]

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

For $\text{Cl}_2(g) \rightleftharpoons 2\text{Cl}(g)$

* Having found $K_p$ at 1400 K, find $K_c$ at 1400 K.
Example from Kinetics II & III

Fast reversible reaction followed by a slow step:

1. $2\text{NO}(g) \leftrightarrow \text{N}_2\text{O}_2 (g)$ fast (equil. const. $K$)
2. $\text{N}_2\text{O}_2 (g) + \text{O}_2(g) \rightarrow 2\text{NO}_2$ slow (rate constant $k$)

$$2\text{NO}(g) + \text{O}_2 (g) \rightarrow 2\text{NO}_2 (g)$$ net reaction

Rate = rate of slow step = $k \left[\text{N}_2\text{O}_2\right]\left[\text{O}_2\right]$ 

From (1), with equilibrium constant, $K = \frac{\left[\text{N}_2\text{O}_2\right]}{\left[\text{NO}\right]\left[\text{NO}\right]}$

$\Rightarrow \left[\text{N}_2\text{O}_2\right] = K \left[\text{NO}\right]^2$

So rate = $k \left[\text{N}_2\text{O}_2\right] \left[\text{O}_2\right] = k K \left[\text{NO}\right]^2 \left[\text{O}_2\right]$

$\Rightarrow$ rate = constant $\times \left[\text{NO}\right]^2 \left[\text{O}_2\right]$

consistent with observed rate law
Catalysts and Equilibrium