Revision Handout

Gases, Liquids & Solids

Kinetics

Equilibrium

Acids & Bases

Thermodynamics

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

Any questions or requests - email to c.kepert@chem.usyd.edu.au
Gases, Liquids and Solids

**Ideal Gas Equation**

\[ P \, V = n \, R \, T \]

- Pressure
- Volume
- Number of moles
- Gas constant
- Absolute temperature

**Density**

\[ \rho = \frac{m}{V} \]
**Gases, Liquids and Solids**

**Dalton’s Law of Partial Pressures:**

Total pressure of mixture of gases = sum of pressures that each would exert if it were alone.

**Graham’s Law of Effusion/Diffusion:**

Rate of gas effusion/diffusion $\propto \frac{1}{\sqrt{\text{molar mass}}}$
Gases, Liquids and Solids

Molecular Velocities vs Temperature:
- Not all gas molecules travel at the same velocity (see distribution)
- Increasing temperature increases the average molecular velocity

Molecular Velocities of Different Gases:
- All gases have the same average kinetic energy
- Lighter molecules have the highest average velocity

Energy = 1/2 mv² ∝ Temperature
don’t learn, but understand
Real Gases: Deviations from Ideality

Real gases do not behave like Ideal Gases for two reasons:

1) Long-range attractive forces (attractive intermolecular forces)
2) Short-range repulsive forces (non-zero size of molecules)

\[ P \times V = nRT \]

\[
\left( P + \frac{n^2a}{V^2} \right) \times (V - nb) = nRT
\]

don’t learn, but understand
Phase Diagrams

**CO₂**
- Critical point: (31°C, 73 atm)
- Melting/Freezing
- Sublimation/Deposition
- Vaporization/Condensation
- Triple point: (-57°C, 5.1 atm)

**H₂O**
- Critical point: (374°C, 218 atm)
- Triple point: (0.01°C, 0.006 atm)
Kinetics

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

Rate (speed) of reaction = \( \frac{d(\text{concentration})}{d(\text{time})} \)

\[
\begin{align*}
= \frac{1}{a} \frac{d[A]}{dt} &= \frac{1}{b} \frac{d[B]}{dt} &= \frac{1}{c} \frac{d[C]}{dt} &= \frac{1}{d} \frac{d[D]}{dt}
\end{align*}
\]

Rate (speed) of reaction = \( k \ [A]^x \ [B]^y \)

\( k = \text{rate constant; } x, y \text{ can have any values (0, 1, } -\frac{1}{2} \ldots) \).

e.g., \( x = 1, y = 2 \) \( \Rightarrow \) first order in A, second order in B, third order overall
Solving the 1st-Order Rate Equation: \( \text{rate} = \frac{d[A]}{dt} = -k[A] \)

\[
[A] = [A]_0 e^{-kt}
\]

\[
\ln[A] = -kt + \ln[A]_0
\]

\[
\text{Half Life, } t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}
\]

learn, or remember how to work out quickly from above
Kinetics

**Elementary Reactions:**
- processes that occur in a single collision or molecular event
- rate law follows the stoichiometry
- unimolecular - single molecule reacting; bimolecular - two molecules colliding; termolecular - three molecules colliding (very unlikely)

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Molecularity</th>
<th>Rate Law</th>
</tr>
</thead>
<tbody>
<tr>
<td>A → product</td>
<td>Unimolecular</td>
<td>Rate = $k[A]$</td>
</tr>
<tr>
<td>2A → product</td>
<td>Bimolecular</td>
<td>Rate = $k[A]^2$</td>
</tr>
<tr>
<td>A + B → product</td>
<td>Bimolecular</td>
<td>Rate = $k[A][B]$</td>
</tr>
<tr>
<td>2A + B → product</td>
<td>Termolecular</td>
<td>Rate = $k[A]^2[B]$</td>
</tr>
</tbody>
</table>

**Multi-step Reactions**
- processes that involve multiple elementary reactions
- rate law usually doesn’t follow the stoichiometry
- rate-determining step - the slowest of the elementary reactions
- kinetics are determined by the rate-determining step
Example

• \( \text{H}_2(\text{g}) + 2\text{ICl}(\text{g}) \rightarrow \text{I}_2(\text{g}) + 2\text{HCl}(\text{g}) \)

• Suggested mechanism:

\[
\begin{align*}
\text{(1) } & \text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl} \quad \text{slow} \\
\text{(2) } & \text{HI} + \text{ICl} \rightarrow \text{I}_2 + \text{HCl} \quad \text{fast}
\end{align*}
\]

\[\text{H}_2 + 2\text{ICl} \rightarrow \text{I}_2 + 2\text{HCl} \quad \text{net reaction}\]

\[
\begin{align*}
\text{Rate (1)} & = k_1[\text{H}_2][\text{ICl}] \\
\text{Rate (2)} & = k_2[\text{HI}][\text{ICl}]
\end{align*}
\]

\(\text{(1) is slow: rate determining step}\)

\(\therefore \text{Overall rate} = k_1[\text{H}_2][\text{ICl}]\)

• Experiment: rate = \(k[\text{H}_2][\text{ICl}]\), supports assumed mechanism

• HI is an \textit{intermediate}, it doesn’t appear in the overall reaction
Fast reversible reaction followed by a slow step:

\[
\begin{align*}
(1) & \quad 2\text{NO}(g) \quad \leftrightarrow \quad \text{N}_2\text{O}_2 \quad \text{(fast \ (equil. \ const. \ } K) \\
(2) & \quad \text{N}_2\text{O}_2 \quad + \quad \text{O}_2(g) \quad \rightarrow \quad 2\text{NO}_2 \quad \text{(slow \ (rate \ const. \ } k) \\
\hline \\
& \quad 2\text{NO}(g) \quad + \quad \text{O}_2 \quad \rightarrow \quad 2\text{NO}_2 \quad \text{(net \ reaction)}
\end{align*}
\]

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

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

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

So rate \( = k \ [\text{N}_2\text{O}_2] \ [\text{O}_2] = k \ K \ [\text{NO}]^2 \ [\text{O}_2] \)

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

consistent with observed rate law
Temperature-dependence of the rate constant given by the Arrhenius Equation:

$$k = Ae^{-\frac{E_a}{RT}}$$
Kinetics

• Speeds up the reaction, but doesn’t alter the equilibrium.

Uncatalysed:
A + B → products  (slow)

Catalysed:
A + catalyst → C  (fast)
C + B → products  (faster)
+ catalyst
Equilibrium

**Equilibrium Constants**

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

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

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

Mixture of different states (consider “activities”):
- e.g. gas & solid  - only consider gas partial pressures
- e.g. liquid & solid  - only consider liquid concentrations

\[ K_p = K_c (RT)^{\Delta n} \]

If an equation is multiplied by \( n \), then \( K_c \) is raised to the \( n \)th power.
### Equilibrium

#### Reaction Quotient

For a reaction not at equilibrium:

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

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

- If \( Q_c < K_c \) - forward occurs more than reverse.
- If \( Q_c = K_c \) - system is at equilibrium.
- If \( Q_c > K_c \) - reverse occurs more than forward.
Le Châtelier’s Principle

“When a chemical system in a state of equilibrium is disturbed, it reattains equilibrium by undergoing a net reaction that reduces the effect of the disturbance”

- Increase reactant concentrations
  ⇒ more products produced
- Increase pressure / decrease volume
  ⇒ less gas produced
- Increase temperature
  ⇒ endothermic reaction favoured

\[ Q_c \text{ changes, then } Q_c \Rightarrow K_c \]
\[ K_c \text{ changes, then } Q_c \Rightarrow K_c \]
Acids and Bases

Definitions

- **Arrhenius:** $H^+ + OH^- \Leftrightarrow H_2O$
- **Brønsted - Lowry:** $H^+ + A^- \Leftrightarrow HA$
- **Lewis:** $A + :B \Leftrightarrow A:B$

Conjugate Acids and Bases

Autoionisation of Water

$$K_w = [H^+] [OH^-] = 1.0 \times 10^{-14} \text{ at } 25 \, ^\circ C$$

The ‘p’ Convention

- $\text{pH} = -\log_{10}[H^+] \Rightarrow [H^+] = 10^{-\text{pH}}$
- $\text{pH} + \text{pOH} = \text{p}K_w = 14 \text{ at } 25 \, ^\circ C$
**Acids and Bases**

**Strong acids**
\[ \text{H}_2\text{SO}_4, \text{HCl}, \text{HBr}, \text{HI}, \text{HNO}_3, \text{HClO}_4 \]

**Strong bases**
All hydroxides of Groups 1 & 2 (except Be):
NaOH, Ca(OH)\(_2\), …

**Weak Acids and Bases** - everything else!
Acids and Bases

HA ⇌ H⁺ + A⁻

- Acid dissociation constant

\[ K_a = \frac{[H^+] [A^-]}{[HA]} \]

\[ pK_a = -\log_{10}K_a \]

More positive pKₐ ⇒ weaker acid (and the stronger the conjugate base)

B + H₂O ⇌ HB⁺ + OH⁻

- Base ionisation constant

\[ K_b = \frac{[BH^+] [OH^-]}{[B]} \]

\[ pK_b = -\log_{10}K_b \]

More positive pKₐ ⇒ weaker base (and the stronger the conjugate acid)
Acids and Bases

• Relationship between $pK_a$ and $pK_b$: $pK_a + pK_b = 14$

• Polyprotic Acids: $K_{a1} > K_{a2} > K_{a3}$

• Henderson-Hasselbalch Equation:

\[
pH \approx pK_a + \log \frac{[\text{added base}]}{[\text{added acid}]}
\]

• Buffers: practise calculations!

• Titrations: end point / equivalence point, buffer region, ...
Thermodynamics


\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \]

- *the energy of the universe is constant.*

Second Law of Thermodynamics:

\[ \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \]

- *in a spontaneous process the entropy of the universe must increase.*

Third Law of Thermodynamics:

At 0 K, all substances have the same entropy

(the “baseline” for entropy – define this as \( S = 0 \))
Thermodynamics

**Entropy** - a quantitative measure of the randomness/freedom/disorder of a system.

- For any given substance:
  \[ S_{\text{gas}} > > S_{\text{liquid}} > S_{\text{solid}} \]
- Same substance:
  higher \( T \) → higher \( S \)
- *etc.*

**Gibbs Free Energy**

\[ \Delta G^0_T = \Delta H^0 - T \Delta S^0 \]

- \( \Delta G > 0 \)  Reaction non-spontaneous
- \( \Delta G = 0 \)  System at equilibrium
- \( \Delta G < 0 \)  Reaction spontaneous
Thermodynamics

To find the “Crossover Temperature”:

$$\Delta G^0_T = \Delta H^0 - T\Delta S^0 = 0$$

$$T = \frac{\Delta H^0}{\Delta S^0}$$

be careful of units!

Relationship Between Free Energy and Equilibrium Constant

$$\Delta G^0 = -RT \ln K$$

learn one of these, and don’t get confused with the Arrhenius Eqtn!

$$K = e^{-\Delta G^0/RT}$$
Between Now and the Exam

• do your tutorial problem sheets and quizzes
• revise them with model answers
• past exam papers from 1st year Service Room (sold for our photocopying costs: $3!!)
• re-do ALL examples given in lectures – without help from your notes
• ask a tutor or me for help
• university counselling service