5.111 Lecture Summary #30    Monday, November 24, 2014

Reading for Lecture #31: 14.6, 17.7 in 5th ed and 13.6, 17.7 in 4th ed.

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**Topic: Introduction to Kinetics**

I. Rates of Chemical Reactions

II. Rate Expressions and Rate Laws

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**Kinetics Versus Thermodynamics**

When considering a chemical reaction, one must ask whether the reaction will go forward spontaneously (thermodynamics), and ______________ the reaction will go (kinetics).

Stable/unstable refers to ______________ (________________ tendency to decompose)

Labile/nonlabile (inert) refers to the ______________ at which this tendency is realized

Rate is important. A chemical kinetics experiment measures the rate at which the concentration of a substance taking part in a chemical reaction changes with time.

Factors affecting rates of chemical reactions

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**Let’s consider the oscillating clock reaction**

To understand this reaction, one must consider thermodynamics, chemical equilibrium, acid-base, oxidation-reaction, kinetics, and the influence of oxidation and liganded state to color.

The overall reaction is:

\[
\text{IO}_3^- + 2 \text{H}_2\text{O}_2 + \text{CH}_2(\text{CO}_2\text{H})_2 + \text{H}^+ \rightarrow \text{ICH(}\text{CO}_2\text{H})_2 + 2 \text{O}_2 + 3 \text{H}_2\text{O}
\]

Its mechanism involves multiple steps, including:

(a) \[
\text{IO}_3^- + \Gamma + 2 \text{H}_2\text{O}_2 + 2 \text{H}^+ \rightarrow 2 \text{O}_2 + 3 \text{H}_2\text{O} + \text{I}_2
\] (spontaneous when [I\text{\textsubscript{2}}] is low)

(b) \[
\text{I}_2 + \text{CH}_2(\text{CO}_2\text{H})_2 \rightarrow \text{ICH(}\text{CO}_2\text{H})_2 + \text{H}^+ + \Gamma
\] (spontaneous when [I\text{\textsubscript{2}}] is high)

Reaction (a): addition of IO\textsubscript{3}\textsuperscript{-} and \Gamma to hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) under acidic conditions, turns a clear solution to amber (\text{I}^\textsuperscript{-} is clear and I\textsubscript{2} is amber).

Reaction (b): addition of I\textsubscript{2} (I\textsubscript{2} is amber) to malonic acid (CH\textsubscript{2}(CO\textsubscript{2}H)\textsubscript{2}), generates a complex that is blue. Thus, the color of I depends on both oxidation and liganded state.

**Let’s think about the oxidation-reduction processes in Reaction (a):**

I in IO\textsubscript{3}\textsuperscript{-} is being ______________ to I\textsubscript{2}; \Gamma is being ______________ to I\textsubscript{2};

O in H\textsubscript{2}O\textsubscript{2} is being ______________ to O\textsubscript{2}; O in H\textsubscript{2}O\textsubscript{2} is being ______________ to H\textsubscript{2}O.

With a large (+) \( E^\circ \), H\textsubscript{2}O\textsubscript{2} is

The reaction rate is also sensitive to temperature.
I. Rates of Chemical Reactions

Measuring average reaction rates
Consider: \( \text{NO}_2 (g) + \text{CO} (g) \rightarrow \text{NO} (g) + \text{CO}_2 (g) \)

Can monitor the changes in concentration of NO average rate = \( \frac{\text{change in concentration}}{\text{change in time}} \)

average rate = \( \frac{0.0288 - 0.0160 \text{ M}}{150. - 50. \text{ sec}} \)

average rate depends on time interval chosen

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Measuring instantaneous reaction rates
Consider: \( \text{NO}_2 (g) + \text{CO} (g) \rightarrow \text{NO} (g) + \text{CO}_2 (g) \)

Instantaneous rate = \( \lim_{\Delta t \to 0} \frac{[\text{NO}]_t + \Delta t - [\text{NO}]_t}{\Delta t} = \frac{d[\text{NO}]}{dt} \)

As \( \Delta t \) approaches 0, the rate becomes the slope of the line tangent to the curve at time \( t \).

Instantaneous rate at \( t=150 \text{ sec} \) is

\[
\frac{0.0326 - 0.0249 \text{ M}}{200. -100. \text{ sec}} = 7.7 \times 10^{-5} \text{ M s}^{-1}
\]

Initial rate = Instantaneous rate at time equals ______ sec
Rate expressions

Consider again: \( \text{NO}_2 (g) + \text{CO} (g) \rightarrow \text{NO} (g) + \text{CO}_2 (g) \)

Can monitor NO or CO\(_2\) increase or NO\(_2\) or CO decrease

\[
\text{rate} = \frac{-d[\text{NO}_2]}{dt} = \frac{-d[\text{CO}]}{dt}
\]

Assuming no intermediate species and/or that the concentration of intermediates is independent of time

Generally \( a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D} \)

\[
\text{rate} = \frac{-1}{a} \frac{d[\text{A}]}{dt} = \frac{-1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt}
\]

Example \( 2\text{HI} (g) \rightarrow \text{H}_2 (g) + \text{I}_2 (g) \)

\[
\text{rate} = \frac{-1}{2} \frac{d[\text{HI}]}{dt} = \frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{I}_2]}{dt}
\]

II. Rate Laws

The rate law is the relationship between the rate and the concentration, which are related by a proportionality constant, \( k \), called the rate constant.

\( a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D} \)

\[ \text{rate} = k [\text{A}]^m [\text{B}]^n \]

\( m \) and \( n \) are order of reaction in \( \text{A} \) and \( \text{B} \), respectively

\( k \) is the rate constant

Truths about rate laws

(1) Rate law is a result of experimental observation. You CANNOT look at the stoichiometry of the reaction and predict the rate law (unless the reaction is an elementary reaction - we will come back to this later).

(2) The rate law is not limited to reactants. It can have a product terms, i.e., \( \text{rate} = k[A]^m[B]^n[C]^c \)
(3) For rate = \( k[A]^m[B]^n \), \( m \) is the order of reaction in A, \( n \) is the order of reaction in B. \( m \) and \( n \) can be integers, fractions, negative or positive.

\[
\begin{align*}
m = 0 & \quad \text{Double concentration/} \\
m = \frac{1}{2} & \quad \text{Double concentration/} \\
m = 1 & \quad \text{First order} \quad k[A] \quad \text{Double concentration/} \\
m = 2 & \quad \text{Second order} \quad k[A]^2 \quad \text{Double concentration/} \text{Triple concentration/} \\
m = -1 & \quad \text{Double concentration/} \\
m = -\frac{1}{2} & \quad \text{Double concentration/}
\end{align*}
\]

(4) The overall reaction order is the sum of the exponents in the rate law. For rate = \( k[A]^2[B] \), the overall reaction order is ________ order.

_______ order in A and _______ order in B

(5) The units for \( k \) vary. Determine units for \( k \) by considering units for rate and for concentration.

**Integrated Rate Laws**

Measuring initial rates can be difficult because it involves determining ________ changes in concentrations that occur during short intervals in time.

An alternative is to use the integrated rate law, which expresses concentrations directly as a function of time.
Integrated first-order rate law

First Order \( A \rightarrow B \)

rate \( = \frac{-d[A]}{dt} = k[A] \)

separate concentration and time terms

\[
\int_{[A]_0}^{[A]_t} \frac{1}{[A]} \cdot d[A] = -k \int_0^t dt
\]

\[
\ln [A]_t - \ln [A]_0 = -kt \quad \text{or} \quad \ln [A]_t = -kt + \ln [A]_0
\]

Equation for straight line

Let’s plot \( \ln [A]_t \) versus time

\[
\ln \frac{[A]_t}{[A]_0} = -kt
\]

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

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

Integrated 1st order rate law

Rate constants can be determined from experiment by plotting data in this manner.
First-order Half-life

Half-life is the time it takes for the original concentration to be reduced by half (______).

From above \[ \ln \left( \frac{[A]_t}{[A]_0} \right) = -kt \]

\[ \ln \left( \frac{[A]_0}{2} \right) = -kt_{1/2} \]

\[ \ln 1/2 = -kt_{1/2} \]

\[ -0.6931 = -kt_{1/2} \]

\[ t_{1/2} = \frac{0.6931}{k} \]

First order half life ________________
depend on concentration.

Half life depends on k, and k depends on the material in question.

For the same material does it take longer to go from 1 ton to a \( \frac{1}{2} \) ton or 1 gram to a \( \frac{1}{2} \) gram?

______________________________
Equation Sheet Exam 4

\[ c = 2.9979 \times 10^8 \text{ m/s} \]
\[ h = 6.6261 \times 10^{-34} \text{ J s} \]
\[ N_A = 6.02214 \times 10^{23} \text{ mol}^{-1} \]
\[ R = 8.314 \text{ J/(K mol)} \]
\[ 1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J} \]
\[ K_w = 1.00 \times 10^{-14} \text{ at 25.0}^\circ \text{C} \]
\[ 14.00 = \text{pH} + \text{pOH} \text{ at 25.0}^\circ \text{C} \]
\[ \aleph (\text{Faraday's constant}) = 96,485 \text{ C mol}^{-1} \]

<table>
<thead>
<tr>
<th>Electromagnetic Spectrum:</th>
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<tbody>
<tr>
<td>Violet ~ 400-430 nm</td>
</tr>
<tr>
<td>Blue ~ 431-490 nm</td>
</tr>
<tr>
<td>Green ~ 491-560 nm</td>
</tr>
<tr>
<td>Yellow ~ 561-580 nm</td>
</tr>
<tr>
<td>Orange ~ 581-620 nm</td>
</tr>
<tr>
<td>Red ~ 621-700 nm</td>
</tr>
</tbody>
</table>

Complementary Colors: red/green, blue/orange, yellow/violet

\[ \Gamma < \text{Br}^- < \text{Cl}^- \] (weak field ligands)
\[ < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} \] (intermediate)
\[ < \text{NH}_3 < \text{CO} < \text{CN}^- \] (strong field ligands)

1 Coulomb • Volt = 1 Joule
1 Bq = 1 nuclei/sec
1 A = 1 C/s \hspace{1cm} 1 W = 1 J/s
\[ \ln = 2.3025851 \log \]
1 J = 1 kgm²s⁻²
\[ x = \frac{-b \pm (b^2 -4ac)^{1/2}}{2a} \]
\[ a \cdot x^2 + b \cdot x + c = 0 \]
\[ E = h \nu = \frac{h c}{\lambda} \]
\[ c = \nu \lambda \]
\[ \Delta G = \Delta H - T \Delta S \]
\[ \Delta G = \Delta G^\circ + R T \ln Q \]
\[ \Delta G^\circ = -RT \ln K \]
\[ \Delta G = RT \ln Q/K \]
\[ \ln \left( \frac{K_2}{K_1} \right) = - \frac{(\Delta H^\circ/R)(1/T_2 - 1/T_1)}{\Delta S} \]
\[ \text{pH} = pK_a - \log (HA/A^-) \]
\[ \text{pH} = -\log [\text{H}_3\text{O}^+] \]
\[ \text{pOH} = -\log [\text{OH}^-] \]
\[ K_w = K_a K_b \]
\[ pK = -\log K \]
\[ Q = It \]
\[ \Delta G^\circ_{\text{cell}} = -(n)(\aleph) \Delta E^\circ_{\text{cell}} \]
\[ \Delta E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode}) \]
\[ \Delta E^\circ_{\text{cell}} = E^\circ(\text{reduction}) - E^\circ(\text{oxidation}) \]
\[ \Delta E_{\text{cell}} = E^\circ_{\text{cell}} - (RT/n\aleph) \ln Q \]
\[ RT/\aleph = 0.025693 \text{ V at 25.0 } ^\circ \text{C} \]
\[ \aleph/RT = 38.921 \text{ V}^{-1} \text{ at 25.0 } ^\circ \text{C} \]
\[ \Delta E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.025693 \text{ V})(\ln Q)/n] \text{ at 25.0}^\circ \text{C} \]
\[ \Delta E_{\text{cell}} = E^\circ_{\text{cell}} - [(0.0592 \text{ V})(\log Q)/n] \text{ at 25.0}^\circ \text{C} \]
\[ \ln K = (n\aleph/RT) \Delta E^\circ \]
\[ A = A_o e^{-kt} \]
\[ N = N_o e^{-kt} \]
\[ A = kN \]
\[ [A] = [A]_o e^{kt} \]
\[ t_{1/2} = \ln 2 / k \]
\[ 1/[A] = 1/[A]_o + kt \]
\[ t_{1/2} = 1 / k[A]_o \]