5.111 Lecture Summary #30 **Monday, November 24, 2014**

Reading for Today: 14.1-14.5 in 5th ed and 13.1-13.5 in 4th ed.
Reading for Lecture #31: 14.6, 17.7 in 5th ed and 13.6, 17.7 in 4th ed.

Topic: Introduction to Kinetics
I. Rates of Chemical Reactions
II. Rate Expressions and Rate Laws

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

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: $IO_3^- + 2\ H_2O_2 + CH_2(CO_2H)_2 + H^+ \rightarrow ICH(CO_2H)_2 + 2\ O_2 + 3\ H_2O$

Its mechanism involves multiple steps, including:

(a) $IO_3^- + I^- + 2\ H_2O_2 + 2\ H^+ \rightarrow 2\ O_2 + 3\ H_2O + I_2$ (spontaneous when $[I_2]$ is low)

(b) $I_2 + CH_2(CO_2H)_2 \rightarrow ICH(CO_2H)_2 + H^+ + I^-$ (spontaneous when $[I_2]$ is high)

Reaction (a): addition of IO_3^- and I^- to hydrogen peroxide (H_2O_2) under acidic conditions, turns a clear solution to amber (I^- is clear and I_2 is amber).

Reaction (b): addition of I_2 (I_2 is amber) to malonic acid ($CH_2(CO_2H)_2$), 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):

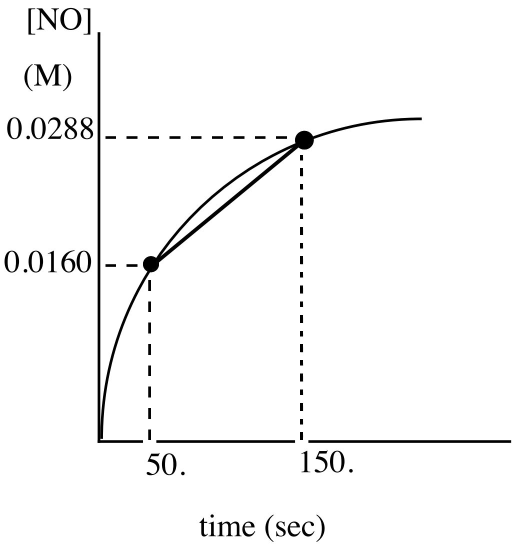
I in IO_3^- is being ___________________ to I_2; I^- is being ___________________ to I_2;
O in H_2O_2 is being ________________ to O_2; O in H_2O_2 is being _________________ to H_2O.
With a large (+) $E°$, H_2O_2 is

The reaction rate is also sensitive to temperature.

I. Rates of Chemical Reactions

Measuring average reaction rates

Consider: NO_2 (g) + CO (g) → NO (g) + CO_2 (g)



Can monitor the changes in concentration of NO

average rate = $\dfrac{\text{change in concentration}}{\text{change in time}}$

average rate = ________

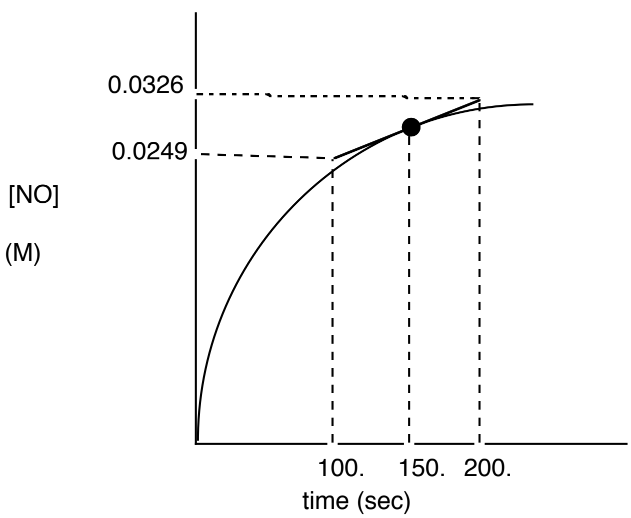
average rate = $\dfrac{0.0288 - 0.0160 \text{ M}}{150. - 50. \text{ sec}}$ =

average rate depends on time interval chosen

Measuring instantaneous reaction rates

Consider: NO_2 (g) + CO (g) → NO (g) + CO_2 (g)

$$\text{Instantaneous rate} = \text{limit}_{\Delta t \to 0} \frac{[NO]_{t+\Delta t} - [NO]_t}{\Delta t} = \frac{d[NO]}{dt}$$



As Δt approaches 0, the rate becomes the slope of the line tangent to the curve at time t.

Instantaneous rate at t=150 sec is

$\dfrac{0.0326 - 0.0249 \text{ M}}{200. - 100. \text{ sec}}$ = 7.7 x 10^{-5} M s^{-1}

Initial rate = Instantaneous rate at time equals _______sec

Rate expressions

Consider again: NO_2 (g) + CO (g) → NO (g) + CO_2 (g)

Can monitor NO or CO_2 increase or NO_2 or CO decrease

$$\text{rate} = \frac{-d[NO_2]}{dt} = \frac{-d[CO]}{dt} = \qquad = $$

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

Generally aA + bB → cC + dD

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

Example 2HI (g) → H_2 (g) + I_2 (g)

rate = = =

II. Rate Laws

The rate law is the relationship between the rate and the concentration, which are related by a proportionality constant, _______ ,called the ______________________________________ .

aA + bB → cC + dD

rate = k $[A]^m[B]^n$.....

m and n are order of reaction in A and 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., 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.

m = 0			Double concentration/
m = ½			Double concentration/
m = 1	First order	k[A]	Double concentration/
m = 2	Second order	$k[A]^2$	Double concentration/
			Triple concentration/
m = -1			Double concentration/
m = -1/2			Double concentration/

(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

$$\text{rate} = \frac{-d[A]}{dt} = k[A]$$

separate concentration and time terms

$$\frac{1}{[A]} \bullet d[A] = -k\,dt$$

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

$\ln [A]_t - \ln [A]_0 = -kt$ or $\boxed{\ln [A]_t = -kt + \ln [A]_0}$ **Equation for straight line**

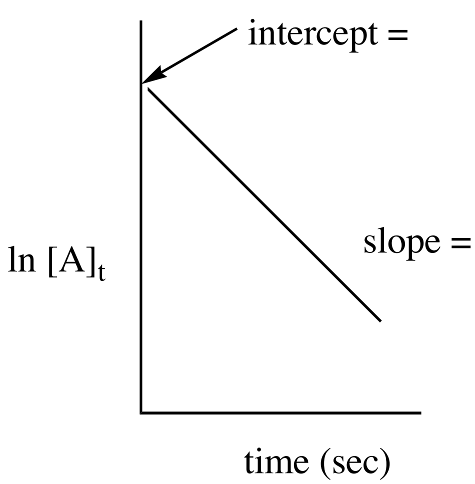
$$\ln \frac{[A]_t}{[A]_0} = -kt$$

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

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

Integrated 1st order rate law

Let's plot $\ln [A_t]$ versus time



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

$$y = mx + b$$

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

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

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

$$\ln 1/2 = -kt_{1/2}$$

$$-0.6931 = -kt_{1/2}$$

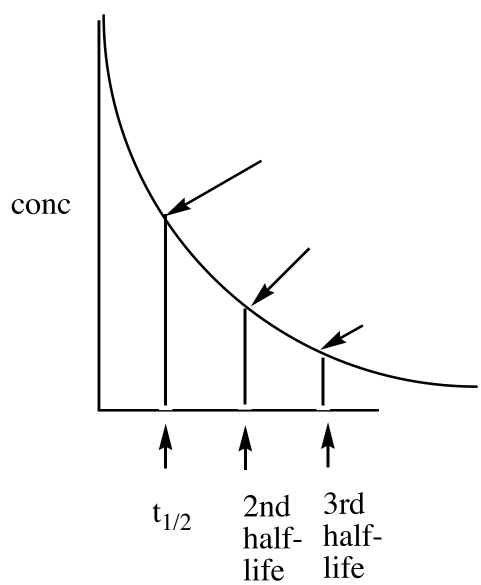
$$t_{1/2} = \frac{0.6931}{k}$$

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 ½ ton or 1 gram to a ½ gram?

________________________________ .



Equation Sheet Exam 4

$c = 2.9979 \times 10^8$ m/s

$h = 6.6261 \times 10^{-34}$ J s

$N_A = 6.02214 \times 10^{23}$ mol^{-1}

R = 8.314 J/(K mol)

1 eV = 1.60218×10^{-19} J

$K_w = 1.00 \times 10^{-14}$ at 25.0°C

14.00 = pH + pOH at 25.0°C

ℑ (Faraday's constant) = 96,485 C mol^{-1}

Electromagnetic Spectrum:
Violet ~ 400-430 nm Blue ~ 431-490 nm
Green ~ 491-560 nm
Yellow ~ 561-580 nm Orange ~ 581-620 nm
Red ~ 621-700 nm

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

$I^- < Br^- < Cl^-$ (weak field ligands)
$< F^- < OH^- < H_2O$ (intermediate)
$< NH_3 < CO < CN^-$ 9 (strong field ligands)

1 Coulomb • Volt = 1 Joule

1 Bq = 1 nuclei/sec

1A = 1C/s 1W = 1 J/s

ln = 2.3025851log

1 J = 1 kgm^{2}s^{-2}

$x = [-b \pm (b^2 - 4ac)^{1/2}]/2a$

$ax^2 + bx + c = 0$

$E = h\nu = hc/\lambda$

$c = \nu\lambda$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta G = RT \ln Q/K$

$\ln (K_2/K_1) = -(\Delta H°/R)(1/T_2 - 1/T_1)$

$pH \approx pK_a - \log (HA/A^-)$

$pH = -\log [H_3O^+]$ $pOH = -\log [OH^-]$

$K_w = K_aK_b$ $pK = -\log K$

$Q = It$

$\Delta G°_{cell} = -(n)(\Im)\ \Delta E°_{cell}$

$\Delta E°(cell) = E°(cathode) - E°(anode)$

$\Delta E° = E°(reduction) - E°(oxidation)$

$\Delta E_{cell} = E°_{cell} - (RT/n\Im)\ln Q$

$RT/\Im = 0.025693$ V at 25.0 °C
$\Im/RT = 38.921$ V^{-1} at 25.0 °C

$\Delta E_{cell} = E°_{cell} - [(0.025693\ V)(\ln Q)/n]$ at 25.0°C

$\Delta E_{cell} = E°_{cell} - [(0.0592\ V)(\log Q)/n]$ at 25.0°C

$\ln K = (n\Im/RT)\ \Delta E°$

$A = A_o e^{-kt}$

$N = N_o e^{-kt}$

$A = kN$

$[A] = [A]_o e^{-kt}$ $t_{1/2} = \ln 2 / k$

$1/[A] = 1/[A]_o + kt$ $t_{1/2} = 1 / k[A]_o$