Chemistry 1B, Fall 2016
Topics 21-22

Chemistry 1B

Fall 2016

Topics 21-22
Chemical Kinetics

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Chemistry 1B so far: STRUCTURE
of atoms and molecules

Chemistry 1B now: DYNAMICS
chemical kinetics

2

Thermodynamics: Whether a reaction will occur
?? spontaneously
and "how far" it will proceed
[*equilibrium conditions*]

$2H_2(g)+O_2(g) \rightarrow 2H_2O(g)$

$\Delta H = -484\ kJ$ **very exothermic**

equilibrium chem 1A-1C

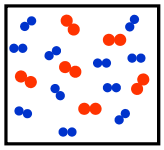
$$K_p = \frac{\left(\frac{P_{H_2O}}{1\text{ atm}}\right)^2}{\left(\frac{P_{H_2}}{1\text{ atm}}\right)^2\left(\frac{P_{O_2}}{1\text{ atm}}\right)} = 2\times10^{80}$$

'all' products at equilibrium

3

HOWEVER:

O_2 + H_2



nada (no reaction) almost forever

Kinetics: How **fast** a reaction proceeds, and
the molecular steps involved in a
reaction [*the mechanism of a reaction*].

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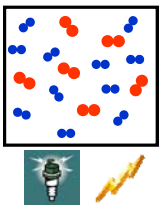
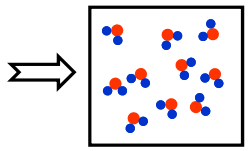
BUT:

O_2 + H_2





H_2O

Kinetics: How **fast** a reaction proceeds, and
the molecular steps involved in a
reaction [*the mechanism of a reaction*].

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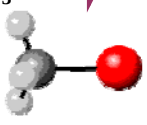
$CN^- + CH_3I \rightarrow CH_3CN + I^-$

$N\equiv C^-$ → $H_3C\text{-}I$ → $N\equiv C\text{-}CH_3 + I^-$



$N\equiv C\text{-}CH_3 + I^-$

Kinetics: How **fast** a reaction proceeds, **and**
the molecular steps involved in a
reaction [*the mechanism of a reaction*].

http://www.bluffton.edu/~bergerd/classes/CEM221/sn-e/SN2_alternate.html

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specific objectives for final exam material

- Concepts and definitions
  - Lecture notes
  - HW10 Z15.55, Z15.52, Z15.68

  } HW10 #67, S19-S20

- Numerical Problem Solving
  - Lecture notes
  - HW10 Z15.17, Z15.20, Z15.57, Z15.73, Z15.82

  } HW10 #64,#65,#68, #69,#71

- Graphical interpretations
  - Lecture notes
  - HW10 Z15.36a, Z15.81

  } HW10 #66,#70

HW#10 DUE SUNDAY, 4th DECEMBER (last WebAssign)

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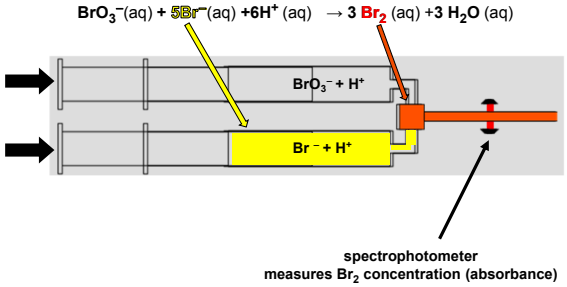
measuring how fast a reaction goes

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(aq)$



spectrophotometer measures Br_2 concentration (absorbance)

http://www.chm.davidson.edu/vce/kinetics/BromateBromideReaction.html

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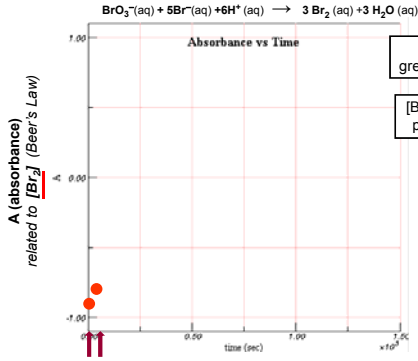
[Br_2] (absorbance) vs time
(for set of initial [BrO_3^-], [Br^-], [H^+]) and fixed Temperature

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(aq)$



more $[Br_2] \Rightarrow$ greater absorbance

$[Br_2]$ increasing as product appears

time *(t=0 when reactants mixed)*

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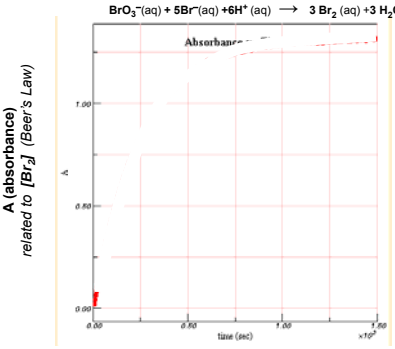
[Br_2] (absorbance) vs time
(for set of initial [BrO_3^-], [Br^-], [H^+]) and fixed Temperature

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(aq)$



more $[Br_2] \Rightarrow$ greater absorbance

$[Br_2]$ increasing as product appears

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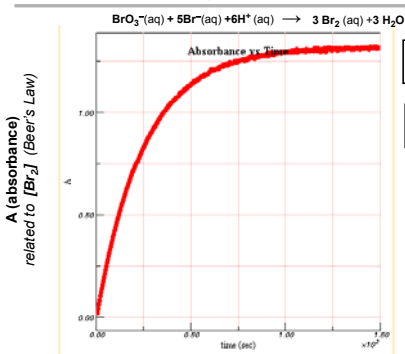
[Br_2] (absorbance) vs time
(for set of initial [BrO_3^-], [Br^-], [H^+]) and fixed Temperature

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3\,Br_2(aq) + 3\,H_2O(aq)$



more $[Br_2] \Rightarrow$ greater absorbance

$[Br_2]$ increasing as product appears

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Zumdahl Sec.15.1

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

TABLE 15.1

Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ (at 300°C)

Time (±1 s)	Concentration (mol/L) NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

t=0 only reactant

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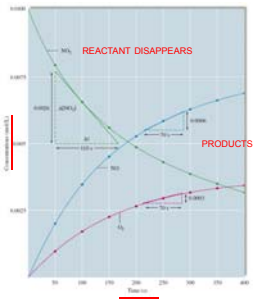
Zumdahl section 15.1

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$



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DIFFERENTIAL rate of chemical reaction (appearance of product)

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

reaction rate: [disappearance of $NO_2(g)$] $= -\frac{change\ of\ [NO_2]}{change\ of\ time} = -\frac{\Delta[NO_2]}{\Delta t}$

DIFFERENTIAL reaction rate $= \lim_{\Delta t \to 0} -\frac{\Delta[NO_2]}{\Delta t} = -\frac{d[NO_2]}{dt}$

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"initial rate" at t=0 *(0→ 50 s)*

$\Delta t = t_2 - t_1 = (50 - 0)s = 50s$

$-\Delta[NO_2] = -(0.0079 - 0.0100)$ mol/L=0.0021 mol/L

$rate \approx -\frac{\Delta[NO_2]}{\Delta t} = \frac{0.0021}{50}$ mol $L^{-1}s^{-1} = 4.2 \times 10^{-5}$ mol $L^{-1}s^{-1}$

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reaction rate changes as reaction proceeds (Z fig.15.1, Table 15.2)

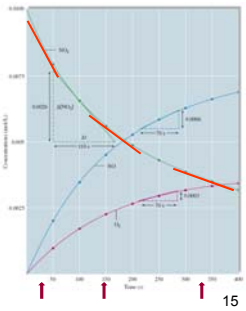
reaction rate $= -\frac{d[NO_2]}{dt} = -$ (slope of $[NO_2]$ vs t)

slope=tangent to curve

TABLE 15.2
Average Rate (in mol L^{-1} s^{-1}) of Decomposition of Nitrogen Dioxide as a Function of Time

$-\frac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	0 → 50
2.8×10^{-5}	50 → 100
2.0×10^{-5}	100 → 150
1.4×10^{-5}	150 → 200
1.0×10^{-5}	200 → 250

Note: The *rate* decreases with time.



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relations among rates of chemical reaction based on different components

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

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400	0.0031	0.0069	0.0035

in each Δt=50s interval

- $\Delta[NO_2] = \Delta[NO] = 2\Delta[O_2]$

disappearance	appearance	
NO_2	NO	O_2
-0.021	0.021	0.011
mol L^{-1} at t=0		

$-\frac{d[NO_2]}{dt} = +\frac{d[NO]}{dt} = +\ ?\ \frac{d[O_2]}{dt}$

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relations among rates of chemical reaction based on different components

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Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ (at 300°C)

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disappearance	appearance	
NO_2	NO	O_2
-0.021	0.021	0.011
mol L^{-1} at t=0		

$-\frac{d[NO_2]}{dt} = +\frac{d[NO]}{dt} = +\ \mathbf{2}\ \frac{d[O_2]}{dt}$

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rate will (may) generally depend on concentrations

higher concentrations ⇒ more collisions

more collisions ⇒ more reactions occurs

rate depends on concentrations

$a\ A + b\ B \rightarrow c\ C + d\ D$

$-\frac{d[A]}{dt} = k[A]^m[B]^n$

rate constant for a given Temperature

concentrations of reactants each raised to a power *(usually integers)*

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generalized (differential) rate expression

$aA + bB \xrightarrow{k_f} cC + dD$ forward reaction

$aA + bB \xleftarrow{k_r} cC + dD$ reverse reaction (products recombine)

general differential rate expression *(can get more complicated):*

$$-\frac{d[A]}{dt} = k_f[A]^m[B]^n - k_r[C]^k[D]^l$$

forward rate (loss of [A])
k_f *rate constant of forward reaction*

reverse rate (increase of [A])
k_r *rate constant of reverse reaction*

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initial (differential) rate expression

$aA + bB \xrightarrow{k_f} cC + dD$ forward reaction

$aA + bB \xleftarrow{k_r} cC + dD$ reverse reaction

$$-\frac{d[A]}{dt} = k_f[A]^m[B]^n - k_r[C]^k[D]^l$$

INITIAL RATE (initially only reactants present):

$[A]_o, [B]_o \neq 0$ $\quad -\frac{d[A]_0}{dt} = k[A]_0^m[B]_0^n$

$[C]_o, [D]_o = 0$

- k is rate constant (for eqn written as disappearance of A)
- **DEFINITION OF RATE ORDER** rate is:
  - m^{th} order in reactant [A]
  - n^{th} order in reactant [B]

Note: *Only in certain instances (discuss soon) will the order of a reactant or product (m,n) be the same as its stoichiometric coefficient (a,b)*

- overall rate order is $[m+n]^{th}$ order (i.e. total order of reaction rate)

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rate laws: initial rate

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ forward reaction

~~$2NO_2(g) \leftarrow 2NO(g) + O_2(g)$~~ reverse reaction

initial rate:
- only reactants present
- $[NO]_o = [O_2]_o = 0$
- no reverse reaction

$$-\frac{d[NO_2]_0}{dt} = k[NO_2]_0^n$$

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skills for HW and final (HW10 #64-#65)

DIFFERENTIAL RATE EXPRESSIONS

- Write rate expression in terms of reactant concentrations
- Determine order for each reactant from initial rate data
- Determine overall rate order
- Determine rate constant

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determining rate order from initial rate (table 15.4 p 723 Z)

$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(\ell)$

$$-\frac{d[NH_4^+]_0}{dt} = k[NH_4^+]_0^m[NO_2^-]_0^n$$ differential initial rate

TABLE 15.4
Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

to determine the order in a reactant (e.g. m or n):
identify two initial conditions (experiments) where the concentration of only one reactant has changed

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determining rate order from initial rate (table 15.4 p 723 Z)

$NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(\ell)$

$$-\frac{d[NH_4^+]_0}{dt} = k[NH_4^+]_0^m[NO_2^-]_0^n$$

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1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

$(x \text{ rate}) = [x \text{ conc}]^n$
$(2) = (2)^1$

for $[NO_2^-]^n$ 1 vs 2: $[NH_4^+]$ const, double $[NO_2^-]$ rate doubles ⇨ n=1

for $[NH_4^-]^m$ 2 vs 3: $[NO_2^-]$ const, double $[NH_4^+]$ rate doubles ⇨ m=1

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order of reaction

NH_4^+ (aq) + NO_2^- (aq) → N_2 (g) +2H_20 (ℓ)

$$\text{initial rate of disappearance}\left[NH_4^+\right] = -\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^1\left[NO_2^-\right]_0^1$$

first order in [NH_4^+]

first order in [NO_2^-]

second order overall

given rate law: determine k (rate constant) HW10 #64-65

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

now that we know the order of the reaction
to get k use any 'experiment' (or average of all)

$$\{\text{initial rate of disappearance of } NH_4^+\} = -\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^1\left[NO_2^-\right]_0^1$$

from exp 1 $1.35\times10^{-7}\,mol\,L^{-1}s^{-1} = k(0.100\,mol\,L^{-1})^1(0.0050\,mol\,L^{-1})^1$

$$k = 2.70\times10^{-4}\,mol^{-1}L\,s^{-1}$$

from exp 3 $5.40\times10^{-7}\,mol\,L^{-1}s^{-1} = k(0.200\,mol\,L^{-1})^1(0.010\,mol\,L^{-1})^1$

$$k = 2.70\times10^{-4}\,mol^{-1}L\,s^{-1}$$

more complicated

BrO_3^-(aq) **+ 5Br^-**(aq) **+6H^+** (aq) → **3 Br_2** (aq) **+3 H_2O** (aq)

remember same reaction in stop-flow apparatus, earlier slide

more complicated (see Table 15.5)

BrO_3^-(aq) **+ 5Br^-**(aq) **+6H^+** (aq) → **3 Br_2** (aq) **+3 H_2O** (aq)

TABLE 15.5
The Results from Four Experiments to Study the Reaction
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol L^{-1} s^{-1})
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

from initial rate data determine n, m, and p

$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^n\left[Br^-\right]^m\left[H^+\right]^p$$

[BrO_3^-]^n: exp 1-2 [BrO_3^-] doubles, rate x2 ⇒ n= 1 $2=[2]^1$

[Br^-]^m: exp 2-3 [Br^-] doubles, rate x2 ⇒ m= 1

[H^+]^p: exp 1-4 [H^+] doubles, rate x4 ⇒ p= 2 $4=[2]^2$

(x rate)=[x conc]^n

order of the reaction

$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

first order in [BrO_3^-]

first order in [Br^-]

second order in [H^+]

fourth order overall

after determining order, evaluate rate constant

BrO_3^-(aq) **+ 5Br^-**(aq) **+6H^+** (aq) → **3 Br_2** (aq) **+3 H_2O** (aq)

$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol L^{-1} s^{-1})
1	0.10	0.10	0.10	8.0×10^{-4}

$rate = k \times (0.10\,mol\,L^{-1})^1 \times (0.10\,mol\,L^{-1})^1 \times (0.10\,mol\,L^{-1})^2 = 8.0\times10^{-4}\,L^{-1}s^{-1}$

$$k = 8.00\,L^3\,mol^{-3}s^{-1}$$

will be identical (within experimental) using any of the 'experiments'

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skills for HW and final

differential rate expressions

- ✓ • Write rate expression in terms of reactant concentrations
- ✓ • Determine order for each reactant from initial rate data
- ✓ • Determine overall rate order
- ✓ • Determine rate constant

integral rate expression

- Determine order of reaction from plot of 'concentration' vs time
- Half-life of a reaction

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integrated rate expression

differential rate gives **change** of reactant or product concentrations with time

$$-\frac{d[\text{reactant}]}{dt} = \cdots$$

integrated rate gives **value** of reactant or product concentrations with time

$$[\text{reactant}] = f(t)$$

from calculus $x = \int dx$ and $t = \int dt$

(value, change, value, change)

INTEGRATE !!!

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math 11 or 19

$$\int dt = ?$$

$$\int \frac{dx}{x} = ?$$

$$\int \frac{dx}{x^2} = ?$$

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integrated rate expression for first-order reaction

differential rate law: $-\frac{d[A]}{dt} = k[A]$ first order disappearance of reactants

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

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

$$\ln[A] = -kt + C$$

(slope, intercept)

integrated rate law: $\ln[A] = -kt + \ln[A]_0$ *when* $t = 0$ $[A] = [A]_0$

first order: a plot of ln[*A*] vs t would be a straight line with slope –k and intercept ln $[A]_o$

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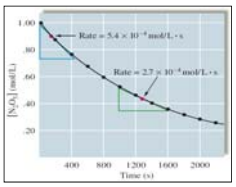
integrated first order reaction

$2N_2O_5$ (soln) → $4NO_2$(soln) + O_2(g)

$$\text{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]^n$$



$[N_2O_5]$ vs t

How could we tell if n=1 (first order in N_2O_5)?
[not using multiple experiments with various initial concentrations]

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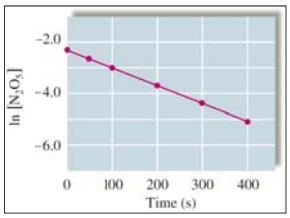
integrated rate law (first-order)

$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$ *(if reaction is first order)*

plot **ln $[N_2O_5]$** vs **t**

do we get straight line ??

(yes n=1, no n≠ 1)



YES !!
n=1
it is first-order

slope = ***-k***
t=0 intercept is ***ln $[N_2O_5]_o$***

$$\text{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]^1$$

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Topics 21-22

other integrated rate laws

$-\frac{d[A]}{dt} = k$ zero-th order reaction; differential rate law

$\int d[A] = -k\int dt$ $\quad [A] = -kt + [A]_0$ zeroth order reaction; integrated rate law

plot [A] vs t gives straight line

$-\frac{d[A]}{dt} = k[A]^2$ second order reaction; differential rate law

$\int \frac{d[A]}{[A]^2} = -k\int dt$ $\quad \frac{1}{[A]} = +kt + \frac{1}{[A]_0}$ second order reaction; integrated rate law

plot $[A]^{-1}$ vs t gives straight line

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more complicated integrated rate laws **(don't fret)**

$$-\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

more complicated to get integrated rate-laws for rate expressions which depend on several reactant concentrations :

use $[Br^-]_o$ and $[H^+]_o >> [BrO_3^-]_o$; plot ln $[BrO_3^-]$ vs t

$[Br^-]$ and $[H^+]$ change relatively little **(constant)**

reaction 'pseudo' first-order; i.e rate≈ ***(k $[Br^-]$ $[H^+]^2$)*** $[BrO_3^-]^1$

≈≈ ***constant = (k $[Br^-]_o$ $[H^+]_o^2$)***

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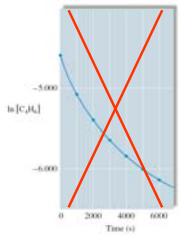
first order or second order ??? Example 15.5 and (HW10 #66)

$2C_4H_6 \longrightarrow C_8H_{12}$ $\quad -\frac{d[C_4H_6]}{dt} = k[C_4H_6]^?$

same rate data plotted two ways



ln $[C_4H_6]$ vs t

or

$\frac{1}{[C_4H_6]}$ vs t

$-\frac{d[C_4H_6]}{dt} = k[C_4H_6]^2$

straight line ⇒ first order

straight line ⇒ second order

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$t_{½}$ half-life vs rate constant

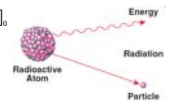
time for concentration of reactant to drop by factor of 2

$[A]_{t+t_{½}} = \frac{1}{2}[A]_t$ e.g. when half the original reactant left $[A]_{t_{½}} = \frac{1}{2}[A]_o$

first-order reaction (e.g. radioactive decay)

$\ln[A]_t = -kt + \ln[A]_0$ and $\ln[A]_{t+t_{½}} = -k(t + t_{½}) + \ln[A]_0$

$\ln[A]_t - \ln[A]_{t+t_{½}} = \ln\left(\frac{[A]_t}{[A]_{t+t_{½}}}\right) = k\,t_{½}$



$\frac{[A]_t}{[A]_{t+t_{½}}} = 2$ *def of* $t_{½}$

$\ln(2) = kt_{½}$

$t_{½} = \frac{\ln(2)}{k} = \frac{0.693}{k}$ eqn 15.3

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$t_{½}$ half-life vs rate constant zeroth and 2nd order

still the definition of half-life

time for concentration of reactant to drop by factor of 2

$[A]_{t+t_{½}} = \frac{1}{2}[A]_t$ e.g. when half the original reactant left $[A]_{t_{½}} = \frac{1}{2}[A]_o$

but:

order	0th	1st	2nd
$t_{1/2}$	$\frac{[A]_{at\,t}}{2k}$	$\frac{0.693}{k}$	$\frac{1}{k[A]_{at\,t}}$

larger k ⇒ shorter $t_{½}$

only for 1st order is the half the same throughout the reaction *(independent of the 'current' concentration of [A])*

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summary (also understand section 15.5; 1-5, 6)*

TABLE 15.6

Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of the straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

know how to use; ***all needed formulas given on exam***

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Chemistry 1B, Fall 2016
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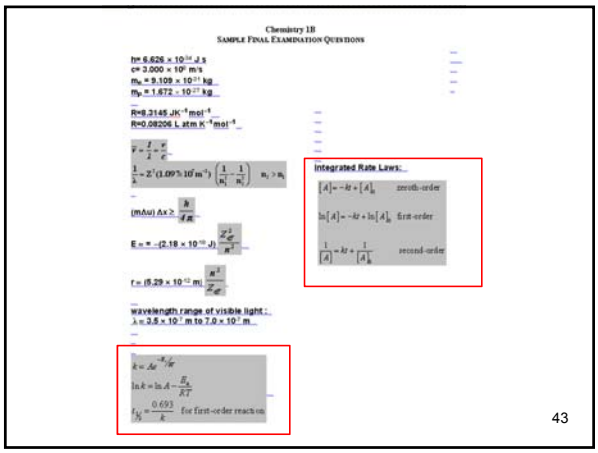

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end of topics 21-22

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initial rate (2 vs 3)

initial rate of disappearance $\left[NH_4^+\right] = -\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^m\left[NO_2^-\right]_0^n$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

rate $= k\ [NH_4^+]^m\ [NO_2^-]^n$

3: $5.40\times10^{-7} = k[0.200M]^m[.010M]^n$

2: $2.70\times10^{-7} = k[0.100M]^m[.010M]^n$

divide 3/2 $\frac{3}{2}$: $\frac{5.40\times10^{-7}}{2.70\times10^{-7}} = \frac{k[0.200M]^m[.010M]^n}{k[0.100M]^m[.010M]^n}$

$\frac{3}{2}$: $2.00 = [2]^m \Rightarrow m = 1$

(x rate)= [x conc]^n

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initial rate (x rate)= [x conc]^n

initial rate = ….. $[A]_0^n$ n^{th} order in A

double initial concentration of A i.e. [2 x]

and initial rate changes by ⇒ implies order n $\frac{rate\,2}{rate\,1} = \left(\frac{conc\,2}{conc\,1}\right)^n$

if the initial concentration of one **reactant doubles [2x]** and the reaction rate

doubles (x2) ⇒ n=1 $2=[2]^1$

quadruples (x4) ⇒ n=2 $4=[2]^2$

octuples (x8) ⇒ n=3 $8=[2]^3$

(x rate)= [x conc]^n also holds for other concentration multiples e.g. [3x] triple initial concentration , n=2, rate 9 times faster

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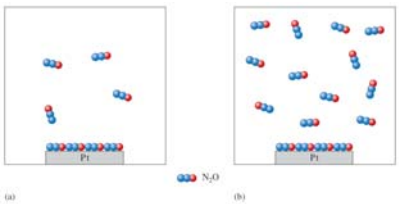
zeroth order reaction: fully occupied surface catalyst

decomposition of N_2O on platinum surface

$2N_2O\,(g) \xrightarrow{Pt(surface)} 2N_2\,(g) + O_2\,(g)$

$-\frac{d[N_2O]}{dt} = k = k[N_2O]^0$ zeroth order



after surface covered, higher $[N_2O]$ leads to no greater rate of decomposition

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