CHEM 206 section 01

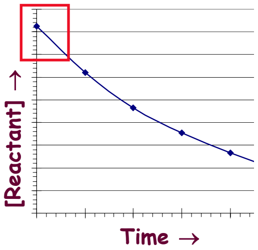
LECTURE #11 Fri. Feb.08, 2008

LECTURE TOPICS:

TODAY'S CLASS: 15.3-15.4

NEXT CLASS: 15.6 (doing 15.5 last…)

Determining the form of the rate law:
Method 1: Method of Initial Rates



EXPERIMENT'S PURPOSE:

- to determine how changing EACH reactant's conc. <u>on its own</u> affects the rate of the reaction
- to find each reactant's "order"

A TYPICAL INITIAL RATES EXPERIMENT: aA + bB → product

1st: DATA ACQUISITION:

- RUN 1: use known [A] and [B]… **measure initial rate of reaction**
- RUN 2: change ONE of [A] *OR* [B], & measure initial rate
- RUN 3: change other reactant's concentration, & repeat…

2nd: ANALYSIS: compare 2 runs at a time (only 1 [ ] changed)

Determine rate's dependence on concentration:

- 1ST ORDER: [A] x n causes x n^1 change in rate
- 2ND ORDER: [A] x n causes x n^2 change in rate

most common

- ZERO ORDER: [A] x n causes x n^0 = NO change in rate
- HALF ORDER: [A] x n causes x $n^{1/2}$ change in rate (RARE)

EXAMPLE: redox rxn between ammonium & nitrite ions

Zumdahl's

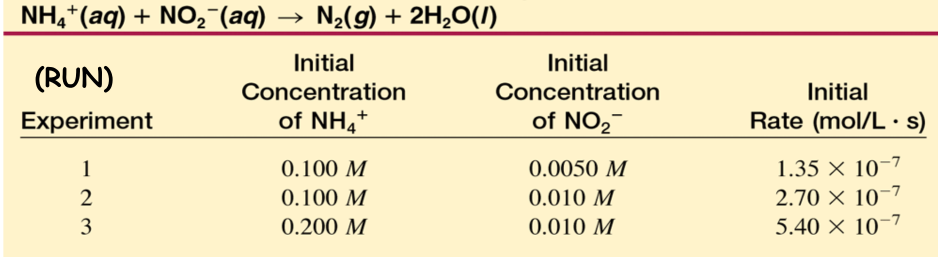


TABLE 12.4 Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \rightarrow N_2(g) + 2H_2O(l)$

(RUN) Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L · s)
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}

General form of rate law: rate = $k[NH_4^+]^m[NO_2^-]^n$

where m & n are most likely 1 or 2…

AFTER ANALYSIS: rate $\propto [NH_4^+]^1$ linear dependence
rate $\propto [NO_2^-]^1$ linear dependence

⇨ rate = $k[NH_4^+][NO_2^-]$

⇨ reaction is "first order in" ammonium and in nitrite
or "first order with respect to" NH_4^+ and NO_2^-

OVERALL, this reaction is 2nd order: m + n = 2

Also: Initial rates data let us calculate rate constant, *k*

…useful later – provides link to size of energy barrier (activation E)

Using experimentally derived rate law: *e.g.*, rate = $k[NH_4^+][NO_2^-]$

- Sub in rate$_o$ & $[\ ]_o$ data & solve for *k* !
- Best: calculate average value for all rxn runs you did
- NOTE: rate constants change with temperature…
  so important to report T along with *k*

For last example:
Take run #1's data:

Best: find <u>average</u> *k* for all 3 runs
(do that yourselves & verify…)

$[NH_4^+]_o$ = 0.100M,
$[NO_2^-]_o$ = 0.0050 M
initial rate = 1.35×10^{-7} Ms^{-1}

$$k = \frac{\text{initial rate}}{[NH_4^+]_o[NO_2^-]_o} = \frac{1.35\times10^{-7}\ Ms^{-1}}{[0.100\ M][0.0050\ M]} = 2.70\times10^{-4}\ M^{-1}s^{-1}$$

a second-order rate constant

Summary: how to derive a differential rate law

1.) Differential Rate Law: rate = k[reactant]^n

Via EXPERIMENT: "method of initial rates"

→ SEVERAL RUNS: change [reactant] ⇒ measure rate

ANALYSIS:

$$\frac{\text{RUN } \textcircled{2}}{\text{RUN } \textcircled{1}} \Rightarrow \frac{\text{rate}_{\textcircled{2}} = \cancel{k}[\text{reactant}]_{\textcircled{2}}^{n}}{\text{rate}_{\textcircled{1}} = \cancel{k}[\text{reactant}]_{\textcircled{1}}^{n}}$$

But remember:
- commonly: n = 1 or 2
- visible by inspection!

$$\Rightarrow \frac{(\cancel{\text{rate}_{\textcircled{1}}})\cdot x}{\cancel{\text{rate}_{\textcircled{1}}}} = \frac{(\cancel{[\text{reactant}]_{\textcircled{1}}}\cdot y)^{n}}{\cancel{[\text{reactant}]_{\textcircled{1}}}^{n}}$$

$$\Rightarrow x = y^{n}$$

Solve for ORDER (n) of rxn with respect to <u>one reactant at a time</u>

EX: Using initial rates data, determine the rate law for

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

	Reactant Concentration (M)		**Reaction rate (M/s)**
Run	**$[NO]_o$**	**$[Cl_2]_o$**	**$RATE_o$**
1	0.13	0.20	1.0×10^{-2}
2	0.26	0.20	4.0×10^{-2}
3	0.13	0.10	5.0×10^{-3}

There are two ways to summarize rxn order: two forms of the rate law, related by calculus

1.) Differential Rate Law: "the rate law"

- Expresses how rxn rate changes with [ ], for each reactant
- How to derive it: method of initial rates

rate = $k[\text{reactant}]^n$ *means:* $\frac{-d[\text{reactant}]}{dt} = k[\text{reactant}]^n$

= instantaneous rate: change in [reactant] over <u>very small time period</u>

i.e., dt & d[reactant] = **"differentials "**

= **infinitesimally small changes**

Thus: can use calculus to figure out how [ ] varies with time

2.) Integrated Rate Law

- Expresses how one [reactant] varies with time
- HOW TO DERIVE IT:
  - a) by calculus: integrate the differential rate law
  - b) by exp't: plot [ ] *vs.* time over a long time period

15.4 Concentration-time relationships: Integrated rate laws

a) Via CALCULUS: integrate the differential rate law

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

1st separate the differential variables & group like terms…

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

Now: integrate !

Treat 1st & 2nd order cases separately…

FIRST ORDER:

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

Integral of $(1/x)\,dx = \ln x$

Integral of $1\,dx = x$

Then evaluate over time $0 \rightarrow t$

$$\ln[A]_t - \ln[A]_o = -k\,t$$

⇨ $\ln[A]_t = -k\,t + \ln[A]_o$

This defines a line! Convenient!

SECOND ORDER:

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

Integral of $(-1/x^2)\,dx = (1/x)$

Integral of $1\,dx = x$

Then evaluate over time $0 \rightarrow t$

$$1/[A]_t - 1/[A]_o = k\,t$$

⇨ $1/[A]_t = k\,t + 1/[A]_o$

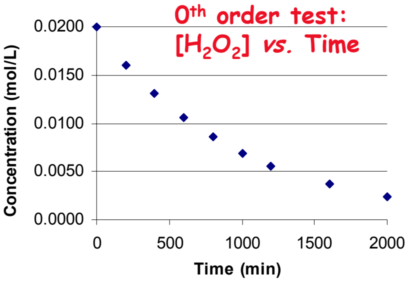
Also defines a line! Convenient!

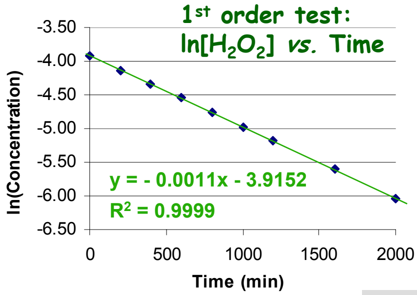
$2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$ **Decomposition of hydrogen peroxide**

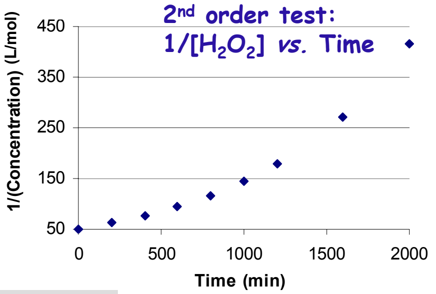
Time (min)	$[H_2O_2]$ mol/L
0	0.0200
200	0.0160
400	0.0131
600	0.0106
800	0.0086
1000	0.0069
1200	0.0056
1600	0.0037
2000	0.0024

By inspecting data:
$[H_2O_2]$ *vs. t* plot
will <u>not</u> be linear

What is this rxn's:
1.) rate law?
2.) rate constant?


0th order test:
$[H_2O_2]$ *vs.* Time


1st order test:
$\ln[H_2O_2]$ *vs.* Time


2nd order test:
$1/[H_2O_2]$ *vs.* Time

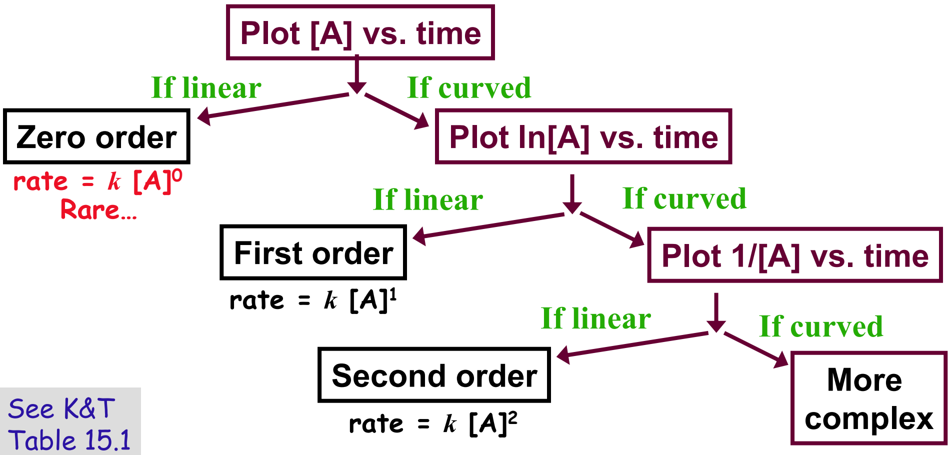
See K&T Fig.15.8

Method 2 for determining rate laws = Graphical method

RXN: $aA + bB \rightarrow cC + dD$ **GOAL: determine** rate = $k\,[A]^m[B]^n$

To find order of rxn *wrt* [A] :

- Use large $[B]_o$ ⇨ rate ≈ $k_{eff}\,[A]^m$ *…if Δ[B] ≈ 0, all rate Δs due to [A]*
- Monitor [A] ⇨ follow rxn rate for long time
- DATA ANALYSIS: trial-and-error test for common orders



rate = $k\,[A]^0$
Rare…

rate = $k\,[A]^1$

rate = $k\,[A]^2$

See K&T Table 15.1

FOR NOW: we have learned…

A. Two ways to determine the reaction's order

1.) method of initial rates ⇨ differential rate law

2.) graphical trial & error method ⇨ integrated rate law

And: we can calculate the rate constant *k* once rxn order is known.

REMEMBER WHY WE CARE ABOUT THIS:

The RATE LAW will help us:

1. figure out the rxn's step-by-step mechanism (later)
2. understand how our system's composition changes with time

NEXT:

B. How to use integrated rate laws: *practical…*

Example: RADIOACTIVE DECAY is a 1st order process

Radioactive atom: nucleus unstable, due to p^+ to n^0 ratio

- nucleus spontaneously splits apart
  - ⇨ releases daughter atom(s), plus high E:
    - *α-particles = He nuclei* OR
    - *β-particles = electrons* OR
    - *gamma-rays = γ photons* OR
    - *other more complex possibilities…*

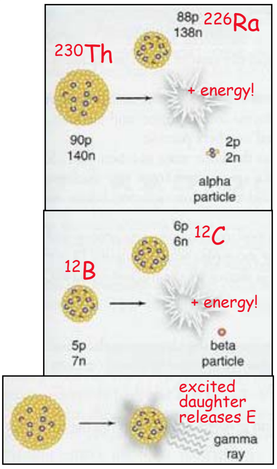
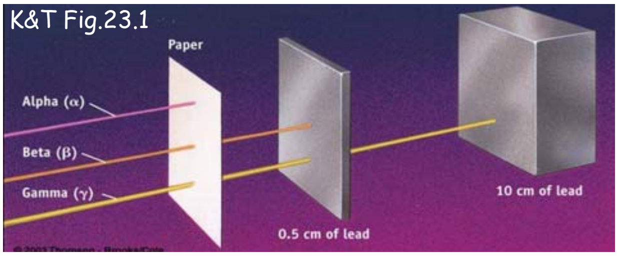


Fig.2.10, *Gen., Org. & Biol. Chem.*, K.W. Raymond, Wiley, 2006.


K&T Fig.23.1

DANGER LEVEL depends on:

- type & energy of emitted particles
- stability of daughter atoms…
- how long the dangerous decay process will continue
  - *rate constant = characteristic of isotope*
  - *slow decay (small k) ⇨ long half-life!*

If interested in radioactivity: see Ch.23

How long will this sample remain radioactive?

Sample exam question: from W04 MT#2, Q#4

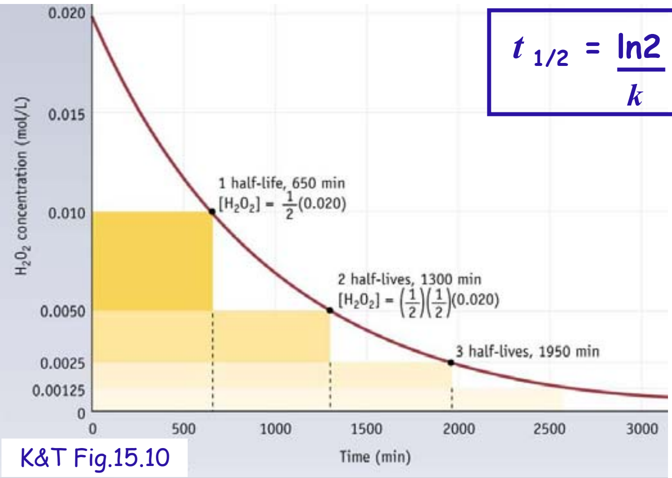
Radioactive ^{32}P is used in biochemical experiments as a way to label phosphate-containing molecules such as DNA. Imagine you are working with ^{32}P-labeled DNA and spill some on your favorite shoes (similar to my friend’s experience). The laboratory Health and Safety Officer says that you must keep the contaminated shoes “in containment” until the level of radioactivity has decayed from its initial value of 4125 disintegrations per minute to 125 disintegrations per minute.

How long must your shoes be kept in containment?

Half-life: a characteristic value for any 1st order process

1.) First-Order Processes: see exponential decay of [ ]

$$\boxed{t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}}$$



K&T Fig.15.10

⇨ **half-life for 1st order rxns does NOT depend on how much is initially present!**

VERY USEFUL …

NOTE: It takes ~5 half-lives for ANY exponential decay process (1st order) to reach ~completion $5\text{x}\ t_{1/2} \rightarrow [\ ] \approx 0$

Deriving mathematical expressions for Half-Life ($t_{\frac{1}{2}}$)

$t_{\frac{1}{2}}$ = time it takes for half the material to be consumed by the rxn	*i.e.*, for [A] to ↓ to $\frac{[A]_o}{2}$

Take definition of half-life: $[A]_t = [A]_o/2$ when $t = t_{\frac{1}{2}}$

sub into 1st order integ'd rate law: $\ln[A]_t = \ln[A]_o - k\,t$

then rearrange to solve for $t_{1/2}$:

(apply log rules…)

$$\ln\left(\frac{[A]_o}{2}\right) = \ln[A]_o - k\,t_{\frac{1}{2}}$$

$$\ln[A]_o - \ln 2 = \ln[A]_o - k\,t_{\frac{1}{2}}$$

$$\cancel{\ln[A]_o} - \cancel{\ln[A]_o} - \ln 2 = -\,k\,t_{\frac{1}{2}}$$

$$-\ln 2 = -\,k\,t_{\frac{1}{2}}$$

➡ $\frac{\ln 2}{k} = t_{\frac{1}{2}}$ **= a constant!**

For any 1st-order process: $t_{\frac{1}{2}}$ depends only on k (constant)

How long will this sample remain radioactive?

Sample exam question: from W04 MT#2, Q#4

Radioactive ^{32}P is used in biochemical experiments as a way to label phosphate-containing molecules such as DNA. Imagine you are working with ^{32}P-labeled DNA and spill some on your favorite shoes (similar to my friend's experience). The laboratory Health and Safety Officer says that you must keep the contaminated shoes "in containment" until the level of radioactivity has decayed from its initial value of 4125 disintegrations per minute to 125 disintegrations per minute.

How long must your shoes be kept in containment (in days)?

Look up: $t_{1/2}$ of ^{32}P = 14.3 days

APPROACH: 1.) Use half-life to find decay rate constant
2.) Use integrated rate law to find time

NOTE: can use # disintegrations (or # atoms, or mass) directly.
WHY? The units will cancel out during the calculation…

What about non-first-order processes?

2.) Second-Order Reactions:

→ half-life depends on initial concentration.

Thus: must know what you have in order to use this…

$t_{1/2}$ concept NOT AS USEFUL as it is for 1st order

sub into $1/[A]_t = 1/[A]_o + kt$:

$[A]_t = [A]_o/2$ for time $t = t_{1/2}$

and solve for $t_{1/2}$…

$$t_{1/2} = \frac{1}{k[A]_o}$$

0.) Zero-Order Reactions:

→ half-life depends on initial concentration…

sub into $[A]_t = [A]_o - kt$

and solve for $t_{1/2}$…

$$t_{1/2} = \frac{[A]_o}{2k}$$

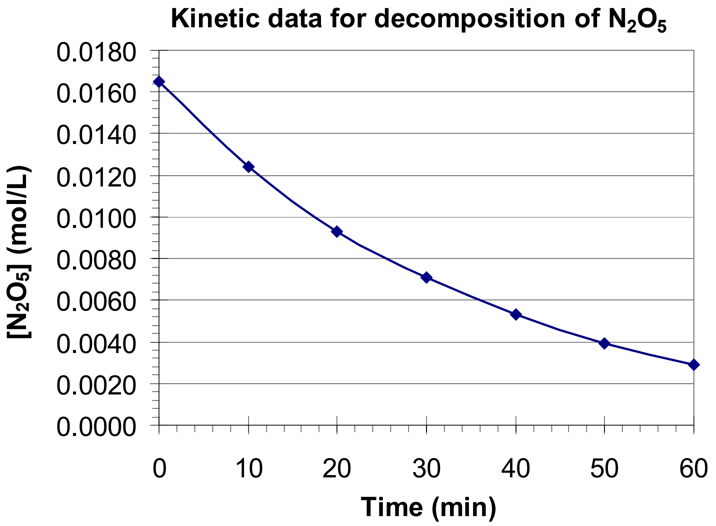
THUS: Half-lives tabulated only for 1st order processes

⇨ definitely not worth memorizing the other $t_{1/2}$ formulas!

⇨ can derive them easily if really need to use them

Use an analysis of half-lives to determine the order of…

$2N_2O_5(soln) \rightarrow 4NO_2(soln) + O_2(g)$



Data from Silberberg's *Chemistry*, 4th Ed., McGraw-Hill, 2006.

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.15 up to section 15.4

+ **WORK ON Problems from Ch.14-15**

Next class: Ch.15…

Extra Ex.: **Thyroid cancer therapy: radioactive iodine**

You undergo radiation therapy with ^{131}I after recovering from a thyroid tumour operation. If you start with a dose of 1.6×10^{15} atoms, how many ^{131}I atoms remain after 2.0 days?

^{131}I = a β-emitter; half-life = 8.065 days

APPROACH: 1.) Use half-life to find decay rate constant
2.) Use integrated rate law to find [^{131}I]

1.) $t_{1/2} = \ln 2 / k \Rightarrow k = \ln 2 / t_{1/2}$

$= 0.693 / 8.065\ \text{d}$

$= 0.08593\ \text{d}^{-1}$ disintegrations per day

2.) $\ln[^{131}\text{I}] = -kt + \ln[^{131}\text{I}]_o$

$= -(0.0859\ \text{d}^{-1})(2.0\text{d}) + \ln(1.6\times10^{15})$

$= 34.837$ *(SF for logs: digits <u>after</u> decimal are sig.; here 2 + 1 extra)*

$[^{131}\text{I}] = e^{34.837} = 1.3\times10^{15}$ atoms remaining after 2.0d

(SF…rounds to 2SF)

NOTE: can ignore volume & use # atoms only since rate constant doesn't include a conc. term…