Establishing the Rate Law

- A typical rate law for the general reaction,

  $aA + bB \rightarrow gG + hH$ might be :

  rate of reaction = $k[A]^m[B]^n$

  in which [A] and [B] represent reactant molarities and the exponents m and n are generally small, positive integers. (but may be zero, fractional and/or negative in more complex cases).

- The rate law is established by analysing experimental data.
- Three methods will be considered:

1. initial rates
2. graphical methods
3. successive half-lives.

1) Method of Initial Rates

- at the start of an experiment (t = 0), the initial concentration of each reagent is known - since you measured them.
- a tangent to the concentration-time curve at t = 0 will provide the ***initial rate of reaction***

The simplest example is when one concentration is doubled while the others are held constant.

- measure initial rates for two different concentrations of every reactant keeping concentrations of other reactants constant
- compare relative rates and initial concentrations to find m, n and k

- What's special about the initial rate?

Once the reaction starts it is very difficult to know what the concentrations are at any given time unless you already know the stoichiometry and the rate law. Further reactions of the products or reversibility can complicate matters at later stages of a reaction.

TABLE 15.3 Kinetic Data for the Reaction:
$2\ HgCl_2 + C_2O_4^{2-} \longrightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$

Experiment	$[HgCl_2]$, M	$[C_2O_4^{2-}]$, M	Initial rate, M min^{-1}
1	$[HgCl_2]_1 = 0.105$	$[C_2O_4^{2-}]_1 = 0.15$	1.8×10^{-5}
2	$[HgCl_2]_2 = 0.105$	$[C_2O_4^{2-}]_2 = 0.30$	7.1×10^{-5}
3	$[HgCl_2]_3 = 0.052$	$[C_2O_4^{2-}]_3 = 0.30$	3.5×10^{-5}

4 $[HgCl_2] = 0.21$ $[C_2O_4^{2-}] = 0.75$?

$$\text{rate of reaction} = k[HgCl_2]^m[C_2O_4^{2-}]^n$$

- consider experiments 2 & 3 where $C_2O_4^{2-}$ is unchanged : rate doubles as $[HgCl_2]$ doubles, Thus the rate varies as the first power of $[HgCl_2]$. m =1

- consider experiments 1 & 2 with Hg constant: rate quadruples as $[C_2O_4^{2-}]$ doubles. Thus rate varies as the square of oxalate. n =2. What is the expected rate for expt # 4 ?

Mathematically, one solves the following equation involving the ratio of expts 2 & 3. This eliminates k which is unknown at this point.

$$\frac{R_2}{R_3} = \frac{k(0.105)^m(0.3)^n}{k(0.052)^m(0.3)^n} = \left(\frac{0.105}{0.052}\right)^m = 2.0^m$$

$$\frac{R_2}{R_3} = \frac{7.1 \text{ X } 10^{-5}}{3.5 \text{ X } 10^{-5}} = 2.0$$

$2 = 2^m$, therefore **m = 1** $\{\log(2) = m \log(2)\}$

in general : rate ratio = (conc. ratio)^m is solved by taking logs

log(rate ratio) = m log (conc. ratio)

- and from experiments 1 & 2

  $[HgCl_2]$ remains constant while $[C_2O_4^{2-}]$ doubles

From the rate law

$$\frac{R_2}{R_1} = \frac{k(0.105)(0.30)^n}{k(0.105)(0.15)^n} = 2.0^n = \frac{7.1 \text{ X } 10^{-5}}{1.8 \text{ X } 10^{-5}} = 3.94$$

$2^n \approx 4$, n = 2 (by inspection)

or, take logs of both sides of the equation

n log(2.0) = log(3.94)

n (0.30) = 0.595, **n = 1.99 ≈ 2**

- More Generally : for rate = $[A]^m[B]^n[C]^o$

$\log[\text{rate}(1)/\text{rate}(2)] = m \log[A_1/A_2] + n \log[B_1/B_2] + o \log[C_1/C_2]$

you need at least 4 rates to solve for the 3 unknowns m,n,and o.

Determination of "k"

- The rate law thus is

$$\text{rate of reaction} = k[HgCl_2][C_2O_4^{2-}]^2$$

- to determine the rate constant, k, use data from any one of the experiments (or better take an average of several).

$$k = \text{initial rate}/\{[HgCl_2][C_2O_4^{2-}]^2\}$$

expt 1. $k = 1.8 \times 10^{-5}/\{(0.1050)(.15)^2\}$

$$\mathbf{k = 7.6 \times 10^{-3}\ M^{-2}\ min^{-1}}$$

$$\mathbf{\text{rate of reaction} = 7.6 \times 10^{-3}\ [HgCl_2][C_2O_4^{2-}]^2}$$

(rate of reaction in M min^{-1})

note : RXN rate = $-\frac{1}{2}\, d[Hg]/dt = -d[ox]/dt = k[Hg][ox]^2$ so the rate constant for loss of Hg would be 2k !

What gives?

The reaction is: $2\ HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$

but the rate law is : $\text{rate} = k[HgCl_2][C_2O_4^{2-}]^2$

Clearly the kinetic orders are totally unrelated to the stoichiometry!!!

Why? The mechanism of the reaction provides the explanation, a subject we will address in more detail later.

fast step $Hg^{2+} + 2\ C_2O_4^{2-} \rightarrow [Hg(C_2O_4)_2]^{2-}$

slow step $[Hg(C_2O_4)_2]^{2-} \rightarrow\rightarrow$ products

2 oxalates and 1 Hg^{2+} come together forming a dioxalatomercurate (II) ion before the rate determining step. This explains the rate law.

Factoids: Hg_2Cl_2 is calomel, an insoluble white solid used in calomine lotion for treating poison ivy and in the "standard calomel electrode".

Oxalate is the CB of oxalic acid, a toxic substance found in rhubarb.

2. Method of Integrated Rate Laws

For the general reaction **aA → products** we can write

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^n$$

"**n**" is the order of the reaction wrt the reactant "**A**"

- the integration of this expression for different values of "n" gives the "integrated rate laws"

Integrated rate laws give concentrations vs time.

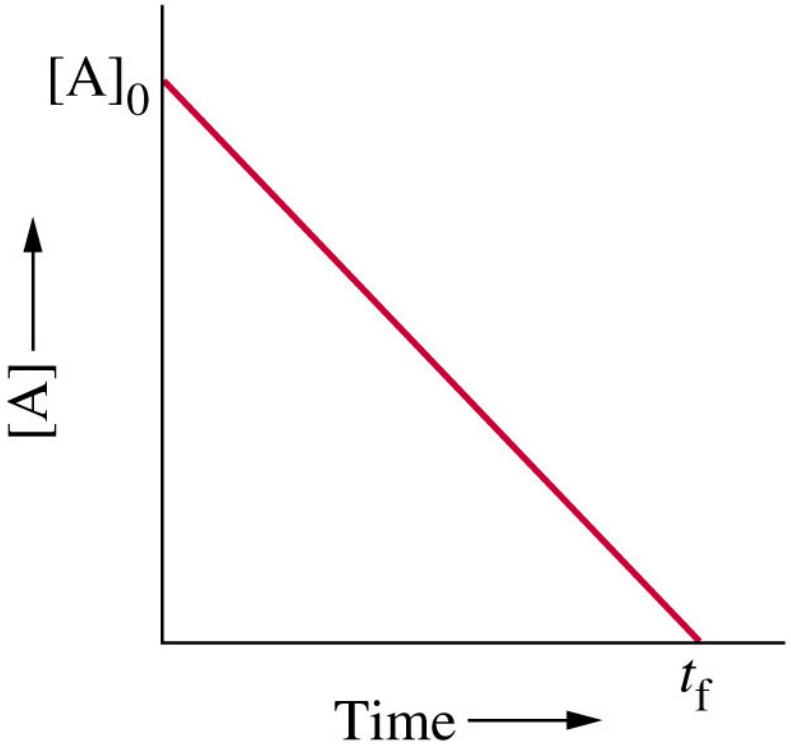
Rate laws give rate vs concentrations

Note: Your text, like many, do not include the stoichiometric "a" factor. It is a common source of trivial mistakes. Be careful as often the "rate of what" is not explictly stated.

Zero Order Reactions: n=0

rate of reaction = $k[A]^0 = k$ = constant

$$-\frac{1}{a}\frac{d[A]}{dt} = k \quad \rightarrow \quad d[A] = -akdt \quad \rightarrow \quad [A] = [A]_0 - akt$$



zero order is a trivial case rarely seen in chemistry. If you give me $1 every minute your money obeys zero order kinetics. k = $1 per minute and $P = P_o - kt$.

concentration vs time graph is linear with slope = – ak

$t_{1/2} = [A_o]/2ak$ it gets shorter as $[A_o]$ decreases. see $ / minute example.

First Order Reaction

$H_2O_2 \rightarrow H_2O + \frac{1}{2} O_2$

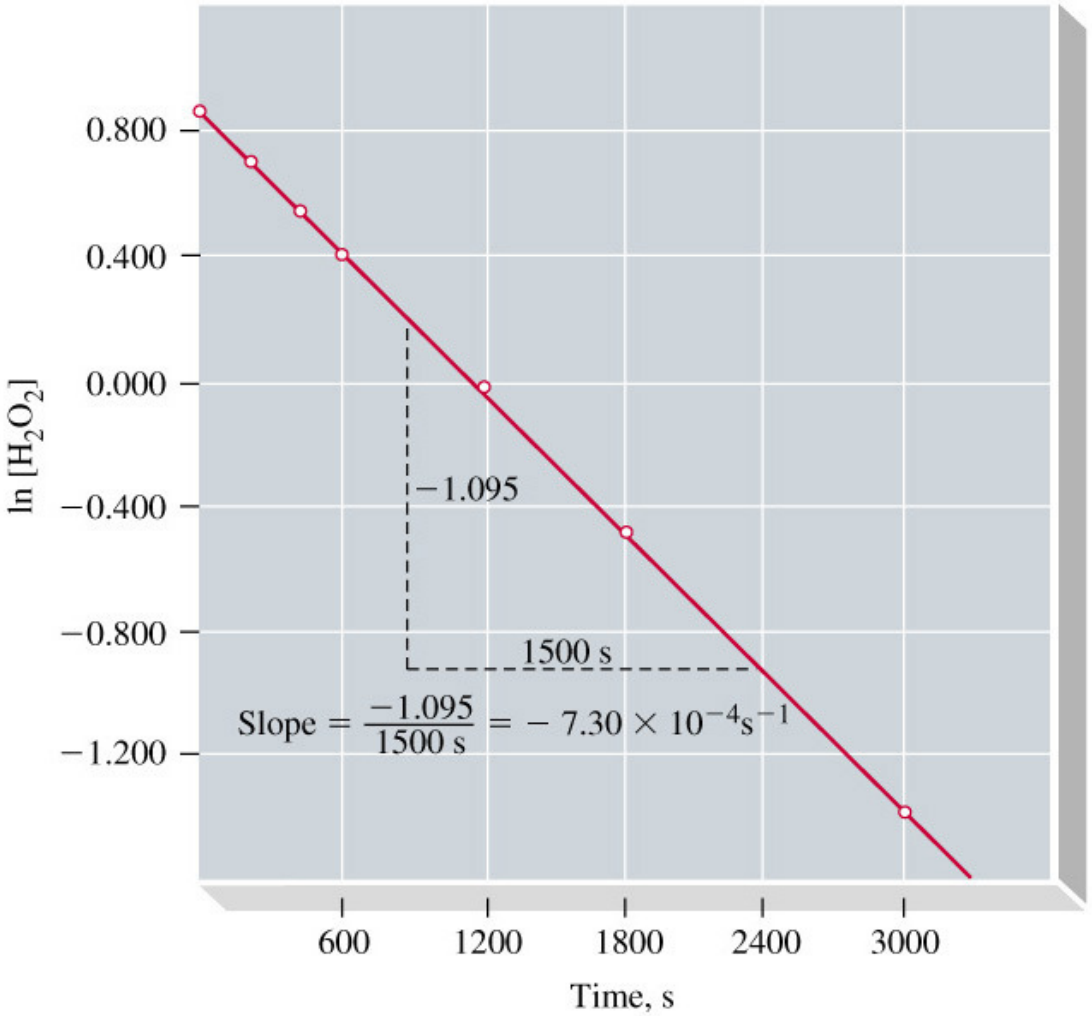
$$[A] = [A]_0 e^{-akt} \quad \textbf{(exponential decay)}$$

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

$$\ln \frac{[A]_0}{[A]} = akt$$

For a first order reaction a plot of ln[A] vs t is linear with slope = ak

Does it matter that $\ln[H_2O_2]$ is plotted. Not $\ln [H_2O_2]_o / H_2O_2]$? How would it differ?



Examples of First Order Processes		half life	k in seconds^{-1}
radioactive decay of	^{238}U	10^9 yrs	4.87×10^{-18}
	^{14}C	10^3 yrs	3.8×10^{-12}
	^{90}Sr	28 yrs	
	^{3}H	12.26 yrs	
	^{126}I	13 days	
sucrose + H_2O → glucose + fructose		8.4 hr	2.3×10^{-5}
N_2O_5 → 2 N_2O_4 + O_2 (CCl_4/45 C)		18.6 min	6.2×10^{-4}
$CH_3COOH \rightarrow CH_3COO^- + H^+_{(aq)}$		8.9×10^{-7}	7.8×10^5
$MbO_2 \rightarrow Mb + O_2$		0.07 s	10
Mb CO → Mb + CO		35 s	0.02

? In nuclear fallout, is radioactive iodine, strontium or uranium a bigger problem?

- Compound interest. $P = P_o(1+ RdT)^{t/dt}$ gives the principal after time t compounded every dt at interest rate R. The limit as $dt \rightarrow 0$ becomes $P = P_o\, e^{+Rt}$

- The growth phase for bacteria is exponential but then levels off as nutrients are depleted. {limits to growth}

$$N = N_o e^{+Gt}$$

- First order kinetics derives from cases where the probability of growth or decay is proportional to the time interval dT . $dN/N = k\, dT$.

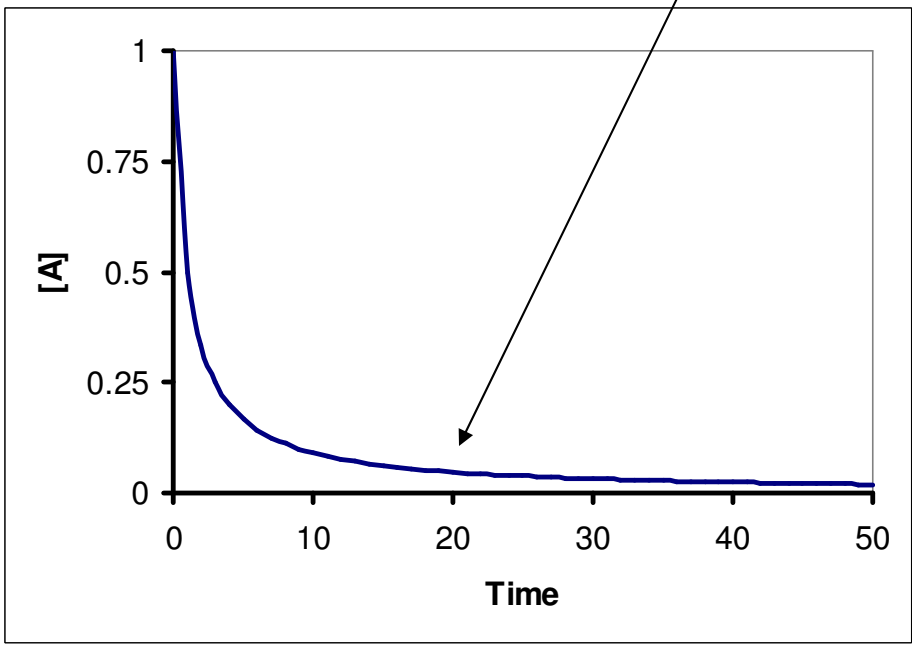
? Consider the consequences of 10 deaths/year vs a 10% death rate in a sterile population of 100 after say 10 years. Ans. zero vs $100/e = 37$ survivors.

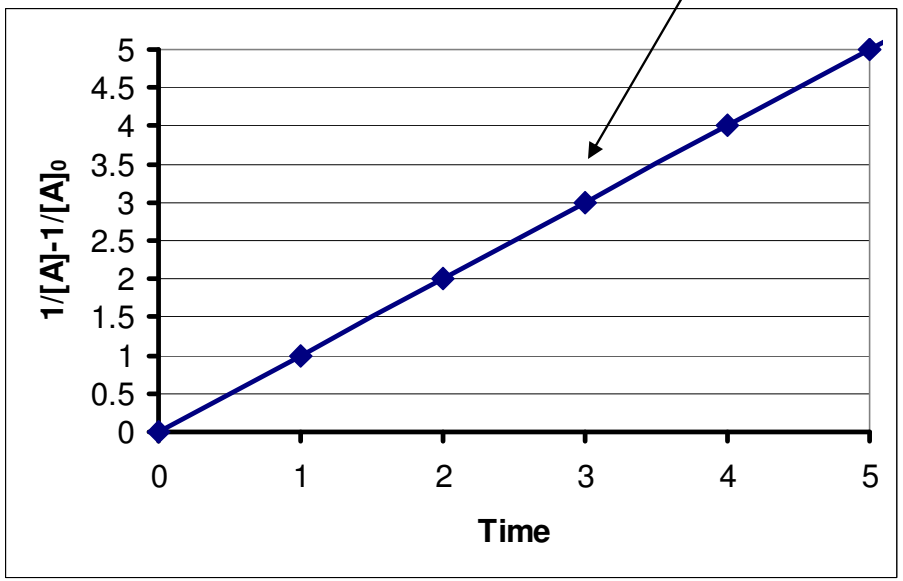
Second Order Reactions: n = 2

$$\textbf{rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = k[A]^2$$

Integrated rate law : $[A] = \dfrac{[A]_0}{[A]_0 akt + 1}$

Integrated rate law in linearized form : $\dfrac{1}{[A]} - \dfrac{1}{[A]_0} = akt$





3. Method of Successive half lives.

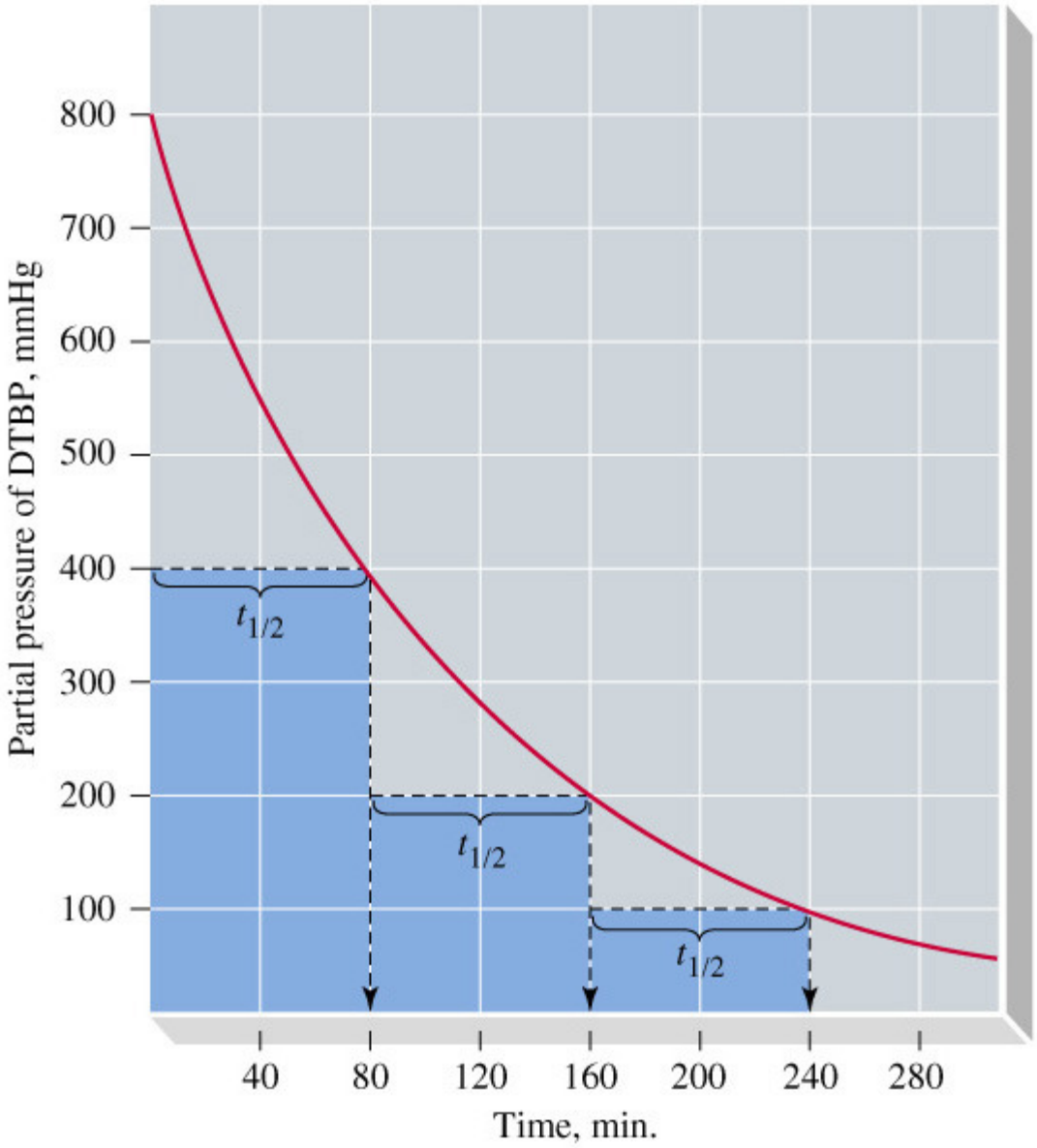


Fig. 15-5. DTBP decay in gas phase.

half life = 80 min , independent of P.

1st ORDER !!!

rate = k [P_{DTBP}]

k = .693/80 = 0.0086 min^{-1}

? how long would it take half of DTBP to decay if P_o were 1 torr ?

Summary of Rate Laws

	zero order	1st order	2nd order
Linear Plot	[A] vs t	ln[A] vs t	1/[A] vs t
slope	k Ms^{-1}	k s^{-1}	k $M^{-1}s^{-1}$
Half life	$[A_o]/2k$	.693/k	$1/(k[A_o])$
1st	$t_{1/2}$	$t_{1/2}$	$t_{1/2}$
2nd	$1/2\ t_{1st}$	$t_{1/2}$	$2\ t_{1st}$
3rd	$¼\ t_{1st}$	$t_{1/2}$	$4\ t_{1st}$

* For second order if we hit $[A_o]/2$ at say t= 10 minutes, then $[A_o]/4$ at t = 30 minutes and $[A_o]/8$ at t= 70 minutes. For 87.5% completion ($A_o/8$ left) it would take 1.75 $t_{1/2}$ for zero order, 3 half lives for first order and 7 for 2nd order.

Summary of Methods

Getting a rate

- Slope of [A] vs t
- Δ[A]/ Δt over a small range
- Plug conc and k into rate law where known

Deducing a rate law

- Initial rate data at various concentrations
- Linear plots of ln A or 1/A vs time
- Trial and error to find one which gives constant k.
- Pseudo-first order data

Simplifying more complex rate laws.

1. **Pseudo-first Order Conditions** - It is convenient to have only one species changing with time. This is accomplished by using a large excess of all other reactants.

$$A + B \rightarrow AB \quad \text{rate} = k_2 [A][B]$$

initial $[A_o] = 0.1M$ and $[B_o] = .001M$

final $[A_f] = 0.099\ M$ and $[B_f] = 0\ M$ [A] hardly changes at all !

$-d[B]/dt = k_2 [A][B]$ and thus $\int d[B]/[B] = \int k_2 [A]\, dt$

since A is independent of t, we can integrate to give

$\ln (B_o/B) = k_2[Ao]\, t = kobs\ t$ a pseudo-first order rate law.

$kobs = k_2[A_o]$ is the pseudo-first order constant and $t_{1/2} = .693/k_2[A_o]$

Typically one carries out a series of experiments varying A_o while keeping [A] >> [B]. A plot of kobs vs [A] has a slope k_2 and is linear if first order in [A]. If second order you would plot kobs vs $[A]^2$ etc.

A big advantage of first order in B is that you don't need to know B_o to get k. You could start measurements whenever you like after mixing and still obtain k. Not true for 2nd order.

Pseudo-first order conditions for the reaction :

$$2\ HgCl_2 + C_2O_4^{2-} \rightarrow 2\ Cl^- + 2\ CO_2 + Hg_2Cl_2$$

rate = $k[HgCl_2][C_2O_4^{2-}]^2$ $\quad k = 7.6 \times 10^{-3}\ M^{-2}min^{-1}$

A) conditions : $[HgCl_2] = 0.001$ M $\quad [C_2O_4^{2-}] = 0.1$ M

$d[Hg]/dt = 2k[Hg][ox]^2 = .0152\ [Hg][0.1]^2$

$d[Hg]/[Hg] = 0.000152\ dt$ $\quad$ reduces to simple 1st order kinetics

$[Hg] = [Hg]_o\ e^{-0.000152\ t}$ $\quad$ and $t_{1/2} = .693/0.000152 = 4560$ min

B) conditions: $[HgCl_2] = 0.001$ M $\quad [C_2O_4^{2-}] = 1.0$ M

kobs = $0.0152\ [1]^2\ min^{-1}$ and $t_{1/2} = 45.6$ min

* in each case a plot of ln [Hg] vs time would be linear with slope kobs

where kobs = $0.0152\ [ox]^2\ min^{-1}$ $\quad$ units ($M^{-2}\ min^{-1} \times M^2$) = min^{-1}

Pseudo-first order conditions can be applied to simplify even the most complex rate laws.

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

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

if $[Br^-]_0$=0.3 M, & $[BrO_3^-]_0$= 0.0001 M, and the reaction is run in a pH =2 buffer, then the reaction rate reduces to a first order decay of bromate ion:

$$\text{Rate} = k\,[BrO_3^-][0.3][.01]^2 = (3 \times 10^{-5})\,k\,[BrO_3^-]$$

$$\text{Rate} = \text{kobs}\,[BrO_3^-] \quad \text{where kobs} = (3 \times 10^{-5})\,k$$

* note units of k are $M^{-3}s^{-1}$ while those of kobs are s^{-1}

plot $\ln[BrO_3^-]$ vs time to get kobs.

For several expts all at $[Br^-]$ = 0.3 M and $[BrO_3^-]$ = 0.0001 M but in different pH buffers, a plot of kobs vs $[H^+]^2$ would be linear with slope = 0.3 k.

OR you could do 4 expts at pH =2 and $[BrO_3^-]$ = 0.0001 M with $[Br^-]$ of 0.1, 0.2 , 0.3 , and 0.4 M. A plot of kobs vs $[Br^-]$ would be __ ??

14-89. The rate of the reaction $2CO_{(g)} \rightarrow C_s + CO_{2\,(g)}$ was studied by injecting CO gas into a vessel and monitoring the total pressure at constant volume.

Data below in black. Solution in blue.

- note that 2 gas molecules become one. Thus the pressure will drop in half on completion. let $x = P_{co2}$ produced

$P_{total} = P_{co} + P_{co2} = (250 - 2x) + x = 250 - x$.

we need to extract the reactant pressure , $P_{co} = P_{tot} - 2x$

Then plot ln P_{co} if 1st order or $1/P_{co}$ if 2nd order.

time (s)	P_{TOT} (torr)	P_{CO}	P_{CO2}
0	250	250	0
398	238	226	12
1002	224	198	26
1801	210	170	40
infinite	125	0	125

Plot $1/P_{co}$ vs t is linear with slope $= -ak = -1.05 \times 10^{-6}$ $torr^{-1}s^{-1}$ so $k = 5 \times 10^{-7}$ $torr^{-1}s^{-1}$

check $-dP_{co}/dt \sim 24/398 = 1.05 \times 10^{-6}$ $[250]^2$. so $0.065 \sim 0.06$

$dP_{co2}/dt \sim 12/398 = 0.03$ ☺

14-90 The kinetics of phosphine decomposition at 950 K was followed in a closed flask by monitoring the total pressure. Find the rate constant.

$$4\ PH_3\ (g) \rightarrow P_4\ (g) + 6\ H_2\ (g)$$

$$P_o - 4x \qquad x \qquad 6x$$

$$P_{tot} = P_o - 4x + 7x = P_o + 3x \quad \text{so} \quad x = (P_{tot} - P_o)/3$$

Table of Data (torr) and calcd (blue)

t (s)	P tot	x	PH_3	P_4	H_2
0	100	0	100	0	0
40	150	50/3	33.3	16.7	100
80	167	67/3	10.7	22.3	134
120	172	72/3	4	24	144
inf	175	75/3	0	25	150

Plot ln $[PH_3]$ vs t is linear.

slope = 0.0275 s^{-1} =4k

$t_{1/2}$ = 25.2 s =.693/4k

rate = k$[PH_3]$
= ¼ d$[PH_3]$ /dt

RQ 13. In the first order reaction A→ P, initial [A] = 0.816 M and after 16.0 min [A] = 0.632 M .

a) What is the rate constant?

Plug into integrated rate expression $A = A_o e^{-kt}$

$\ln A/Ao = -kt$

$\ln (.632/.816) = -.255 = - k (16 \text{ min})$

$k = 1.59 \times 10^{-2} \text{ min}^{-1}$

b) What is the half life? $t_{1/2} = 0.693/0.0159 = 43.6 \text{ min}$

c) When will [A] = 0.235 ?

$\ln(.235/.816) = -1.24 = - 0.0159\ t$ $t = 78 \text{ min}$.

Radiocarbon dating. Ex 25-4

^{14}C forms in the upper atmosphere via cosmic radiation. Living things take up this isotope as CO_2. Once dead the level of ^{14}C drops through radioactive decay $t_{1/2} = 5730$ years.

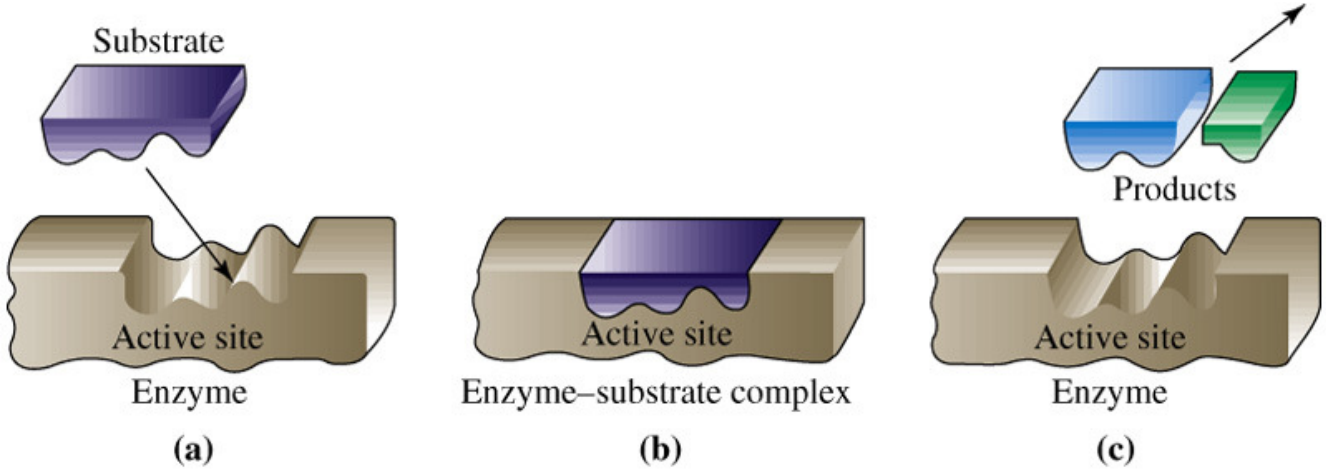
If living things have 15 disintegrations/minute/gram of carbon , how old is a mummy with an activity of 8.5 dis/min/g ?

$k = 0.693/5730 = 1.21 \times 10^{-4}\ yr^{-1}$

$\ln N/No = -kt$

$\ln 8.5/15 = -0.567 = - k t \qquad t = .567/1.21 \times 10^{-4}$

$t = 4686$ years.

Enzymes as Catalysts

- the most impressive examples of homogeneous catalysis occur in nature where complex reactions are made possible by enzymes
- catalytic action of enzymes is extremely **specific**
- enzyme activity often described by a **lock-and key model**; only a reacting substance, the **substrate** (the key), that fits into an active site on the enzyme (the lock), will undergo a reaction