12.4 The Integrated Rate Law

Reactant concentration vs. time

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1. First Order Rate Laws (For a general reaction with a single reactant)

A plot of natural log of A vs. time gives a straight line.

Rate = $\Delta[A]/\Delta t = k[A]$, if concentration doubles, so does rate

First Order Integrated Rate Law

Fits the expression: (linear form y = mx+b) as …

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

$\ln[A]_0$ is the initial concentration (b = y intercept)
$\ln[A]$ is concentration of A at time t (y)
k is the slope, m
t is time (x)

or $\ln\left(\frac{[A]_0}{[A]}\right) = kt$ **or** $kt = \ln[A]_0 - \ln[A]$

Calculator Usage and Integrated Rate Law for Graphing with TI-83	
	1.) stat4, clear list L1-L6
	2.) Stat edit:
	a.) L1 time
	b.) L2 concentration
	c.) L3 Ln L2 (Ln [ ])
	d.) L4 1/L2 (1/[ ])
	3.) Graph: 2nd StatPlot
	4.) Set Graph 1 ON <Enter>
	5.) Type: line
	6.) X List: Li (time)
	7.) Y List
	a.) L2: if straight line = 0 order, [A] vs. time
	b.) L3: if straight line = 1 order, ln[A] vs. time
	c.) L4: if straight line = 2 order, 1/[A] vs. time
	8.) Graph
	9.) Zoom Stat (9)
	10.) Stat Calc 4 (Linear Regression) plots of L1 vs. L2, L3 or L4 as appropriate
	11.) Analysis as y=mx+b

Ex. 12.2 with Graphing Calculators:

1st order

k = -slope = 6.93×10^{-3}/s

Ex. 12.3

Concentration of reactant, N_2O_5, after 150s = 0.0354 mol/L

Half Life of a First Order Reaction

$T_{1/2}$ Time required to reach half the original concentration.
For 1st order the half life time remains the same
For a 1st order reaction, $t_{1/2}$ depends only on k.

Derived as: $\ln\left(\frac{[A]_0}{[A]_{1/2}}\right) = \ln 2 = kt_{1/2}$ or since ln 2 = 0.693, then

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

Ex. 12.4:

If half life is 20.0 minutes, then k = 0.0347/min
75% complete is 2 half lives. Each $t_{1/2}$ is equal, so 40.0 minutes.

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2. Second Order Rate Laws (For a general reaction with a single reactant)

In General: Rate = $\Delta[A]/\Delta t = k[A]^2$

Integrated Second Order Rate Law: fits the form y=mx+b

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

A plot of 1/[A] vs. time gives a straight line
[A] can be calculated at any time provided k and original $[A_0]$ is known.

Half Life of Second Order:

Derived as: $t_{1/2} = \frac{1}{k[A]_0}$

Half life depends on rate constant and $[A]_0$,initial concentration of reactant.
For each successive half life, [A] is halved (in denominator), so $t_{1/2}$ doubles.
Each $t_{1/2}$ is 2x the preceding ½ life.

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3. Zero Order Rate Laws

Rate = $k[A]^0 = k(1) = k$
Zero order often encountered when a metal surface or enzyme is required for a reaction to occur.
Rate is constant and does not change with concentration.

Integrated form of Zero Order Rate Law:

$$[A] = -kt + [A]_0$$

Half-Life of zero order reaction:

$$t_{1/2} = \frac{[A]_0}{2k}$$

Half life is determined by concentration of A and k
Each successive half life is half as long.

Integrated Rate Laws for Reactions with more than one Reactant

Maintain levels of other reactants very high relative to the one being studied.

Ex. Rate = k[A][B][C], 3rd order overall

Ex. $[A]_0 = 1.0 \times 10^{-3}$ *M*, $[B]_0 = 1.0$ *M*, $[C]_0 = 1.0$ *M*, so that $[B]_t$ over time = $[B]_0$ and $[C]_t = [C]_0$

Then rate law can be written as: Rate = k'[A], since [B] and [C] are constant.

Psuedo 1st order rate law:

$$k' = k[B]_0\,[C]_0$$

Then k can be calculated since the slope = $-k'$ (if 1st order) and [B] [C] are known.

$$k = \frac{k'}{[B][C]}$$

12.5 Rate Laws: A Summary

The value of k is determined by the appropriate plot.

Summary of the Kinetics for Reactions of the Type aA → 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 straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Table 12.6

Practice Problems:

Set 2: P. 567 #16, 31, 32, 34, 35, 36, 38, 39, 40, 41, 43, 44, 46, 47, 77, 86

Lab: Determination of a Rate Law, The Iodine Clock Reaction

Quiz: 12:1-5, Rate Laws