THE RATES OF CHEMICAL REACTIONS

Chapter 21 Outline

HW: Questions are below. Solutions are in separate file on the course web site.

Sect.	**Title and Comments**	**Required?**
1.	Experimental Techniques	YES
2.	The Rates of Reactions	YES
3.	Integrated Rate Laws Note: You are NOT responsible for equations that are first order in both [A] and [B] {Eqns. 21.18 and 21.19 on pg.794)	YES
4.	Reactions Approaching Equilibrium NO - We'll just comment on "Reversible" First-Order Reactions. YES - Instead, we'll discuss "Competitive" First-Order Reactions.	NO and YES
5.	The Temperature Dependence of Reaction Rates In addition to giving the Arrhenius Theory, we will also present the Transition-State Theory of rate constants, given in Chapter 22 of the text (Sects. 22.4-22.5).	YES
6.	Elementary Reactions	YES
7.	Consecutive Elementary Reactions You do NOT have to memorize the equations for the concentrations of the species.	YES
8.	Unimolecular Reactions	YES
9.	Polymerization Kinetics	NO
10.	Photochemistry	YES

Note: We will also include a section on Enzyme Kinetics in the PowerPoint and supplementary homework.

Chapter 21 Homework Questions

21.1 The rate of formation of C in the reaction 2 A + B $\rightarrow$ 2 C + 3 D is 2.7 Ms^{-1}. State the reaction rate, and the rates of formation or consumption of A, B, and D.

21.2 The rate law for the reaction, A + B $\rightarrow$ Products, is of the form, $r = k[A]^x[B]^y$. From the initial rate data for this reaction given below, determine the reaction orders, "x" and "y", and the rate constant, k (give units).

$[A_o]$	**$[B_o]$**	**r_o**
0.10 M	2.0 M	8.50 Ms^{-1}
0.30	2.0	2.83
0.30	3.0	7.80

21.3 At 518 ^oC, the half-life for the decomposition of gaseous acetaldehyde (aka ethanal, CH_3CHO) is 410 s when the initial pressure is 363 torr. The half-life is 880 s when the initial pressure is 169 torr. Determine the order of the reaction.

21.4 The reaction, A $\rightarrow$ P, is of order "x"; i.e. Rate = $k[A]^x$. When $[A_o]$= 0.4 M, the half-life of the reaction is 200 s. When $[A]_o$= 0.2 M, the half-life of the reaction is 50 s. What is the order of this reaction (i.e. what is "x")?

21.5 The reaction, A $\rightarrow$ P, is of order "x"; i.e. Rate = $k[A]^x$. When $[A_o]$= 0.1 M, the half-life of the reaction is 200 s. When $[A]_o$= 0.25 M, the half-life of the reaction is 126 s. What is the order of this reaction (i.e. what is "x")?

21.6 Consider a second order reaction, A $\rightarrow$ Products. When $[A]_o$ = 1.30 M, the half life of the reaction is 42 seconds.

(a) What is the rate constant, k, for this reaction?

(b) When $[A]_o$ = 1.30 M, what will the concentration be 60 seconds after the start of the the reaction.

(c) When $[A]_o$ = 1.30 M, how long will it take for the concentration of A to decrease to 0.80 M?

21.7 Consider a third order reaction, A $\rightarrow$ Products. When the initial concentration is $[A]_0$ = 0.80 M, it takes 6.40 seconds for the concentration to decrease to [A] = 0.50 M.

(a) Calculate the rate constant, k.

(b) When $[A]_0$ = 0.80 M, what is the concentration after 20 seconds.

(c) When $[A]_0$ = 0.80 M, how long does it take for the concentration to decrease to 0.30 M

21.8 Consider a reaction, A → Products, which is of order 3/2; i.e. $Rate = -\frac{d[A]}{dt} = k[A]^{3/2}$. The rate constant for this reaction is k = 0.03 $M^{-1/2}s^{-1}$.

(a) Determine the half-life for this reaction when $[A]_0$ = 0.50 M

(b) If the initial concentration of A is 0.50 M, what will the concentration of A be after 25 s?

(c) If the initial concentration of A is 0.50 M, how long will it take for the concentration to decrease to 0.20 M?

21.9 Consider the competitive first-order reactions,

$$A \xrightarrow{k_1} B$$

$$A \xrightarrow{k_2} C$$

(a) If one begins an experiment with $[A]_o$ = 1.20 M, it is found that [B] = 0.90 M at the conclusion of the experiment.
What is the ratio of the two rate constants, k_1/k_2?

(b) It is found that the rate constant for the first reaction is k_1 = 0.60 s^{-1}. what is the concentration, [C], 2.0 seconds after the start of the reaction?

21.10 The rate constant for a first order reaction is $1.5x10^{-3}$ s^{-1} at 40 °C and $8.6x10^{-2}$ s^{-1} at 80 °C.

(a) Calculate the Arrhenius parameters, A and E_a, for this reaction.

(b) Calculate the rate constant of this reaction at 130 °C.

(c) Calculate the temperature at which the half-life of this reaction is 200 s.

21.11 The Transition State Theory Equation for the rate constant is:

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$$

R, N_A and h are universal constants:

$$\frac{R}{N_A h} = \frac{8.31}{(6.02x10^{23})(6.63x10^{-34})} = 2.1x10^{10}$$

For a given kinetics experiment, a plot of ln(k/T) vs. 1/T was a straight line with
Slope = -5450 K and Intercept = +12.80

Calculate the reaction's Activation Enthalpy, $\Delta H^{\ddagger}$ (in kJ/mol), and the Activation Entropy, $\Delta S^{\ddagger}$ (in J/mol-K).

21.12 One theory of rate constants for bimolecular gas phase reactions is “Collision Theory”. The collision theory form for the rate constant is: $k = C\sqrt{T}e^{-\frac{E_o}{RT}}$, where C is a constant, and E_o is the threshold energy for reaction.

Develop and expression relating the threshold energy, E_o, to the Arrhenius Activation Energy.

21.13 The reaction mechanism for the reaction, $A_2 + 2\ B \rightarrow 2\ P$ is:

$A_2 \rightleftharpoons 2\ A$	Rapid Pre-Equilibrium
$A + B \rightarrow P$	Slow RDS (this reaction occurs twice)

Deduce the rate law for d[P]/dt for this mechanism.

21.14 The reaction, $2\ A + B \rightarrow P$ (P is the product) proceeds by the following mechanism.

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB$$

$$AB + A \xrightarrow{k_2} P$$

“AB” is an intermediate present in steady-state concentration. Use the steady-state approximation on [AB] to develop an expression for the rate of formation of P as a function of [A], [B], k_1, k_{-1} and k_2.

Note: For Photochemistry questions: On an exam, you would be given the following relationship between photon wavelength (λ) and energy (E_{ph}):

$$E_{ph} = \frac{hc}{\lambda} \qquad h = 6.63\text{x}10^{-34}\ \text{J s}\ ,\ c = 3.00\text{x}10^{8}\ \text{m/s}$$

21.15 In a photochemical reaction, $A \rightarrow 2\ B + C$, the quantum yield with 500 nm light is 210 mol A reacted/mol photon absorbed. After exposure of 300 mmol of A to light, 2.28 mmol of B is formed.

How many photons were absorbed?

21.16 In an experiment to determine the reaction quantum yield of a photochemical reaction, A → Products, the reactant was exposed to 490 nm radiation from a 100 W source for 45 ,inin. The intensity of the transmitted light was 40% of the intensity of the incident light. As a result of the radiation, 0.344 mol of the reactant decomposed.

Determine the quantum yield, Φ_R, for this reaction.

21.17 Consider the quenching of an organic fluorophore with a fluorescent lifetime, τ_0 = 6.0 ns. A quenching agent with a quenching rate constant, $k_Q = 3.0x10^8\ M^{-1}s^{-`1}$, is added to the solution.

Predict the quencher concentration, [Q], required to obtain 60% quenching of the fluorescence.

21.18 In a pulsed laser fluorescence experiment on Napthalene (dissolved in hexane), the fluorescence intensity 35 ns after the experiment begins is 65% of the intensity at the beginning of the experiment.
In a separate experiment, it was determined that the fluorescence rate constant is:
$k_F = 4.8x10^6\ s^{-1}$.
Calculate (a) the singlet state lifetime, τ_0 (in ns), and (b) the fluorescence quantum yield of napthalene.

21.19 The hydrolysis of the substrate, N-glutaryl-L-phenylalanine-p-nitroanilide [GPNA], to p-nitroaniline and N-glutaryl-L-phenylanine is catalyzed by α-chymotrypsin.
When $[E]_o = 4.0x10^{-6}$ M, it is found that v_o=$3.7x10^{-8}$ M/s when [S]=$2.5x10^{-4}$ M and v_o=$9.8x10^{-8}$ M/s when [S]=$1.0x10^{-3}$ M.

Determine the slope and intercept of the Lineweaver-Burk plot and, from these, K_M, V_m, and k_2 for this reaction.

21.20 Consider an enzyme catalyzed reaction with $[E]_o$= 2 mM, K_M= 20 mM, and V_M= 80 mM/s

(a) The slope of the Lineweaver-Burk plot is
(A) 0.013 s/mM (B) 4 s-1 (C) $6.3x10^{-4}$ mM/s (D) 0.25 s

(b) The intercept of the Lineweaver-Burk plot is
(A) 0.013 s/mM (B) 4 s-1 (C) $6.3x10^{-4}$ mM/s (D) 0.25 s

(c) The "turnover number", k_2, is
(A) 10 (B) 0.10 s-1 (C) 40 s-1 (D) 0.025 s

Chapter 21

The Rates of Chemical Reactions

Spontaneous Reactions Don't Always Occur

Consider: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

At 298 K, $\Delta G^o = -237.1$ kJ/mol $\longrightarrow$ $K = 4\text{x}10^{41}$

Therefore, this reaction proceeds ~100% to completion.

But, how long does it take? Forever!!!

Without a catalyst, the formation of water from hydrogen and oxygen proceeds infinitesimally slowly.

Thus, we see that thermodynamics tells us only whether a reaction ***can*** occur. It cannot tell us whether it ***will*** occur, or if it will, how ***fast*** is the reaction.

That is the subject of Chemical Kinetics.

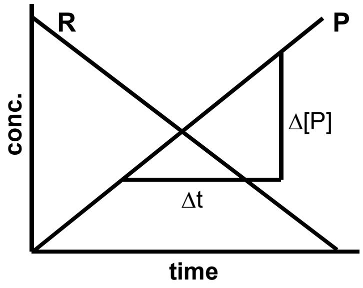
The Reaction Rate

$R \rightarrow P$

$$\text{Rate} = \frac{[P_2]-[P_1]}{t_2-t_1} = \frac{\Delta[P]}{\Delta t}$$

OR

$$\text{Rate} = -\frac{[R_2]-[R_1]}{t_2-t_1} = -\frac{\Delta[R]}{\Delta t}$$



Example: Rate = (0.1 M - 0.0 M) / (10 s - 0 s) = 0.01 $M \cdot s^{-1}$

or: Rate = - (0.0 M – 0.1 M) / (10 s - 0 s) = 0.01 $M \cdot s^{-1}$

Note: the text uses "v" for velocity of a reaction. In accordance with common notation, we will use "Rate" or "R" to denote the reaction rate.

Rates actually change with time

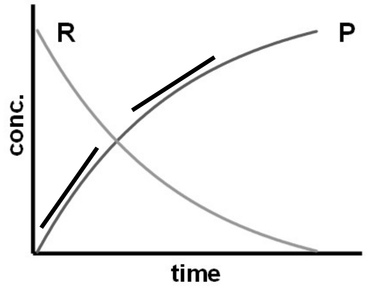
$R \rightarrow P$

$$\text{Rate} = \frac{d[P]}{dt}$$

The derivative, d[P]/dT, is the tangent of the curve.

OR

$$\text{Rate} = -\frac{d[R]}{dt}$$



One must consider stoichiometry when writing rates using different species.

Consider: $A \rightarrow B + 2C$

In $\Delta t = 1$ sec: $\Delta[A] = -0.1$ M $\quad \text{Rate} = -\frac{\Delta[A]}{\Delta t} = -(-0.1\ \text{M}/1\ \text{s}) = 0.1\ \text{M•s}^{-1}$

$\Delta[B] = +0.1$ M $\quad \text{Rate} = +\frac{\Delta[B]}{\Delta t} = +(+0.1\ \text{M}/1\ \text{s}) = 0.1\ \text{M•s}^{-1}$

$\Delta[C] = +0.2$ M $\quad \cancel{\text{Rate} = +\frac{\Delta[C]}{\Delta t}} = \cancel{+(+0.2\ \text{M}/1\ \text{s}) = 0.2\ \text{M•s}^{-1}}$

$$\text{Rate} = +\frac{1}{2}\frac{\Delta[C]}{\Delta t} = 0.1\ \text{M•s}^{-1}$$

General Rule: Divide by Stoichiometric Coefficients when comparing rates of change of different species.

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Thus, for the reaction: $aA + bB \rightarrow cC + dD$

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

Monitoring the Concentration

In order to study the rate of a reaction, one must be able to measure the concentration of one of the reactants or products as a function of time.

There are a number of ways to accomplish this depending upon the nature of the reaction. These methods include:

- Chemical titration: e.g. if Cl^- is formed, one may determine the concentration by titration with $AgNO_3(aq)$.
- pH measurement: Good for reactions in which H^+ or OH^- is produced or consumed.
- Pressure: Good if number of gas phase moles changes; e.g. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

- Optical Rotation: Good if reactant or product is optically active.
- Spectrophotometry: Useful if reactant or product has characteristic absorption band;

  e.g. IR C=O absorption in ketone decomposition.

  Vis. absorption of Br_2 in: $H_2 + Br_2 \rightarrow 2HBr$.
- Gas Chromatography
- NMR Spectra
- Mass Spectrometry

Experimental Methods

The experimental procedures used in the laboratory are dependent upon the time scale of the reaction.

- Hours, days, weeks, etc.

  Extract aliquots (~10) and analyze.

- ~1/2 Hour

  Reaction will continue during analysis of aliquot.

  Extract aliquots, quench (cool or dilute) and analyze.

- 1 - 5 minutes

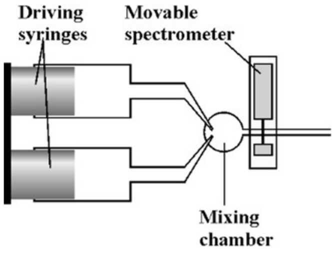
  Insufficient time to extract and quench a suitable number (~10) of samples to analyze.

  In situ concentration measurements; e.g. spectroscopy, pH, etc.

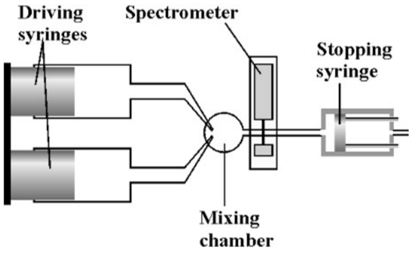
- 1 millisecond - 1 minute

  If reactants mixed in normal fashion by pouring together, the reaction would be over by the time you finished mixing.

  Use rapid mixing, ***flow*** methods.



Standard Flow



Stopped Flow

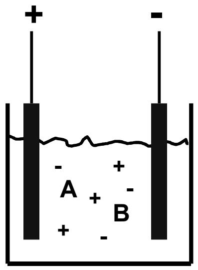
Requires less reactant.

- 1 microsecond - 1 millisecond

No time to mix reactants.

Relaxation Methods: Use a sudden "shock" to perturb a system from equilibrium and measure the relaxation to the new equilibrium concentrations

Temperature Jump (T-Jump)



- Let reactants and products reach reach equilibrium in aqueous solution.
- Add electrolyte [e.g. NaCl(aq)] and capacitor.
- Discharge capacitor quickly (~1 μs). Temperature "jumps".
- Measure relaxation to new equilibrium.

$A \leftrightarrow B$

$\Delta H \neq 0$

Analogous Methods: P-Jump, E-Jump

- 1 picosecond - 1 microsecond

Flash Photolysis

- Create excited state reactant photochemically with ultrashort laser pulse (< 1 ns).
- Measure decay of reactant or production of product.

Rate Laws: Order of a Reaction

$aA + bB \rightarrow \text{Products}$

$\text{Rate} = k[A]^x[B]^y[C]^z$

- [A], [B], [C] can be reactants, products or catalysts
- x = order of reaction w.r.t. [A]
  y = order of reaction w.r.t. [B]
  z = order of reaction w.r.t. [C]
  n = x + y + z = overall order of reaction
- x, y, z are ***not*** necessarily equal to the stoichiometric coefficients
- x, y, z can be: positive integers, negative integers, non-integers
- Not all rate laws are of the form above
  e.g. $\text{Rate} = k_1[A][B] / (k_2 + [B])$ (rate law for Enzyme Cat. Rxns.)
- The rate changes with time because the concentrations change with time

Units of the Rate Constant

$\text{Rate} = k[A]^x[B]^y[C]^z$

or $\text{Rate} = k[\text{conc}]^n$ $n = x + y + z$

$$k = \frac{1}{[\text{conc}]^n}\text{Rate} = \frac{1}{[\text{conc}]^n}\frac{\Delta[\text{conc}]}{\Delta(\text{time})}$$ (Unit Analysis Only)

$$k = \frac{1}{[\text{conc}]^{n-1}} \bullet \frac{1}{\text{time}} = \frac{1}{M^{n-1}} \bullet \frac{1}{s}$$

If [conc] = M
and time = s

$n = 1 \longrightarrow k = 1 / (M^{1-1} \bullet s) = s^{-1}$

$n = 2 \longrightarrow k = 1 / (M^{2-1} \bullet s) = M^{-1}s^{-1}$

$n = 5/2 \longrightarrow k = 1 / (M^{5/2-1} \bullet s) = M^{-3/2}s^{-1}$

Determination of Reaction Order

The Initial Rate Method

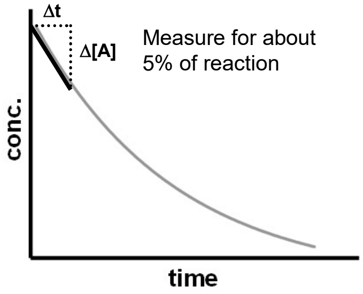
$$A \rightarrow \text{Products}$$

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

The rate changes with time because [A] changes with time.

It is often convenient to measure the ***initial rate*** $[R_o]$ for only a small amount of time after the reaction begins.

$$R_o = k[A]_o^n$$



Measure for about 5% of reaction

Principle of the Method

Experiment 1: $(R_o)_1 = k([A]_o^n)_1$

Experiment 2: $(R_o)_2 = k([A]_o^n)_2$

$$\frac{(R_o)_2}{(R_o)_1} = \frac{k([A]_o)_2^n}{k([A]_o)_1^n} = \left\{\frac{([A]_o)_2}{([A]_o)_1}\right\}^n$$

When $[A]_o$ is doubled, R_o is doubled.

$$\frac{2(R_o)_1}{(R_o)_1} = \left\{\frac{2([A]_o)_1}{([A]_o)_1}\right\}^n$$

$$2 = 2^n$$

$$\boxed{n = 1}$$

When $[A]_o$ is doubled, R_o is quadrupled.

$$\frac{4(R_o)_1}{(R_o)_1} = \left\{\frac{2([A]_o)_1}{([A]_o)_1}\right\}^n$$

$$4 = 2^n$$

$$\boxed{n = 2}$$

When $([A]_o)_1 = 0.5$ M , $(R_o)_1 = 0.10$ Ms^{-1}

When $([A]_o)_2 = 1.25$ M , $(R_o)_2 = 1.56$ Ms^{-1}

$$\frac{(R_o)_2}{(R_o)_1} = \left\{\frac{([A]_o)_2}{([A]_o)_1}\right\}^n$$

$$\frac{1.56\,\mathrm{Ms^{-1}}}{0.10\,\mathrm{Ms^{-1}}} = \left\{\frac{1.25\,\mathrm{M}}{0.5\,\mathrm{M}}\right\}^n \longrightarrow 15.6 = (2.5)^n$$

Method of Logarithms

$\ln(15.6) = \ln(2.5)^n = n \cdot \ln(2.5)$ $[\ln(a)^b = b \cdot \ln(a)]$

$n = \ln(15.6) / \ln(2.5) = 2.75 / 0.92 = 2.99$

$$\boxed{n = 3}$$

Note: Can use either natural or common logs.

Generalization to Multiple Concentrations

$$A + B \rightarrow C$$

$$R_o = k\,[A]_o^{\mathbf{x}}\,[B]_o^{\mathbf{y}}\,[C]_o^{\mathbf{z}}$$

$$\frac{(R_o)_2}{(R_o)_1} = \frac{k([A]_o^x)_2([B]_o^y)_2([C]_o^z)_2}{k([A]_o^x)_1([B]_o^y)_1([C]_o^z)_1}$$

$$= \left\{\frac{([A]_o)_2}{([A]_o)_1}\right\}^x \left\{\frac{([B]_o)_2}{([B]_o)_1}\right\}^y \left\{\frac{([C]_o)_2}{([C]_o)_1}\right\}^z$$

Can isolate a given species by holding other concentrations constant.

e.g. Double $[A]_o$ while holding $[B]_o$ and $[C]_o$ constant.

Example: Consider the reaction, $2A + B \rightarrow 2C$

$$R_o = k\,[A]_o^{\mathbf{x}}\,[B]_o^{\mathbf{y}}\,[C]_o^{\mathbf{z}}$$

Use the experimental data below to determine x, y, z and the rate constant, k.

Expt.	$[A]_o$	$[B]_o$	$[C]_o$	R_o
#1	0.50 M	0.10 M	0.80 M	78 Ms^{-1}
#2	0.75	0.05	0.20	176
#3	0.75	0.10	0.80	176
#4	0.75	0.05	0.80	352

$x = 2$
$y = -1$
$z = 1/2$

$$\longrightarrow \quad R_o = k\,\frac{[A]_o^2[C]_o^{1/2}}{[B]_o}$$

$k = 35\ M^{-1/2}s^{-1}$

Determination of Reaction Order

Use of the Integrated Rate Equation

A → Products and $R = -\frac{d[A]}{dt} = k[A]^n$

One may integrate the rate equation to obtain [A] as a function of k, $[A]_o$ and t.

$$A = A([A]_o, k, t)$$

The form of the function depends upon the order of the reaction, n.

The order, n, and the rate constant, k, can be calculated by determining which order equation fits the experimental data.

First Order Reactions

A → Products

$$R = -\frac{d[A]}{dt} = k[A]^1$$

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

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

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

$$e^{\ln\left(\frac{[A]}{[A]_o}\right)} = e^{-kt}$$

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

$$\boxed{[A] = [A]_o e^{-kt}}$$

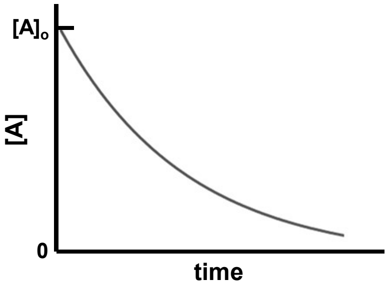
$$\int_{x_1}^{x_2} \frac{1}{x} dx = \ln(x_2 / x_1)$$

$$\int_{x_1}^{x_2} C dx = C(x_2 - x_1)$$

$$[A] = [A]_o e^{-kt}$$

At t = 0 , $[A] = [A]_o$

As $t \to \infty$, $[A] \to 0$



A Linear Equation

It is not straightforward to use plots of [A] vs. t to determine k.

It would be better to have a linear relation.

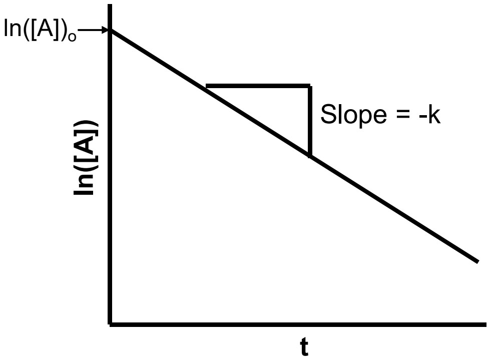
$$\ln\left(\frac{[A]}{[A]_o}\right) = -kt$$

Let's start again at this point.

$$\ln([A]) - \ln([A_o]) = -kt$$

$$\boxed{\ln([A]) = \ln([A_o]) - k\,t}$$

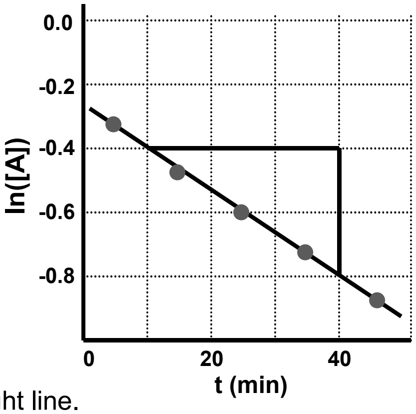
$$\underbrace{\boxed{\ln([A])}}_{y} = \ln([A_o]) - k\underbrace{\boxed{t}}_{x}$$



A → Products

The following data were obtained:

t	[A]	ln([A])
5 min	0.72 M	-0.33
15	0.63	-0.47
25	0.55	-0.60
35	0.48	-0.73
45	0.42	-0.87



Is this reaction first order?

Yes! Because ln([A]) vs. t is a straight line.

What is k?

$\text{Slope} = \frac{-0.80-(-0.40)}{(40-10)\,\text{min}}$ = -0.0133 min^{-1} = -k

$\boxed{k = 0.0133\ \text{min}^{-1}}$

Half-Life of a First Order Reaction

The Half-Life ($t_{1/2}$) of a reaction (any order) is defined by:

$t = t_{1/2}$ when $[A] = ½ [A]_o$

For a first order reaction: $\ln\left(\frac{[A]}{[A]_o}\right) = -kt$

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

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

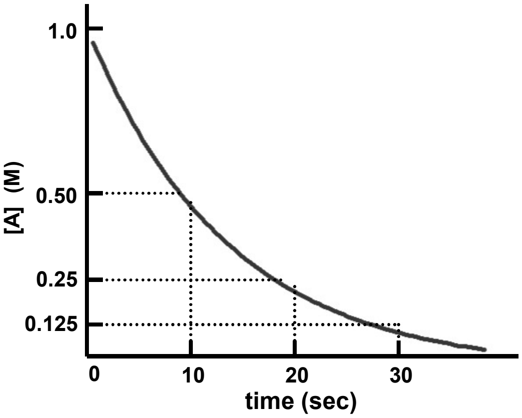
$$-0.693 = -kt_{1/2}$$

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

Notes: (a) $t_{1/2} \propto 1/k$
(b) $t_{1/2}$ is independent of $[A]_o$

$[A]_o$	**$t_{1/2}$**
1.0 M	10 - 0 = 10 s
0.5	20 - 10 = 10 s
0.25	30 - 20 = 10 s

Note that $t_{1/2}$ is independent of $[A]_o$



$k = 0.693 / t_{1/2}$
$= 0.693 / 10\ s$
$= 0.0693\ s^{-1}$

Example: For a first order reaction, A → Products, the half-life is 150 s.

(a) What is the rate constant, k?

$k = 4.62 \times 10^{-3}\ s^{-1}$

(b) If $[A]_o = 0.40$ M, what is [A] after 240 s?

$[A] = 0.13$ M

(c) If $[A]_o = 0.40$ M, how long does it take for [A] to decrease to 0.08 M?

t = 350 s

Second Order Reactions

A → Products

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

$$-\frac{1}{[A]^2}d[A] = k\,dt$$

$$-\int_{[A]_o}^{[A]} \frac{1}{[A]^2}d[A] = \int_0^t k\,dt$$

$$-\left(\frac{1}{[A]_o} - \frac{1}{[A]}\right) = kt$$

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt$$

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

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

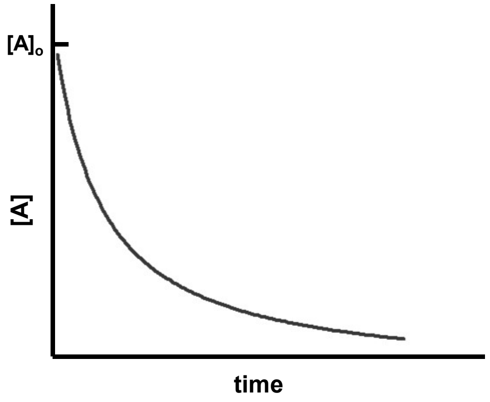
$$\int_{x_1}^{x_2} \frac{1}{x^2}dx = \frac{1}{x_1} - \frac{1}{x_2}$$

$$\int_{x_1}^{x_2} C\,dx = C(x_2 - x_1)$$

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

At t = 0 , $[A] = [A]_o$

As $t \to \infty$, $[A] \to 0$



It is not straightforward to use the above curve to determine the rate constant, k.

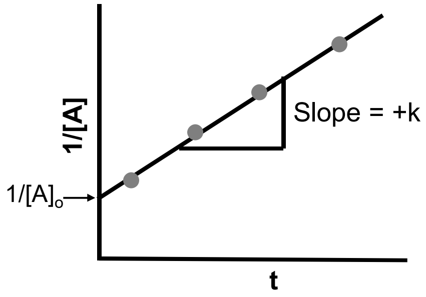
It would be better to have a linear relation.

A Linear Equation

We ALREADY have a linear relation!!!

$$\underbrace{\boxed{\frac{1}{[A]}}}_{y} = \frac{1}{[A]_o} + k\underbrace{\boxed{t}}_{x}$$

This is the step just before solving for [A].



If you believe a reaction may be second order, plot 1/[A] vs. t.

If the plot is a straight line, you have verified the order. The rate constant can be obtained from the slope.

Half-Life of a Second Order Reaction

As before, the Half-Life ($t_{1/2}$) of a reaction (any order) is defined by:

$t = t_{1/2}$ when $[A] = ½ [A]_o$

For a second order reaction: $\frac{1}{[A]} - \frac{1}{[A]_o} = kt$

$$\frac{1}{1/2 \bullet [A]_o} - \frac{1}{[A]_o} = kt_{1/2}$$

$$\frac{2}{[A]_o} - \frac{1}{[A]_o} = kt_{1/2}$$

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

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

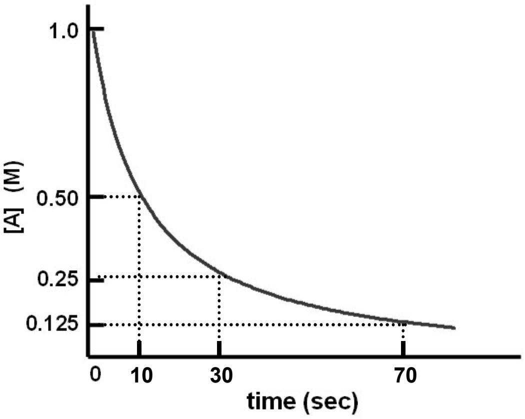
Notes: (a) $t_{1/2} \propto 1/k$

(b) $t_{1/2} \propto 1/[A]_o$

Not Independent of $[A]_o$

$[A]_o$	$t_{1/2}$
1.0 M	10 - 0 = 10 s
0.5	30 - 10 = 20 s
0.25	70 - 30 = 40 s

Note that $t_{1/2} \propto 1/[A]_o$



$k = 1/t_{1/2}\bullet[A]_o = 1/(10\text{ s}\bullet 1\text{ M}) = 0.1\text{ M}^{-1}\text{s}^{-1}$

or $k = 1/t_{1/2}\bullet[A]_o = 1/(20\text{ s}\bullet 0.5\text{ M}) = 0.1$ M-1s-1

or $k = 1/t_{1/2}\bullet[A]_o = 1/(40\text{ s}\bullet 0.25\text{ M}) = 0.1\text{ M}^{-1}\text{s}^{-1}$

Third Order Reactions

A → Products

$$R = -\frac{d[A]}{dt} = k[A]^3$$

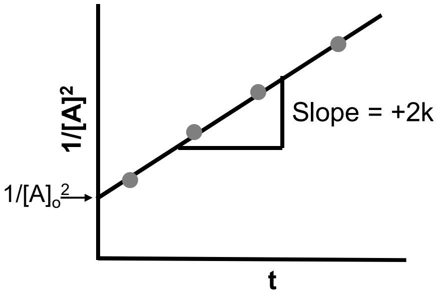
↓ **In Class**

$$\boxed{\frac{1}{[A]^2} = \frac{1}{[A]_o^2} + 2kt}$$

↓ **In Class**

$$t_{1/2} = \frac{3}{2k[A]_o^2}$$

What should we plot to get a straight line?



Notes: (a) $t_{1/2} \propto 1/k$

(b) $t_{1/2} \propto 1/[A]_o^2$

Not Independent of $[A]_o$

Example: The reaction, A → Products, is third order;
i.e. $-d[A]/dt = k[A]^3$

(a) When $[A]_o = 0.40$ M, it takes 75 s for the concentration to decrease to 0.10 M.

What is the rate constant, k?

$k = 0.625\ M^{-2}s^{-1}$

(b) When $[A]_o = 0.40$ M, what is the concentration of A after 315 s?

$[A] = 0.05$ M

Zeroth Order Reactions

A → Products

$$R = -\frac{d[A]}{dt} = k[A]^0$$

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

What???

How can the rate of a reaction be independent of the concentration of reactant??

Photochemical Reactions

Rate limited by photon flux

Surface Catalyzed Reactions

Rate limited by number of active sites on surface

Enzyme Catalyzed Reactions

At high substrate concentration, rate limited by enzyme concentration

A → Products

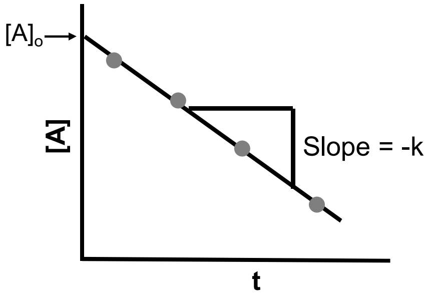
What should we plot to get a straight line?

$$R = -\frac{d[A]}{dt} = k[A]^0 = k$$

$$\Big\downarrow \textbf{ Integrate}$$

$$\boxed{[A] = [A]_o - kt}$$

$$\Big\downarrow$$



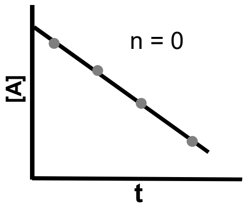
$$t_{1/2} = \frac{[A]_o}{2k}$$

Notes: (a) $t_{1/2} \propto 1/k$

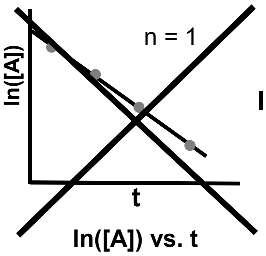
(b) $t_{1/2} \propto [A]_o$

Not Independent of $[A]_o$

Generalization: Linear Plots

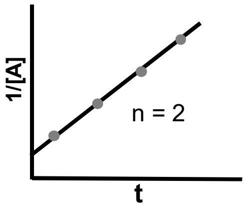


$[A]$ ($=1/[A]^{0-1}$) vs. t

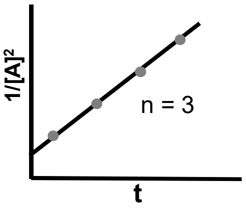


ln([A]) vs. t

Ignore
n = 1



$1 / [A]$ ($=1 / [A]^{2-1}$) vs. t



$1 / [A]^2$ ($=1 / [A]^{3-1}$) vs. t

The Trend in Plots

For ***any*** order (n) ***except*** n = 1, a plot of $\boxed{\frac{1}{[A]^{n-1}} \text{ vs. } t}$ yields a straight line.

For example, if you believe that the reaction order might be n = 3/2, then plot:

$$\frac{1}{[A]^{3/2-1}} = \frac{1}{[A]^{1/2}} \text{ vs. } t$$

A straight line would verify the assumed reaction order.

Generalization: Half-Lives

n = 0 $t_{1/2} = \frac{[A]_o}{2k}$

$$= \frac{1}{2k} \bullet \frac{1}{[A]_o^{0-1}}$$

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

$$= \frac{0.693}{k} \bullet \frac{1}{[A]_o^{1-1}}$$

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

$$= \frac{1}{k} \bullet \frac{1}{[A]_o^{2-1}}$$

n = 3 $t_{1/2} = \frac{3}{2k[A]_o^2}$

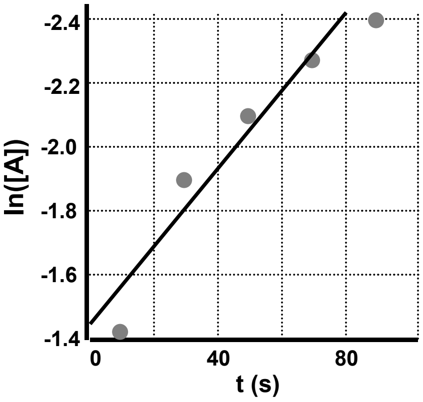
$$t_{1/2} = \frac{3}{2k} \bullet \frac{1}{[A]_o^{3-1}}$$

Trend: For ***all*** orders (***including n = 1***), $\boxed{t_{1/2} \propto \frac{1}{[A]_o^{n-1}}}$

Determining Reaction Order: Trial and Error

A → Products $-d[A]/dt = k[A]^n$

t	**[A]**	**ln([A])**
10 s	0.239 M	-1.43
30	0.153	-1.88
50	0.122	-2.10
70	0.104	-2.26
90	0.092	-2.39

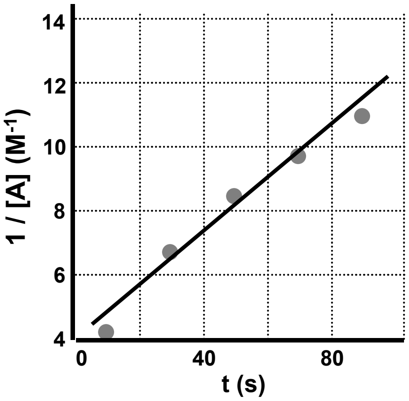


Is this reaction first order?

No Way!!!

A → Products $-d[A]/dt = k[A]^n$

t	**[A]**	**1/[A]**
10 s	0.239 M	4.18 M^{-1}
30	0.153	6.54
50	0.122	8.20
70	0.104	9.62
90	0.092	10.87

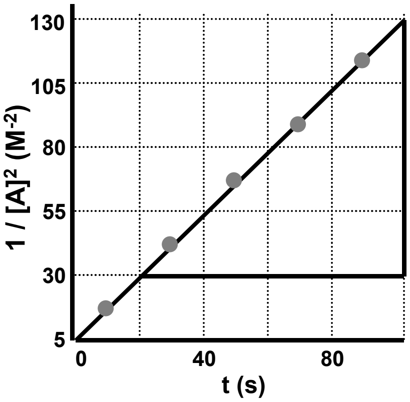


Is this reaction second order?

Close, but no cigar!!

A → Products $-d[A]/dt = k[A]^n$

t	[A]	$1/[A]^2$
10 s	0.239 M	17.5 M^{-2}
30	0.153	42.5
50	0.122	67.5
70	0.104	92.5
90	0.092	118



Is this reaction third order?

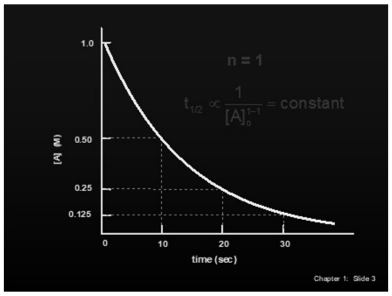
Yes!!!

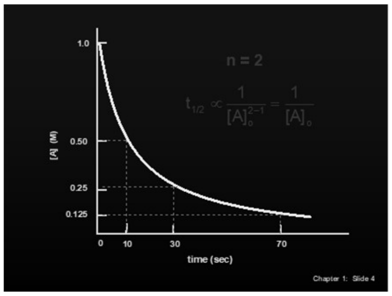
What is k?

$$\frac{1}{[A]^2} = \frac{1}{[A]_o^2} + 2kt \qquad \text{Slope} = \frac{(130-30)\,M^{-2}}{(100-20)\,s} = 1.25\,M^{-2}s^{-1} = 2k$$

$\boxed{k = 0.625\ M^{-2}s^{-1}}$

Direct Determination of Reaction Order: Half-Life Method





In contrast to “trial and error”, there are a number of direct methods to determine the order of a reaction.

One of these is the “Half-Life Method”.

One can determine the reaction order by learning how the half-life depends upon the initial concentration, $[A]_o$

$$t_{1/2} \propto \frac{1}{[A]_o^{n-1}}$$

When $[A]_o = 0.2$ M, $t_{1/2} = 60$ s.
When $[A]_o = 0.4$ M, $t_{1/2} = 15$ s.

What is the order, n?

Note that when $[A]_o$ is doubled, $t_{1/2}$ is reduced by a factor of four.

Therefore,

$$t_{1/2} \propto \frac{1}{[A]_o^2}$$

Hence, 2 = n-1 $\boxed{n = 3}$

The proportionality between $[A]_o$ and $t_{1/2}$ is not always obvious from inspection.

One may use a mathematical method to determine n from the data.

Mathematical Procedure to Determine n

$$(t_{1/2})_1 \propto \frac{1}{([A]_0^{n-1})_1} \quad \text{and} \quad (t_{1/2})_2 \propto \frac{1}{([A]_0^{n-1})_2}$$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{1/([A]_0^{n-1})_2}{1/([A]_0^{n-1})_1}$$

$$\boxed{\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{([A]_o)_1}{([A]_o)_2}\right)^{n-1}}$$

When $[A]_o = 0.2$ M, $t_{1/2} = 60$ s.
When $[A]_o = 0.4$ M, $t_{1/2} = 15$ s.

What is the order, n?

$$\frac{15\text{ s}}{60\text{ s}} = \left(\frac{0.2\text{ M}}{0.4\text{ M}}\right)^{n-1}$$

$$0.25 = (0.50)^{n-1}$$

$$\ln(0.25) = \ln(0.50)^{n-1} = (n-1)\cdot\ln(0.50)$$

$$n-1 = \ln(0.25) / \ln(0.50) = (-1.39) / (-0.69) = 2.0$$

$$\boxed{n = 3}$$

Reactions Approaching Equilibrium (Reversible First-Order Reactions

We'll just discuss this material briefly. You are not responsible for it.

Reversible reactions (first order and more complex reactions) are very important, and can be well studied by relaxation methods (introduced earlier).

Consider the reversible reaction, A ⇌ B, in the case that the rates of the forward and reverse reactions are both first order:

$A \rightarrow B$	$R_F = -d[A]/dt = k_f[A]$
$B \rightarrow A$	$R_R = -d[B]/dt = +d[A]/dt = k_R[B]$

With a bit of algebra, it can be shown that:

$$\Delta[A] = \Delta[A]_o e^{-(k_F+k_B)t} \quad \text{where} \quad \Delta[A] = [A] - [A]_{eq}$$

$$\Delta[A]_o = [A]_o - [A]_{eq}$$

Thus, the deviation of [A] from its equilibrium value decreases exponentially with a rate constant equal to the sum of the forward and reverse first-order rate constants.

$\Delta[A] = \Delta[A]_o e^{-(k_F + k_B)t}$ where $\Delta[A] = [A] - [A]_{eq}$

$\Delta[A]_o = [A]_o - [A]_{eq}$

Thus, the deviation of [A] from its equilibrium value decreases exponentially with a rate constant equal to the sum of the forward and reverse first-order rate constants.

Therefore, measurement of Δ[A] as a function of time (from a relaxation experiment) allows one to determine the sum of the two rate constants, $k_F + k_B$.

The ratio of the two constants, k_F/k_B, can be determined from the equilibrium concentrations:

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_F}{k_B}$$

Thus, measurement of the decay kinetics, and the equilibrium concentrations at infinite time permit determine of both the forward and reverse rate constants for the reversible reaction.

Competitive First Order Reactions

When a synthetic chemist performs a reaction, (s)he will often obtain more than one product (e.g. lovely white crystals + ugly black gunk).

This is an example of multiple reaction pathways for the given reactant. This can be studied using a "Competitive" first order reaction mechanism.

Consider the two first order reactions:

$A \xrightarrow{k_1} B$ (Product #1)

$A \xrightarrow{k_2} C$ (Product #2)

Below, we will develop expressions for [A], [B] and [C] as a function of time.

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$

[A] vs. time

Both reactions cause [A] to decrease with time.

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A] = -(k_1 + k_2)[A] = -k'[A]$$

This is a simple first-order rate law, with the effective rate constant, $k' = k_1 + k_2$

It may be integrated directly to obtain the following equation for [A].

$$[A] = [A]_o e^{-(k_1+k_2)t} = [A]_o e^{-k't}$$

Notice that the rate constant for the disappearance of [A] is the sum of the rate constants for the two competing reactions.

$$A \xrightarrow{k_1} B \qquad [A] = [A]_o e^{-(k_1+k_2)t} = [A]_o e^{-k't}$$
$$A \xrightarrow{k_2} C$$

[B] vs. time

[B] is formed only from the first of the two rate equations.

$$\frac{d[B]}{dt} = +k_1[A]$$

To integrate this equation, we insert the above expression for [A].

$$\frac{d[B]}{dt} = +k_1[A]_o e^{-(k_1+k_2)t} = +k_1[A]_o e^{-k't}$$

$$\frac{d[B]}{dt} = +k_1[A]_o e^{-(k_1+k_2)t} = +k_1[A]_o e^{-k't}$$

With the initial condition, $[B]_o = 0$, we can integrate (**in class**) to get the following equation for [B] vs. time.

$$[B] = \frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right) = \frac{k_1}{k'}[A]_o\left(1-e^{-k't}\right)$$

[C] vs. time

Using the identical procedure for [C], we have:

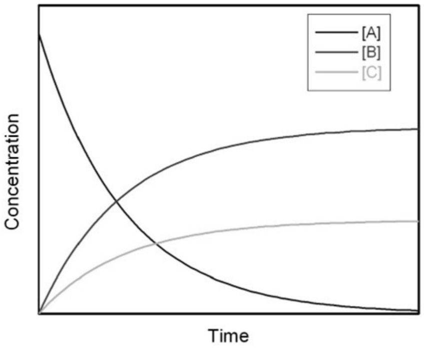
$$\frac{d[C]}{dt} = +k_2[A]$$

This yields: $[C] = \frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right) = \frac{k_2}{k'}[A]_o\left(1-e^{-k't}\right)$

$$[A] = [A]_o e^{-(k_1+k_2)t}$$

$$[B] = \frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)$$

$$[C] = \frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)$$



As one would expect, [A] decreases exponentially with a rate constant equal to the sum, $k_1 + k_2$

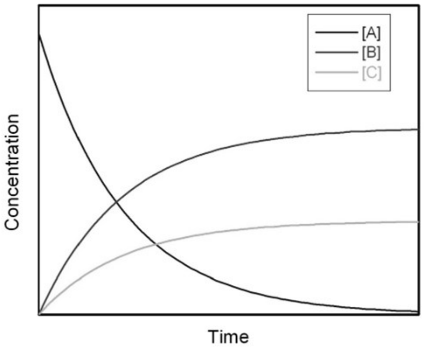
Perhaps surprisingly, [B] and [C] both increase exponentially, with rate constants equal to the sum, $k_1 + k_2$

However, the relative amounts of the two products depend upon their respective rate constants.

$$[A]=[A]_o e^{-(k_1+k_2)t}$$

$$[B]=\frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)$$

$$[C]=\frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)$$



Let's consider the relative concentrations of the two products, [B]/[C].

$$\frac{[B]}{[C]}=\frac{\frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)}{\frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)}=\frac{k_1}{k_2}$$

$$\frac{[B]}{[C]}=\frac{\frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)}{\frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)}=\frac{k_1}{k_2}$$

Thus, we see that the relative yields of two different products in a reaction is a measure of their relative rate constants.

Consider a reactant, [A] which undergoes two first-order reactions to form the products, [B] and [C]

(A) If one begins with an initial concentration of the reactant, 0.90 M. At the conclusion of the experiment, the concentration of C was 0.55 M. What is the value of the ratio, k_1/k_2 ?

$k_1/k_2 = 0.64$

$$\frac{[B]}{[C]} = \frac{\frac{k_1}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)}{\frac{k_2}{k_1+k_2}[A]_o\left(1-e^{-(k_1+k_2)t}\right)} = \frac{k_1}{k_2}$$

Thus, we see that the relative yields of two different products in a reaction is a measure of their relative rate constants.

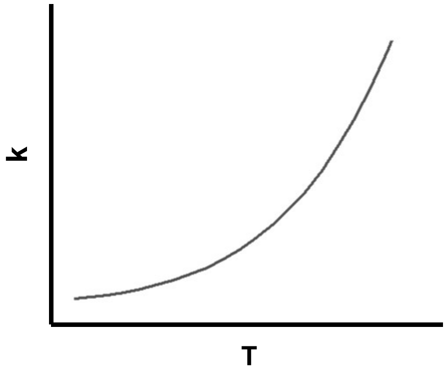
Consider a reactant, [A] which undergoes two first-order reactions to form the products, [B] and [C]

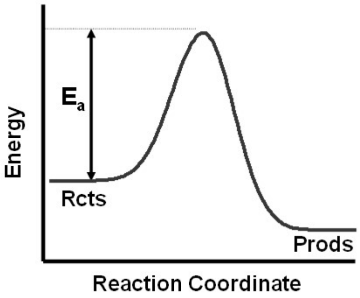
(B) The rate constant, k_1, for the first reaction was found to be $k_1 = 0.050\ s^{-1}$. If one begins with an initial concentration of the reactant of 0.90 M, what will be the concentration of [C] 10 s after the start of the reaction?

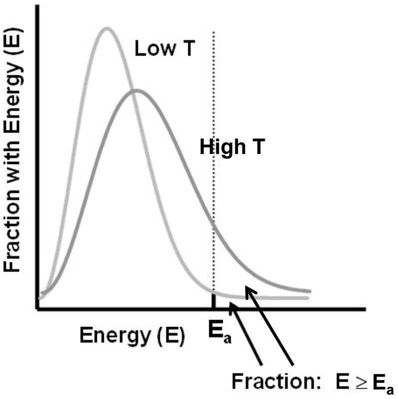
[C] = 0.40 M

Temperature Dependence of the Rate Constant

It is observed for most reactions that the rate constant, k, increases exponentially with rising temperature.







In order for molecules to react, they must overcome an energy barrier, called the Activation Energy (E_a).

At low temperature, only a small fraction of collisions have $E \geq E_a$

At high temperature, a larger fraction of collisions have $E \geq E_a$

The Arrhenius Equation

Svante Arrhenius (1889)

$$k = Ae^{-\frac{E_a}{RT}}$$

Matches observed k vs. T

A = Pre-Exponential Factor

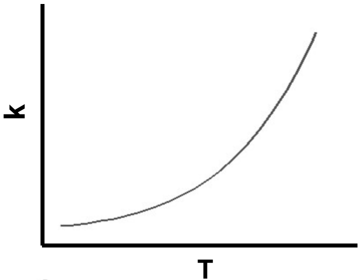
Units: Same as k

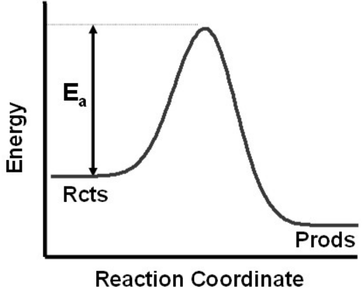
E_a = Activation Energy

Units: kJ/mol

R = 8.31 J/mol-K

T = Temperature (K)



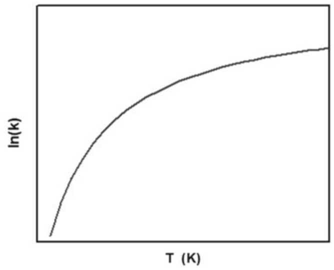


Relation Between E_a and Temperature Dependence of k

$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

$$\frac{d\ln(k)}{dT} = +\frac{E_a}{RT^2}$$



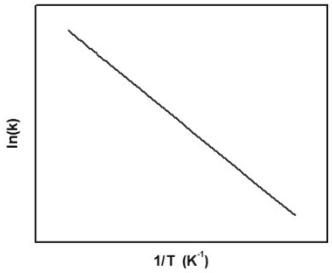
This equation predicts that a plot of ln(k) vs. T will **NOT** be a straight line. Rather the slope will become smaller at higher temperatures.

We will use the above expression for dln(k)/dT in a later section. However, for now let's determine how to obtain a straight line plot

$$\frac{d\ln(k)}{dT} = +\frac{E_a}{RT^2} = \frac{d\ln(k)}{d(1/T} \cdot \frac{d(1/T)}{dT} = -\frac{1}{T^2} \cdot \frac{d\ln(k)}{d(1/T}$$

Therefore: $\frac{d\ln(k)}{d(1/T} = -\frac{E_a}{R}$

Thus, we expect that if ln(k) is plotted vs. 1/T, we should get a straight line with Slope = $-E_a/R$



Determination of the Arrhenius Parameters

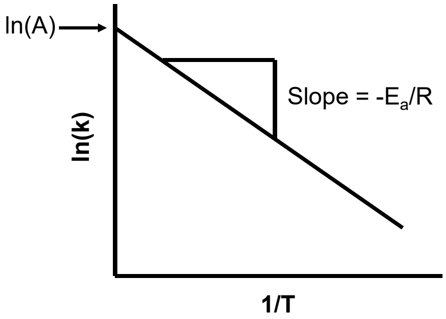
$$k = Ae^{-\frac{E_a}{RT}}$$

$$\ln(k) = \ln\left(Ae^{-\frac{E_a}{RT}}\right)$$

$$\ln(k) = \ln(A) + \ln\left(e^{-\frac{E_a}{RT}}\right)$$

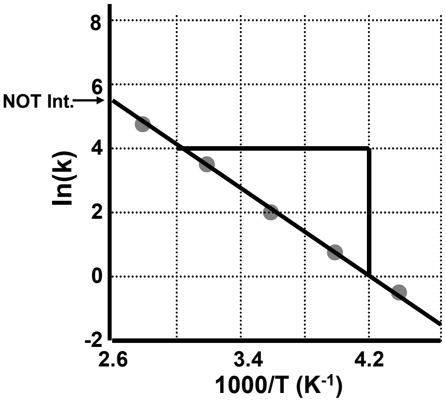
$$\boxed{\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}}$$

$$\underset{y}{\boxed{\ln(k)}} = \ln(A) - \frac{E_a}{R}\underset{x}{\boxed{\frac{1}{T}}}$$



A rate constant was measured as a function of temperature, and the following Arrhenius plot [ln(k) vs. 1000/T] was obtained.

Calculate A and E_a for this reaction.



$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$

$$\text{Slope} = \frac{\Delta\ln(k)}{\Delta(1/T)} = \frac{0.0 - 4.0}{(4.2 - 3.0)\text{x}10^{-3}\ \text{K}^{-1}}$$

Note

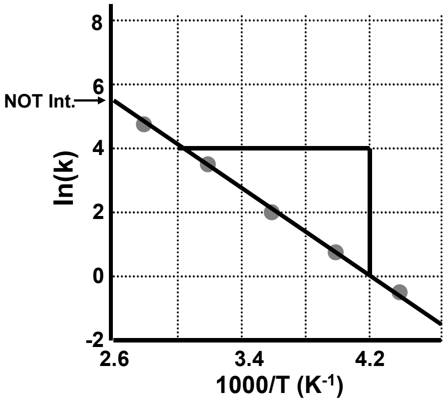
$$\text{Slope} = -3330\ \text{K} = -\frac{E_a}{R}$$

E_a = -R•(-3330 K)

= -8.31 J/mol-K(-3330 K)

= +27690 J/mol

$$\boxed{E_a = 27.7\ \text{kJ/mol}}$$



$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$

$$\text{Int} = \ln(A) = \ln(k_1) + \frac{E_a}{R}\frac{1}{T_1}$$

$$= 4.0 + \frac{27{,}690\ \text{J/mol}}{8.314\ \text{J/mol-K}} \cdot 3.0\text{x}10^{-3}\ \text{K}^{-1}$$

ln(A) = 14.0

$$\boxed{A = 1.2\text{x}10^{6}\ \text{s}^{-1}}$$

Two Point Analysis

$$\ln(k_1) = \ln(A) - \frac{E_a}{R}\frac{1}{T_1}$$

$$\ln(k_2) = \ln(A) - \frac{E_a}{R}\frac{1}{T_2}$$

$$\longrightarrow \ln(k_2)\text{-}\ln(k_1) = -\frac{E_a}{R}\frac{1}{T_2} - \left(-\frac{E_a}{R}\frac{1}{T_1}\right)$$

$$\boxed{\ln(k_2/k_1) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

For a first order reaction, the measured rate constant was 5. s^{-1} at 25 °C and 15. s^{-1} at 35 °C.

Calculate A and E_a for this reaction.

A = 2.5x10^{15} s^{-1}

E_a = 83.8 kJ/mol

A second order reaction has an activation energy of 60 kJ/mol. The rate constant is 3.0 $M^{-1}s^{-1}$ at 25 ^{o}C.

What is the value of k at 50 ^{o}C?

$k = 19.5\ M^{-1}s^{-1}$

A first order reaction has an activation energy of 45 kJ/mol. The half-life is 50 s at 25 ^{o}C.

At what temperature (in ^{o}C) is the half-life equal to 10 s?

$T = 54\ ^{o}C$

Transition State Theory

The material on Transition State Theory can be found in Chapter 22 of the text (Sects. 22.4 and 22.5)

Deficiencies of the Arrhenius Theory

The Arrhenius Equation is basically empirical. Whereas the activation energy, E_a, can be interpreted as the energy barrier to reaction, there is no interpretation of the pre-exponential factor, A.

Furthermore, it is not possible to predict the parameters theoretically.

Transition State Theory (aka Activated Complex Theory)

In 1935, Henry Eyring applied the theoretical methods of equilibrium statistical mechanics to determine the rate constants for elementary reactions.

He assumed that the reactants are in a quasi-equilibrium with a transition state (or activated complex)

$$A + B \overset{K^{\pm}}{\rightleftarrows} AB^{\pm}$$

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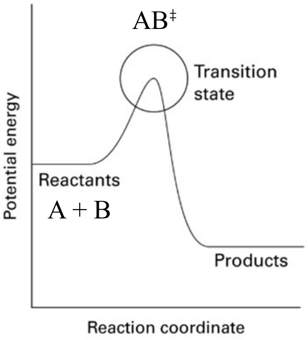


[AB‡] is related to the reaction concentrations by the equilibrium constant, K‡:

$$K^{\pm} = \frac{[AB^{\pm}]}{[A][B]} \quad \text{or} \quad [AB^{\pm}] = K^{\pm}[A][B]$$

One particular vibration of the activated complex, ν‡, leads to conversion of AB‡ to products.

The rate of the reaction is then proportional to the frequency of the vibration, ν‡ , and the concentration of activated complexes, [AB‡].

$$Rate = \nu^{\pm}[AB^{\pm}] = \nu^{\pm}K^{\pm}[A][B]$$

Note: Many treatments of TST include a transmission coefficient, κ, representing the fraction of complexes that proceed to products. It is often assumed that κ ≈ 1, as we have done here.

$$Rate = \nu^{\pm}[AB^{\pm}] = \nu^{\pm}K^{\pm}[A][B] = k_r[A][B]$$

k_r is the reaction rate constant, given by: $k_r = \nu^{\pm}K^{\pm}$

ν‡ is the frequency of the vibration of the activated complex which leads to dissociation into products

K‡ is the equilibrium constant between reactants and activated complex.

Using statistical mechanics formulae for vibrational frequencies, it can be shown that: $\nu^{\pm} = \frac{k_B T}{h} = \frac{RT}{N_A h}$

k_B is Boltzmann's constant, and is related to the gas constant, R, by $k_B = R/N_A$, and h is Planck's Constant (6.63x10^{-34} J-s)

Thus, we have the TST expression for the rate constant:

$$k = \frac{k_B T}{h}K^{\pm} = \frac{RT}{N_A h}K^{\pm}$$

$$k = \frac{k_B T}{h} K^{\pm} = \frac{RT}{N_A h} K^{\pm}$$

One advantage of Transition State Theory over the Arrhenius Theory is that Statistical Mechanical methods have been well studied to predict equilibrium constants.

Thus, one can use the equation above to predict values for the rate constants of elementary reactions.

However, a big advantage of TST for experimental kineticists is that, as we shall see, the TST expression for the rate constant, like the Arrhenius Equation, has two parameters.

Unlike the Arrhenius Equation, **both** TST parameters are interpretable.

Thermodynamic Formulation of TST

$$k = \frac{RT}{N_A h} K^{\pm}$$

The equilibrium constant, $K^{\ddagger}$, may be related to the Gibbs Activation Energy, $\Delta G^{\ddagger}$, and to the Activation Enthalpy, $\Delta H^{\ddagger}$ and Activation Entropy, $\Delta S^{\ddagger}$, by the standard relations:

$$\Delta G^{\pm} = -RT \ln(K^{\pm}) = \Delta H^{\pm} - T\Delta S^{\pm} \longrightarrow \ln(K^{\pm}) = -\frac{\Delta H^{\pm}}{RT} + \frac{\Delta S^{\pm}}{R}$$

Therefore: $K^{\pm} = e^{-\frac{\Delta H^{\pm}}{RT} + \frac{\Delta S^{\pm}}{R}} = e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$

Thus, the TST equation for the rate constant is:

$$\boxed{k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}}$$

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$$

Note: The equation in the text (Eqn. 22.43) differs from the one above:

$$k = \frac{RT}{N_A h}\left(\frac{RT}{p^o}\right) e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$$ Text Eqn. 22.43 after minor manipulation

A comparison shows that the text equation has the additional factor, RT/p^o.

That term arises from the conversion from K_p to K_c. These are different by that factor for bimolecular gas phase reactions.

However, for reactions in solution and for unimolecular gas phase reactions, K_p and K_c are the same. The form of the equation that we present is the correct one for these cases.

It is useful to compare the TST and Arrhenius equations for the rate constant:

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$$

Transition State Theory

$$k = Ae^{-\frac{E_a}{RT}}$$

Arrhenius Theory

Note that TST has two parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) just like the Arrhenius Theory (E_a and A). However, **both** TST parameters have a mechanistic interpretation.

$\Delta H^{\ddagger}$, the Activation Enthalpy, has a meaning qualitatively similar to E_a. It represents the barrier which the colliding molecules must overcome in order to react to form products.

$\Delta S^{\ddagger}$, the Activation Entropy, represents the relative amount of disorder of the activated complex compared to reactants.
This parameter is often very useful in determining the mechanism of the reaction.

$\Delta S^{\ddagger}$, the Activation Entropy, represents the relative amount of disorder of the activated complex compared to reactants.
This parameter is often very useful in determining the mechanism of the reaction.

Metal Carbonyl Substitution

$L + M(CO)_6 \rightarrow ML(CO)_5 + CO$

Associative: $L + M(CO)_6 \rightarrow ML(CO)_6 \rightarrow ML(CO)_5 + CO \quad \Delta S^{\ddagger} < 0$

Dissociative: $L + M(CO)_6 \rightarrow L + M(CO)_5 + CO$
$\rightarrow ML(CO)_5 + CO \quad \Delta S^{\ddagger} > 0$

Ring Opening Reaction

If $\Delta S^{\ddagger} \approx 0$, the ring structure is preserved in the transition state.

If $\Delta S^{\ddagger} > 0$, the ring has opened in the transition state

---

Determination of the TST Parameters

A linearized form of the TST equation can be developed in the following manner.

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}} \longrightarrow k/T = \frac{R}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}$$

$$\ln\left(k/T\right) = \ln\left(\frac{R}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}}\right) = \ln\left(R/N_A h\right) + \frac{\Delta S^{\pm}}{R} - \frac{\Delta H^{\pm}}{RT} = C - \frac{\Delta H^{\pm}}{RT}$$

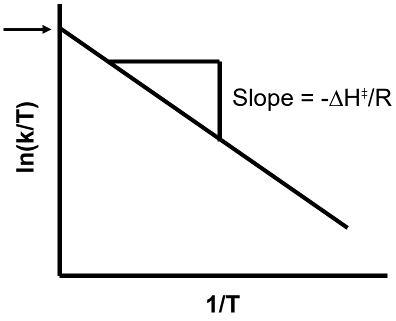
where $C = \ln\left(R/N_A h\right) + \frac{\Delta S^{\pm}}{R}$

One expects a plot of ln(k/T) vs. 1/T will be a straight line

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{R}{N_A h}\right) + \frac{\Delta S^{\pm}}{R} - \frac{\Delta H^{\pm}}{RT} = C - \frac{\Delta H^{\pm}}{RT} \qquad C = \ln\left(\frac{R}{N_A h}\right) + \frac{\Delta S^{\pm}}{R}$$

$$\underset{\textbf{y}}{\boxed{\ln\left(\frac{k}{T}\right)}} = \underset{\text{Int}}{\underset{\uparrow}{C}} - \overset{\text{Slope}}{\overset{\downarrow}{\frac{\Delta H^{\pm}}{R}}} \underset{\textbf{x}}{\boxed{\frac{1}{T}}}$$

$$\text{Int} = \text{C} = \ln\left(\frac{\text{R}}{\text{N}_\text{A}\text{h}}\right) + \frac{\Delta\text{S}^{\pm}}{\text{R}} \longrightarrow$$



Relation Between TST and Arrhenius Parameters

Relation between E_a and $\Delta H^{‡}$

Recall that we showed that the Arrhenius Equation leads to an expression relating E_a to dln(k)/dT.

$$k = Ae^{-\frac{E_a}{RT}} \longrightarrow \frac{d\ln(k)}{dT} = +\frac{E_a}{RT^2}$$

Let's use this to relate E_a to $\Delta H^{‡}$.

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}} \longrightarrow \ln(k) = \ln\left(\frac{R}{N_A h}\right) + \ln(T) + \frac{\Delta S^{\pm}}{R} - \frac{\Delta H^{\pm}}{RT}$$

Therefore: $\frac{d\ln(k)}{dT} = 0 + \frac{1}{T} + 0 + \frac{\Delta H^{\pm}}{RT^2} = \frac{\Delta H^{\pm}}{RT^2} + \frac{1}{T}$

Then: $\frac{E_a}{RT^2} = \frac{\Delta H^{\pm}}{RT^2} + \frac{1}{T} \longrightarrow E_a = \Delta H^{\pm} + RT$

or $\Delta H^{\pm} = E_a - RT$

$$E_a = \Delta H^{\pm} + RT$$

or $\Delta H^{\pm} = E_a - RT$

The difference between the TST Activation Enthalpy and the Arrhenius Activation Energy is not especially large for reactions around room temperature.

For example, if ∆H‡ = 50.0 kJ/mol, then:

At 300 K: $E_a = 50.0\,kJ + (8.31x10^{-3}\,kJ/mol \cdot K)(300\,K) = 52.5\,kJ/mol$

i.e. approximately 5% higher

However, there is a major interest in high temperature kinetics (e.g. in combustion chemistry), in which reactions occur at 1500 K to 2000 K or higher.

At 1500 K: $E_a = 50.0\,kJ + (8.31x10^{-3}\,kJ/mol \cdot K)(1500\,K) = 62.5\,kJ/mol$

i.e. approximately 25% higher.

Thus, one observes a very significant deviation between the two parameters at elevated temperatures.

Relation between A and ∆S‡

$$\Delta H^{\pm} = E_a - RT$$

Let's substitute this relation into the TST Equation:

$$k = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{\Delta H^{\pm}}{RT}} = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{E_a - RT}{RT}} = \frac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{E_a}{RT}} e^{-\frac{-RT}{RT}} = \frac{RTe}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{E_a}{RT}}$$

Thus: $k = \frac{RTe}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{-\frac{E_a}{RT}} = Ae^{-\frac{E_a}{RT}}$

This gives: $A = \frac{RTe}{N_A h} e^{\frac{\Delta S^{\pm}}{R}}$

Therefore, we see that $A \propto \frac{RTe}{N_A h} e^{\frac{\Delta S^{\pm}}{R}}$ showing that the Arrhenius pre-exponential factor is an indirect measure of the Activation Enthalpy.

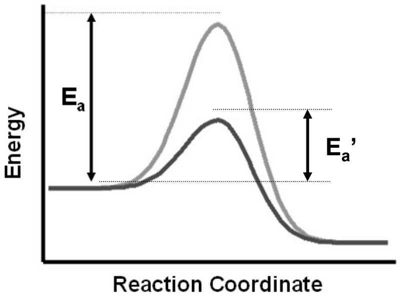
It is instructive to evaluate A (at room temperature) for $\Delta S^\ddagger = 0$:

$$A \propto \frac{RTe}{N_A h} e^{\frac{\Delta S^\ddagger}{R}} = \frac{(8.31\,J/mol\cdot K)(298\,K)(2.72)}{(6.02x10^{23}\,mol^{-1})(6.63x10^{-34}\,J\cdot s)} e^{0} = 1.7x10^{13}\,s^{-1}$$

Therefore, as a rule of thumb, if an experimental activation energy is:
$A < 1.7x10^{13}\ s^{-1} \rightarrow \Delta S^\ddagger < 0$, and
$A > 1.7x10^{13}\ s^{-1} \rightarrow \Delta S^\ddagger > 0$

A	**$\Delta S^\ddagger$**
$1x10^{16}$	+52 J/mol-K
$1x10^{15}$	+34
$1x10^{14}$	+15
$1x10^{13}$	-4
$1x10^{12}$	-24

Catalysis



$$k = Ae^{-\frac{E_a}{RT}}$$

We learned that k, and hence the reaction rate, can be increased by raising the temperature.

At higher temperatures, a greater fraction of collisions have an energy greater than the activation energy, E_a.

A second way to increase the rate of a reaction is to add a ***catalyst***.

This is a species which increases the reaction rate without being consumed in the reaction.

It accomplishes this by providing an alternative reaction pathway with a lower activation energy, E_a'.

Accounting for the Rate Laws

Most reactions require more than a single step. The reaction mechanism is the detailed series of individual steps required for transformation of the reactants to products.

Elementary Reactions

Sometimes, a reaction occurs in a single step. In this case, the rate law can be written immediately by inspection of the reaction stoichiometry.

$$H_2 + I_2 \xrightarrow{k} 2HI$$

$$R = k[H_2][I_2]$$

Note that the converse is ***not*** necessarily true;
i.e. if the experimental rate law follows the stoichiometry of the overall reaction, the mechanism may still be more than a single step.

Elementary First Order Reactions

Consider the simple first order reaction: $A \rightarrow P$

If it is an elementary reaction, the rate law is: $\text{Rate} = -\frac{d[A]}{dt} = k[A]$

Assuming that $[A](t=0) = [A]_o$ and $[P](t=0) = 0$, this equation integrates to:

$$[A] = [A]_o e^{-kt}$$

One can also determine [P] from the relation: $[P] = [A]_o - [A]$

$$[P] = [A]_o - [A] = [A]_o - [A]_o e^{-kt} \quad \text{or} \quad [P] = [A]_o\left(1 - e^{-kt}\right)$$

Thus we see that:

(1) [A] decreases exponentially from $[A]_o$ to 0

(2) Simultaneously, [B] increases exponentially from 0 to $[A]_o$

Consecutive First Order Reactions

Consider two consecutive first order reactions: $A \xrightarrow{k_1} I \xrightarrow{k_2} P$

The initial reactant, A, forms an intermediate, I, when then reacts to form the product, P.

The rate equations for each species are:

$$\frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[I]}{dt} = +k_1[A] - k_2[I] \qquad \frac{d[P]}{dt} = +k_2[I]$$

Reactant Concentration, [A]

This integrates fairly easily

$$\frac{d[A]}{dt} = -k_1[A] \longrightarrow \boxed{[A] = [A]_o e^{-k_1 t}}$$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P \qquad \frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[I]}{dt} = +k_1[A] - k_2[I] \qquad \frac{d[P]}{dt} = +k_2[I]$$

Intermediate Concentration, [I]

Plug in concentration, [A]

$$\frac{d[I]}{dt} = +k_1[A] - k_2[I] \longrightarrow \frac{d[I]}{dt} = +k_1[A]_o e^{-k_1 t} - k_2[I]$$

This is an inhomogeneous first order differential equation, which can be solved using standard (but advanced) techniques to yield:

$$\boxed{[I] = \frac{k_1}{k_2 - k_1}[A]_o \left\{e^{-k_1 t} - e^{-k_2 t}\right\}}$$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P \qquad \frac{d[A]}{dt} = -k_1[A] \qquad \frac{d[I]}{dt} = +k_1[A] - k_2[I] \qquad \frac{d[P]}{dt} = +k_2[I]$$

Product Concentration, [P]

$$\frac{d[P]}{dt} = +k_2[I]$$

One can plug in [I] and solve this differential equation.
However, it's easier to just use: $[P] = [A]_o - [A] - [I]$

This yields: $$\boxed{[P] = [A]_o \left\{ 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right\}}$$

Yecch!!!! However, you do NOT have to memorize these results.

Concentrations at $t = 0$ and $t \to \infty$

$$[A] = [A]_o e^{-k_1 t}$$

$[A](t=0) = [A]_o$

$[A](t\to\infty) = 0$

$$[I] = \frac{k_1}{k_2 - k_1}[A]_o \left\{ e^{-k_1 t} - e^{-k_2 t} \right\}$$

$[I](t=0) = 0$

$[I](t\to\infty) = 0$

$$[P] = [A]_o \left\{ 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right\}$$

$[P](t=0) = 0$

$[P](t\to\infty) = [A]_o$

Note that the concentrations of all three species at the start and end of the reaction are the values that one expects physically.

[A] decreases monotonically towards 0

[I] first increases and then decreases back towards 0

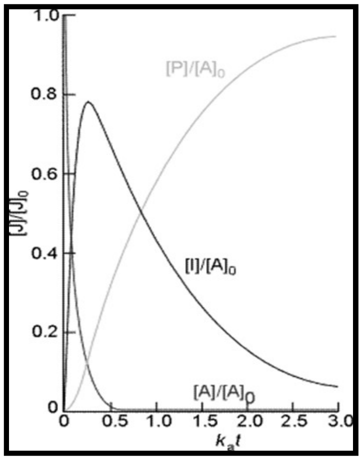
[P] increases monotonically towards $[A]_o$

Limiting Case: $k_1 >> k_2$ $A \xrightarrow{k_1} I \xrightarrow{k_2} P$

One expects that [A] will drop very rapidly towards 0 and [I] should rise quickly up to almost $[A]_o$

One then has a simple first order reaction:
[I] will drop exponentially towards 0

[P] will rise exponentially towards $[A]_o$



Limiting Case: $k_2 >> k_1$ $A \xrightarrow{k_1} I \xrightarrow{k_2} P$

One expects that [I] will rise only very slightly from 0 because it will be used up almost immediately by the second, very fast reaction.

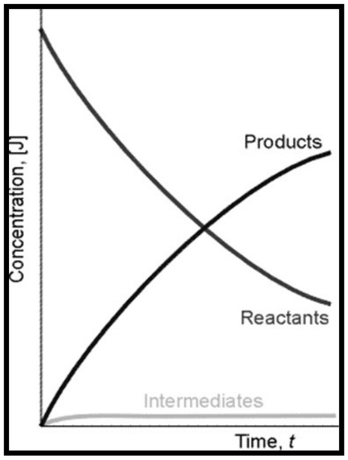
One expects that:

[A] will drop exponentially from $[A]_o$

[I] will rise slightly, but remain constant

[P] will rise exponentially towards $[A]_o$

We shall consider this limiting case in more detail soon. It represents a very good introduction to the Steady State Approximation.



Mechanisms and Rate Laws

We have already seen that if a reaction involves only a single elementary step, then the rate law may be written directly from the reaction stoichiometry.

Sometimes, a reaction occurs in a single step. In this case, the rate law can be written immediately by inspection of the reaction stoichiometry.

$$H_2 + I_2 \rightarrow 2HI$$

$$R = k[H_2][I_2]$$

However, more commonly, a reaction occurs in a **series** of elementary steps, in which case the rate law may differ significantly from the reaction stoichiometry

Slow Rate Determining Step (RDS)

$$2H_2O_2(aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g)$$

$$\cancel{R \neq k[H_2O_2]^2}$$

Observed Rate Law: $R = k[H_2O_2][I^-]$

Mechanism: (1) $H_2O_2 + I^- \xrightarrow{k} H_2O + IO^-$ Slow **RDS**

(2) $IO^- + H_2O_2 \rightarrow H_2O + O_2 + I^-$ Fast

$$R = d[O_2]/dt \approx d[IO^-]/dt \boxed{= k[H_2O_2][I^-]}$$

Pre-Equilibrium: Hydrolysis of Sucrose

$$\text{Sucrose} + H_2O \xrightarrow{[H^+]} \text{Glucose} + \text{Fructose}$$ Catalyzed by $[H^+]$

Observed Rate Law: $R = k[\text{Suc}][H^+][H_2O]$

Mechanism: (1) $\text{Suc} + H^+ \overset{\mathbf{K}}{\rightleftarrows} \text{SucH}^+$ Fast Pre-Equilibrium

(2) $\text{SucH}^+ + H_2O \xrightarrow{\mathbf{k_1}} \text{Glu} + \text{Fru} + H^+$ Slow RDS

$$R = d[\text{Glu}]/dt = k_1[\text{SucH}^+][H_2O] \boxed{= k_1K[\text{Suc}][H^+][H_2O]}$$

$$K = \frac{[\text{SucH}^+]}{[\text{Suc}][H^+]}$$

$$\downarrow$$

$$[\text{SucH}^+] = K[\text{Suc}][H^+]$$

For the reaction, $Hg_2^{2+}(aq) + Tl^{3+}(aq) \rightarrow 2\ Hg^{2+}(aq) + Tl^+(aq)$

the observed rate law is: $r = \frac{d[Tl^+]}{dt} = k'\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]}$

Show that the mechanism below is consistent with the observed rate law.

Mechanism: $Hg_2^{2+} \overset{K}{=} Hg + Hg^{2+}$ Fast Pre-Equilibrium

$Hg + Tl^{3+} \xrightarrow{k_2} Hg^{2+} + Tl^+$ Slow RDS

$$r = \frac{d[Tl^+]}{dt} = k_2K\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]} \boxed{= k'\frac{[Hg_2^{2+}][Tl^{3+}]}{[Hg^{2+}]}}$$

The Steady-State Approximation

In a multi-step reaction, it will often occur that the intermediate is very unstable, and decays rapidly to product.

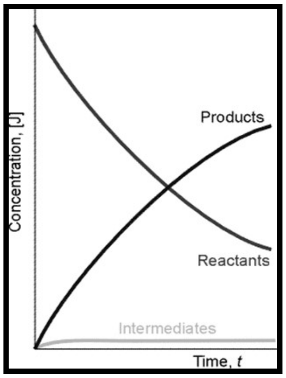
In these cases, it is valid to assume that, after an initial induction period, the concentration of the intermediate will remain approximately constant and very low.

One may then solve for the rate law by assuming that the rate of change of the intermediate is approximately zero.

A classic case where the steady-state approximation is valid is for consecutive first order reactions when the rate constant for the step removing the intermediate, I, is much greater than the rate constant for creating the intermediate:

Limiting Case: $k_2 >> k_1$ $A \xrightarrow{k_1} I \xrightarrow{k_2} P$

Limiting Case: $k_2 >> k_1$ $A \xrightarrow{k_1} I \xrightarrow{k_2} P$



We will use the steady-state approximation on [I] to determine the concentrations, [I] and [P] as a function of time.

We will then compare the result with the exact solution, which was presented earlier.

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

$$\frac{d[A]}{dt} = -k_1[A] \longrightarrow [A] = [A]_o e^{-k_1 t}$$

Apply the Steady-State Approximation: d[**I**]/dt ≈ 0

$$\frac{d[I]}{dt} = +k_1[A] - k_2[I] \approx 0 \longrightarrow [I] = \frac{k_1}{k_2}[A] = \frac{k_1}{k_2}[A_o]e^{-k_1 t}$$

$$\frac{d[P]}{dt} = +k_2[I] = +k_2\left\{\frac{k_1}{k_2}[A]_o e^{-k_1 t}\right\} = k_1[A]_o e^{-k_1 t}$$

This integrates to (in class): $\boxed{[P] = [A]_o\left\{1 - e^{-k_1 t}\right\}}$

$$A \xrightarrow{k_1} I \xrightarrow{k_2} P$$

Exact Solution	**Approximate Solution**
$[A] = [A]_o e^{-k_1 t}$	$[A] = [A]_o e^{-k_1 t}$
$[I] = \frac{k_1}{k_2 - k_1}[A]_o\left\{e^{-k_1 t} - e^{-k_2 t}\right\}$	$[I] = \frac{k_1}{k_2}[A] = \frac{k_1}{k_2}[A_o]e^{-k_1 t}$
$[P] = [A]_o\left\{1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1}\right\}$	$[P] = [A]_o\left\{1 - e^{-k_1 t}\right\}$

As we show **in class**, the exact solutions for the concentrations of [I] and [P] reduce to the approximate solutions using the steady-state approach in the limit that $k_2 >> k_1$

The steady-state approximation is a less restrictive mechanism than assuming a rapid pre-equilibrium. Let's apply this method to a practical example

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

Observed Rate Law: $R = k'[NO]^2[O_2]$ at low $[O_2]$

$R = k''[NO]^2$ at high$[O_2]$

Mechanism: $2NO \xrightarrow{k_1} N_2O_2$ Create Intermediate

$N_2O_2 \xrightarrow{k_{-1}} 2NO$ Reverse of first step

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$ Slow RDS

Shorthand: $2NO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2$

$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$$

$$R = k_2[N_2O_2][O_2] \boxed{= \frac{k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]}}$$

Steady-State Approximation on N_2O_2

$$\Delta[N_2O_2]/\Delta t = 0 = + k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2]$$

$$\downarrow$$

$$[N_2O_2]\{k_{-1} + k_2[O_2]\} = k_1[NO]^2$$

$$\downarrow$$

$$[N_2O_2] = \frac{k_1[NO]^2}{k_{-1} + k_2[O_2]}$$

$$R = \frac{k_1 k_2 [NO]^2 [O_2]}{k_{-1} + k_2[O_2]}$$

Limiting Cases

Low $[O_2]$
$k_2[O_2] << k_{-1}$

$$R = \frac{k_1 k_2 [NO]^2 [O_2]}{k_{-1} + \cancel{k_2[O_2]}} = (k_1 k_2/k_{-1})[NO]^2[O_2] = k'[NO]^2[O_2]$$

Note: If we had employed the approximation of a rapid-preequilibrium to this reaction, we would have obtained the above rate equation.

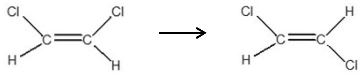
High $[O_2]$
$k_2[O_2] >> k_{-1}$

$$R = \frac{k_1 k_2 [NO]^2 [O_2]}{\cancel{k_{-1}} + k_2[O_2]} = k_1[NO]^2 = k''[NO]^2$$

Unimolecular Gas Phase Reactions

$A(g) \rightarrow$ Products(g)

Examples: $N_2O_5(g) \rightarrow NO_2(g) + NO_3(g)$ **Decompositon**



Isomerization

Observed Rate Law: $R = k'[A]^2$ at low [A]

$R = k''[A]$ at high [A]

Mechanism: $A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$ **A* is an "activated" molecule**

$A^* \xrightarrow{k_2}$ Products

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A^* + A$$

$$A^* \xrightarrow{k_2} \text{Products}$$

If one applies the Steady-State approximation to the concentration, [A*], it can be shown (**in class**) that:

$$R = \Delta[\text{Products}]/\Delta t = \frac{k_1 k_2 [A]^2}{k_2 + k_{-1}[A]}$$

Limiting Cases

low [A]: $k_{-1}[A] \ll k_2$

$$R = \frac{k_1 k_2 [A]^2}{k_2 + \cancel{k_{-1}[A]}}$$

$$R = k_1[A]^2 = k'[A]^2$$

high [A]: $k_{-1}[A] \gg k_2$

$$R = \frac{k_1 k_2 [A]^2}{\cancel{k_2} + k_{-1}[A]}$$

$$R = (k_1 k_2 / k_{-1})[A] = k''[A]$$

Photochemistry

Many important reactions are initiated photochemically; i.e. via the absorption of a photon of light.

Unimolecular Reactions: $A + h\nu \rightarrow A^* \rightarrow$ Products

Bimolecular Reactions: $A + h\nu \rightarrow A^* + B \rightarrow$ Products

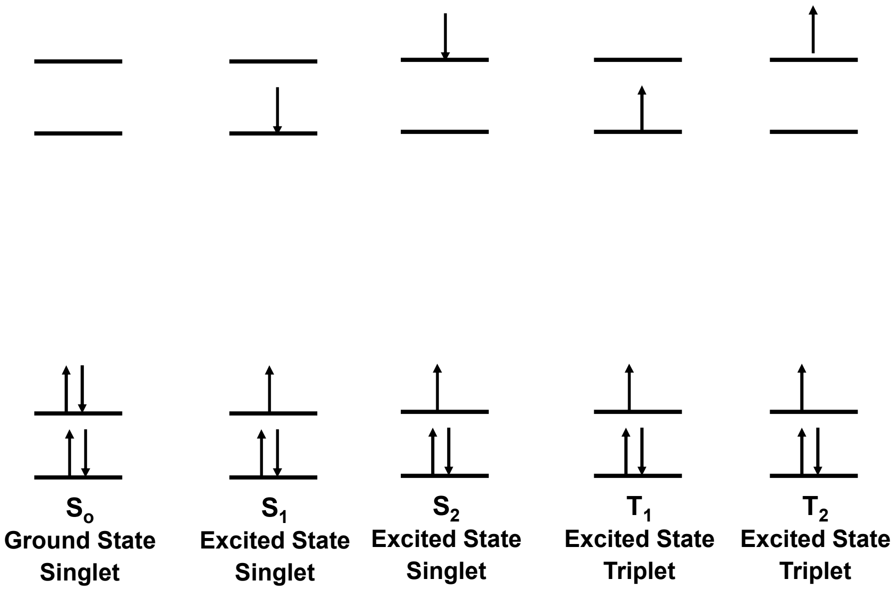
Two advantages of photochemical reactions are that:

1. The reaction may not occur thermally
2. The photochemically induced reaction may be more selective than the thermal reaction of the same substrate(s)

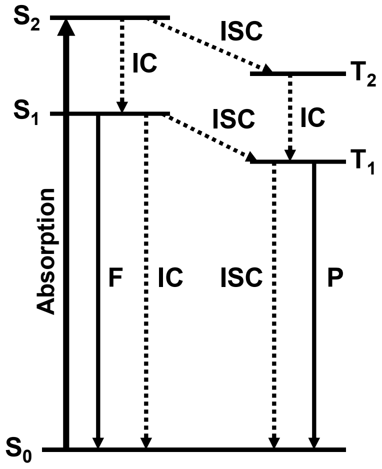
A number of primary photochemical deexcitation processes compete with the formation of products by the excited state.

Therefore, it is important to consider the time scales of the various excitation and decay processes of excited state molecules.

Excited Electronic States



Decay Processes



Non-Radiative Decay

IC Internal Conversion
$S \rightarrow S$ or $T \rightarrow T$

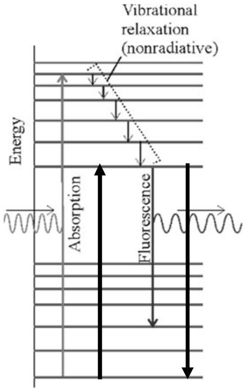
ISC Inter-System Crossing
$S \rightarrow T$ or $T \rightarrow S$

Radiative Decay

F Fluorescence
$S_1 \rightarrow S_0$ Emission

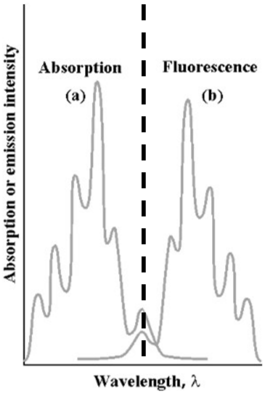
P Phosphorescence
$T_1 \rightarrow S_0$ Emission

Relation Between Absorption and Fluorescence



E_{min} Abs. ν_{min}

E_{max} Fluor. ν_{max}



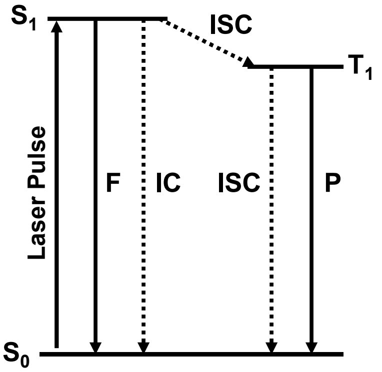
$\lambda \rightarrow$

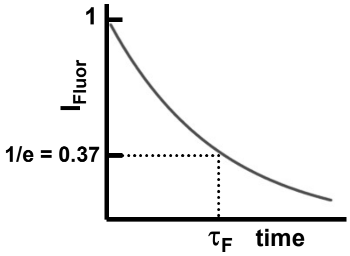
$\leftarrow \nu$

The fluorescence spectrum occurs at lower frequency than the UV (or visible) absorption spectrum.

They are (approximately) mirror images of each other.

Fluorescence and Phosphorescence Lifetimes





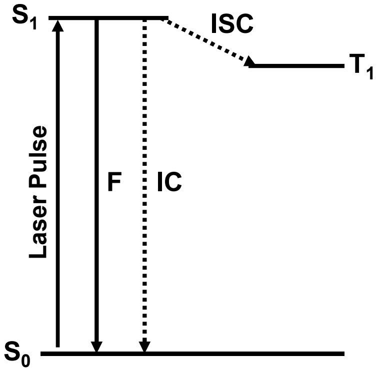
τ_F = Fluorescence Lifetime
τ_F = 1 - 100 nanoseconds (ns)

τ_P = Phosporescence Lifetime
τ_P = 1 ms - days

$\tau_P \gg \tau_F$ because Triplet-Singlet transitions are “spin forbidden”.

Because phosphorescence lifetimes are so extremely long, one rarely observes phosphorescence in aqueous solutions;
the Triplet state is depleted by collisional processes.

Transient Singlet State Kinetics



Once molecules have been excited from S_0 to S_1 by a transient laser pulse, they will have three modes of decays:

1. Fluorescence: $S_1 \xrightarrow{k_F} S_0$
2. Intersystem Crossing: $S_1 \xrightarrow{k_{ISC}} T_1$
3. Internal Conversion: $S_1 \xrightarrow{k_{IC}} S_0$

The overall rate of change of $[S_1]$ is given by:

$$\frac{d[S_1]}{dt} = -k_F[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] = -k_0[S_1]$$

where $k_0 = k_F + k_{ISC} + k_{IC} = \dfrac{1}{\tau_0}$

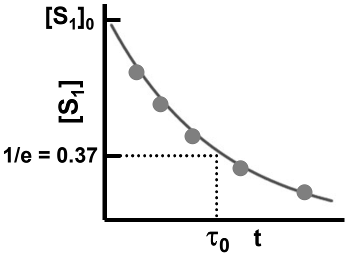
$$\frac{d[S_1]}{dt} = -k_F[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] = -k_0[S_1] \quad \text{where} \quad k_0 = k_F + k_{ISC} + k_{IC} = \frac{1}{\tau_0}$$

This is straightforward to integrate to get:

$$\ln\left(\frac{[S_1]}{[S_1]_0}\right) = -k_0 t \quad \text{or} \quad [S_1] = [S_1]_0 e^{-k_0 t} = [S_1]_0 e^{-k_0 t} = [S_1]_0 e^{-\frac{t}{\tau_0}}$$

Thus $[S_1]$ decays exponentially from its initial value with a decay time, τ_0.

One can monitor $[S_1]$ as a function of time from the fluorescence intensity, I_F.



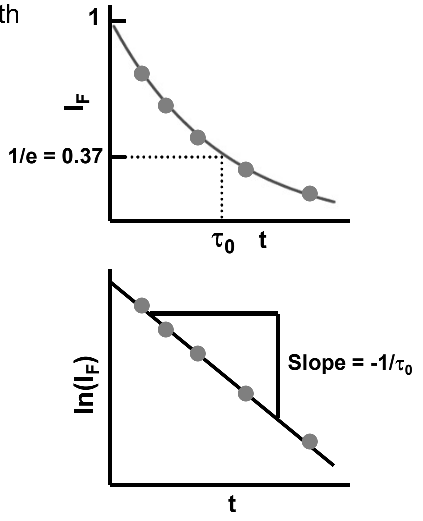
Singlet State Lifetimes From Pulsed Laser Fluorescence

1. Excite molecules from S_0 to S_1 with a short (<1 ns) laser pulse.
2. Monitor the fluorescence intensity as a function of time.

$$I_F = (I_F)_o e^{-\frac{t}{\tau_0}}$$

$$\ln(I_F) = \ln(I_F)_o + \ln(e^{-\frac{t}{\tau_0}})$$

$$\underbrace{\boxed{\ln(I_F)}}_{y} = \ln(I_F)_o - \underbrace{\frac{1}{\tau_0}}_{m = -1/\tau_0}\underbrace{\boxed{t}}_{x}$$



The Quantum Yield (Φ)

The quantum yield for a process is a measure of the efficiency of absorbed photons in inducing the process to occur.

The quantum yield can be defined either in terms of

(a) the rate of the process relative to the rate of photon absorption, or

(b) the number of moles undergoing the process relative to the number of moles of photons absorbed.

Rate: $$\Phi_{proc} = \frac{Rate\ of\ Process}{Rate\ of\ photon\ absorption} = \frac{Rate\ of\ Process}{I_{abs}}$$

Amount:* $$\Phi_{proc} = \frac{Moles\ of\ Molecules\ Undergoing\ Process}{Moles\ of\ Photons\ Absorbed}$$

*Notes: (1) One has an equivalent definition using molecules instead of moles.

(2) 1 mole of photons is often referred to as 1 einstein.

Rate: $\Phi_{proc} = \frac{Rate\ of\ Process}{Rate\ of\ photon\ absorption} = \frac{Rate\ of\ Process}{I_{abs}}$

Amount:* $\Phi_{proc} = \frac{Moles\ of\ Molecules\ Undergoing\ Process}{Moles\ of\ Photons\ Absorbed}$

Primary Processes

These are processes (such as fluorescence, phosphorescence, intersystem crossing, etc.) in which 1 absorbed photon can induce only 1 molecule to undergo the process.

For primary processes, $0 \leq \Phi_{process} \leq 1$

Secondary Processes

These are processes in which 1 absorbed photon can indirectly induce the process to occur multiple times. Typically, these are reactions.

For secondary processes, $0 \leq \Phi_{process} \leq \infty$

Chain reactions often have $\Phi_R > 1$

A Chain Reaction Quantum Yield: Chlorination of Methane

Reaction: $Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$

Mechanism: (1) $Cl_2 + h\nu \rightarrow 2\ Cl\bullet$ Chain Initiation
(2) $Cl\bullet + CH_4 \rightarrow HCl + CH_3\bullet$ Chain Propagation
(3) $CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$ Chain Propagation
(4) $Cl\bullet + Cl\bullet + M \rightarrow Cl_2 + M$ Chain Termination*

*M is an inert body to absorb excess translational energy.

$$\Phi_R = \frac{Moles\ of\ CH_3Cl\ Produced}{Moles\ of\ Photons\ Absorbed} \approx 1{,}000 - 10{,}000$$

Reaction Quantum Yield Examples

Example 1 (like Exer. 21.21a)

In a photochemical reaction, A → B + 3C, the quantum yield with 500 nm radiation is 160 mol/einstein (1 einstein = 1 mol of photons). After exposure of a sample of A to the light for a period of time, 0.36 mol of C was formed.

How many photons of light were absorbed during the time period.

$N_A = 6.02\text{x}10^{23}\ \text{mol}^{-1}$

$N_{ph} = 4.5\text{x}10^{20}$

Reaction Quantum Yield Examples

Example 2 (Exer. 21.22b)

In an experiment to measure the quantum yield of a photochemical reaction, the absorbing substance was exposed to 320 nm radiation from a 87.5 W source for 28.0 min. The intensity of the transmitted light was 25.7% that of the incident light.

As a result of irradiation, 0.324 mol of the absorbing substance decomposed.

Determine the reaction quantum yield, Φ_R.

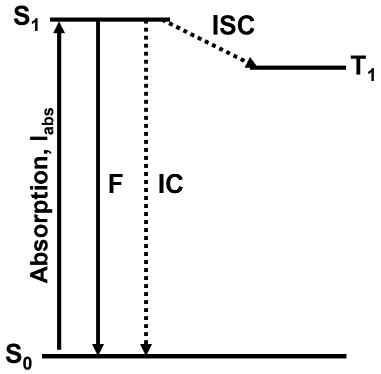
Additional Information:

$$E_{ph} = h\nu = \frac{hc}{\lambda(m)} = \frac{(6.63x10^{-34}\ J\cdot s)(3.00x10^{8}\ m/s)}{\lambda(m)} = \frac{1.99x10^{-25}\ J\cdot m}{\lambda(m)}$$

Note: This relation will be furnished on a test if needed.

$\Phi_R = 1.11$

Steady-State Singlet Kinetics: The Fluorescence Quantum Yield



In an experiment where there is continuous irradiation of the sample, the excited Singlet will reach a steady-state concentration, $[S_1]$.

We will perform the kinetic analysis to solve for the steady-state concentration and use the result to determine the fluorescence quantum yield, Φ_F

Processes

1. Photon Absorption: $S_0 \xrightarrow{I_{abs}} S_1$
2. Fluorescence: $S_1 \xrightarrow{k_F} S_0$
3. Intersystem Crossing: $S_1 \xrightarrow{k_{ISC}} T_1$
4. Internal Conversion: $S_1 \xrightarrow{k_{IC}} S_0$

Note: The rate of the absorption step is: $\frac{d[S_1]}{dt} = +I_{abs}$

---

1. Photon Absorption: $S_0 \xrightarrow{I_{abs}} S_1$
2. Fluorescence: $S_1 \xrightarrow{k_F} S_0$
3. Intersystem Crossing: $S_1 \xrightarrow{k_{ISC}} T_1$
4. Internal Conversion: $S_1 \xrightarrow{k_{IC}} S_0$

Steady-State concentration, $[S_1]$

$$\frac{d[S_1]}{dt} = 0 = +I_{abs} - k_F[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] = I_{abs} - k_0[S_1]$$

where (as before): $k_0 = \frac{1}{\tau_0} = k_F + k_{ISC} + k_{IC}$

Solving for $[S_1]$ yields $[S_1] = \frac{I_{abs}}{k_0} = \frac{I_{abs}}{k_F + k_{ISC} + k_{IC}}$

The Fluorescence Quantum Yield

$$[S_1] = \frac{I_{abs}}{k_F + k_{ISC} + k_{IC}} = \frac{I_{abs}}{k_0}$$

The fluorescence quantum yield is given by:

$$\Phi_F = \frac{Fluorescence\,Rate}{Photon\,Absorption\,Rate} = \frac{k_F[S_1]}{I_{abs}}$$

Substituting the expression for $[S_1]$ then yields:

$$\Phi_F = \frac{k_F[S_1]}{I_{abs}} = \frac{k_F}{I_{abs}}\left(\frac{I_{abs}}{k_F + k_{ISC} + k_{IC}}\right) = \frac{k_F}{k_F + k_{ISC} + k_{IC}} = \frac{k_F}{k_0} = k_F\tau_0$$

This result is intuitively reasonable, and shows that the quantum yield is the ratio of the fluorescence rate constant divided by the sum of rate constants for all S_1 depletion processes.

$$\Phi_F = \frac{k_F[S_1]}{I_{abs}} = \frac{k_F}{I_{abs}}\left(\frac{I_{abs}}{k_F + k_{ISC} + k_{IC}}\right) = \frac{k_F}{k_F + k_{ISC} + k_{IC}} = \frac{k_F}{k_0} = k_F\tau_0$$

Experimental determination of k_F

We saw recently that the singlet state lifetime, τ_0, can be obtained from a pulsed laser fluorescence decay experiment.

The lifetime so determined can be combined with the experimental fluorescence quantum yield to determine the molecule's fluorescence rate constant, k_F.

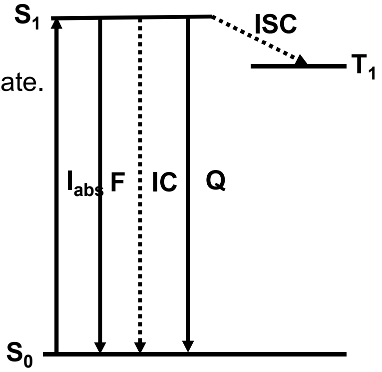
In a pulsed laser fluorescence experiment on liquid benzene the fluorescence intensity 150 ns after the experiment begins is 25% the intensity at the start of the experiment.

In a separate steady-state fluorescence experiment, it was determined that the fluorescence quantum yield in liquid benzene is 0.18

Determine (a) the singlet state lifetime, τ_0 (in ns), and (b) the fluorescence rate constant, k_F (in s^{-1}) in liquid benzene.

(a) τ_0 = 110 ns
(b) $k_F = 1.7\text{x}10^6$ s^{-1}

Excited State Quenching

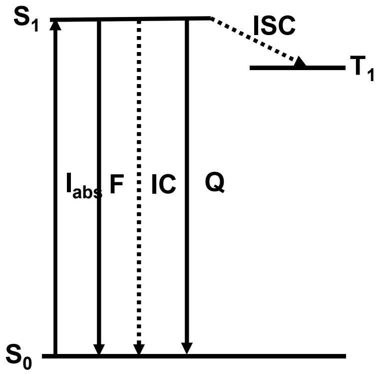


Earlier, we discussed that once a molecule has been excited to S_1, there are three mechanisms for deexcitation of the excited state.

1. Photon Absorption: $S_0 \xrightarrow{I_{abs}} S_1$
2. Fluorescence: $S_1 \xrightarrow{k_F} S_0$
3. Intersystem Crossing: $S_1 \xrightarrow{k_{ISC}} T_1$
4. Internal Conversion: $S_1 \xrightarrow{k_{IC}} S_0$

An additional deexcitation mechanism is the addition of a solute, called a quencher (Q), which can induce depopulation of the excited state.

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q$$



An additional mechanism is the addition of a solute, called a quencher (Q), which can induce depopulation of the excited state.

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q$$

The mechanisms of excited-state quenching include:

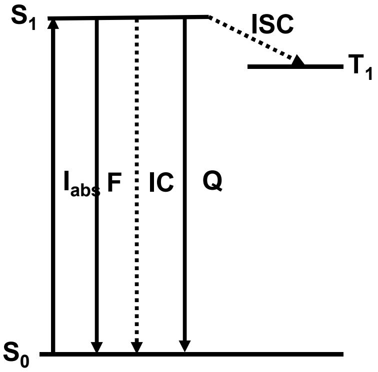
1. Collisional deactivation
2. Resonance Energy Transfer
3. Reaction
4. Spin-orbit coupling (triplet-state quenching)

The net effects of adding a quencher are:

A. The excited state lifetime is reduced (to below τ_0)
B. The fluorescence (or phosphorescence) quantum yield is reduced.

Below, we will develop a relation between the fluorescence yield with no quenching, $\Phi_{F,0}$, and the quantum yield with quencher added, Φ_F

1. Photon Absorption: $S_0 \xrightarrow{I_{abs}} S_1$
2. Fluorescence: $S_1 \xrightarrow{k_F} S_0$
3. Intersystem Crossing: $S_1 \xrightarrow{k_{ISC}} T_1$
4. Internal Conversion: $S_1 \xrightarrow{k_{IC}} S_0$
5. Quenching: $S_1 + Q \xrightarrow{k_Q} S_0 + Q$



We will use a procedure analogous to the one used earlier to obtain an expression for the fluorescence quantum yield in the presence of a quencher.

Steady-State concentration, [S$_1$]

$$\frac{d[S_1]}{dt} = 0 = +I_{abs} - k_F[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] - k_Q[S_1][Q]$$

Steady-State concentration, [S$_1$]

$$\frac{d[S_1]}{dt} = 0 = +I_{abs} - k_F[S_1] - k_{ISC}[S_1] - k_{IC}[S_1] - k_Q[S_1][Q]$$

$$0 = +I_{abs} - [S_1]\left\{k_F + k_{ISC} + k_{IC} + k_Q[Q]\right\} = +I_{abs} - [S_1]\left\{k_0 + k_Q[Q]\right\}$$

where $k_0 = k_F + k_{ISC} + k_{IC} = \frac{1}{\tau_0}$

Therefore: $[S_1] = \frac{I_{abs}}{k_0 + k_Q[Q]}$

The fluorescence quantum yield in the presence of Q is given by:

$$\Phi_F = \frac{Fluorescence\,Rate}{Photon\,Absorption\,Rate} = \frac{k_F[S_1]}{I_{abs}} = \frac{k_F}{I_{abs}}\left(\frac{I_{abs}}{k_0 + k_Q[Q]}\right) = \frac{k_F}{k_0 + k_Q[Q]}$$

The fluorescence quantum yield in the presence of Q is given by:

$$\Phi_F = \frac{Fluorescence\,Rate}{Photon\,Absorption\,Rate} = \frac{k_F[S_1]}{I_{abs}} = \frac{k_F}{I_{abs}}\left(\frac{I_{abs}}{k_0 + k_Q[Q]}\right) = \frac{k_F}{k_0 + k_Q[Q]}$$

With no quencher (i.e. [Q] = 0), the quantum yield is: $\Phi_{F,0} = \frac{k_F}{k_0}$

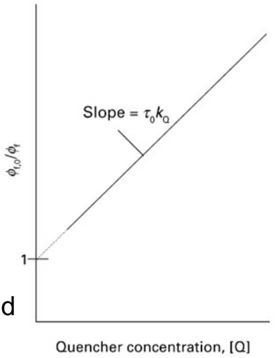
Thus, we see that the presence of a molecule which can quench S_1 reduces the fluorescence quantum yield.

The Stern-Volmer Equation

Let's calculate the ratio, $\Phi_{F,0}/\Phi_F$:

$$\frac{\Phi_{F,0}}{\Phi_F} = \frac{\frac{k_F}{k_0}}{\frac{k_F}{k_0 + k_Q[Q]}} = \frac{k_0 + k_Q[Q]}{k_0} = 1 + \frac{k_Q[Q]}{k_0} = 1 + \tau_0 k_Q[Q]$$

$$\frac{\Phi_{F,0}}{\Phi_F} = 1 + \tau_0 k_Q[Q]$$



Stern-Volmer Equation

We see from this equation that if we measure Φ_F as a function of [Q], one gets a straight line with: Slope = $\tau_0 k_Q$

If the singlet state lifetime, τ_0 , has been measured in a pulsed laser fluorescence experiment, then the Stern-Volmer plot may be used to determine the quenching rate constant, k_Q.

Laser fluorescence experiments require relatively expensive equipment, and are not available to all researchers.

A common application is to estimate k_Q and then use the plot to obtain a value for the singlet state lifetime, τ_0.

One of the methods to estimate k_Q is to use the theory of Diffusion Controlled Reactions (Sect. 22.2 of the text)

Example: Singlet State Lifetime from Fluorescence Quenching

The fluorescence quantum yield for 2-aminopurine in water is 0.32. When a quencher is added to the solution, with [Q] = 0.02 M, the quantum yield is reduced to 0.14

The quenching rate constant is: $k_Q = 2.5\text{x}10^9\ M^{-1}s^{-1}$

Calculate the singlet state lifetime of 2-aminopurine (in ns).

$\tau_0 = 25$ ns

Bimolecular Reactions from S_1

We commented that one mechanism by which a second molecule can quench the fluorescence of a molecule in the excited singlet state is to react with it:

$$A(S_1) + B \xrightarrow{k_R} \mathrm{Pr}\,od \quad \text{or} \quad S_1 + B \xrightarrow{k_R} \mathrm{Pr}\,od$$

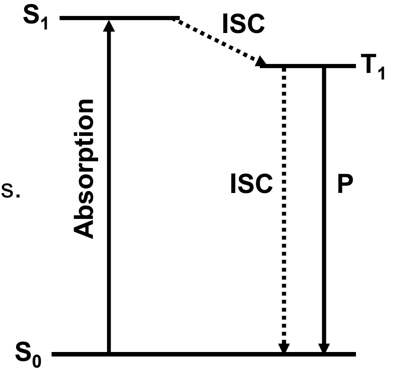
The fluorescence quantum yield from S_1 will be reduced by the presence of the second reactant, B. It is straightforward to show that the Stern-Volmer Equation becomes:

$$\frac{\Phi_{F,0}}{\Phi_F} = 1 + \tau_0 k_R [B]$$

Thus, if one has the measured fluorescence lifetime (in the absence of the second reactant), τ_0 , and measures the fluorescence quantum yield as a function of [B], it is straightforward to use the above equation to determine the bimolecular rate constant, k_R,for the reaction.

The Triplet State (T_1)

Triplet Lifetime, τ_{T1}



After molecules are excited by light from S_0 to S_1, some of the molecules will intersystem cross to T_1.

They can then return to S_0 via two processes.

1. Phosphorescence: $T_1 \xrightarrow{k_P} S_0$
2. Intersystem Crossing: $T_1 \xrightarrow{k_{ISC}} S_0$

The kinetic rate equation is:

$$\frac{d[T_1]}{dt} = -k_P[T_1] - k_{ISC}[T_1] = -k_{T_1}[T_1] = -\frac{1}{\tau_{T_1}}[T_1]$$

This integrates to: $[T_1] = [T_1]_0 e^{-k_{T_1}t} = [T_1]_0 e^{-\frac{t}{\tau_{T_1}}}$

where τ_{T1} is the triplet state lifetime, given by: $\tau_{T_1} = \frac{1}{k_{T_1}} = \frac{1}{k_P + k_{ISC}}$

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Because the $T_1 \rightarrow S_0$ transition is spin-forbidden, triplet state lifetimes, τ_{T1}, are generally many orders of magnitude longer than singlet lifetimes, τ_0

Typical Singlet State Lifetimes: $\tau_0 \approx 1 - 100$ ns

Typical Triplet State Lifetimes: $\tau_{T1} \approx 1$ ms - days

Phosphorescence in Liquid Solution

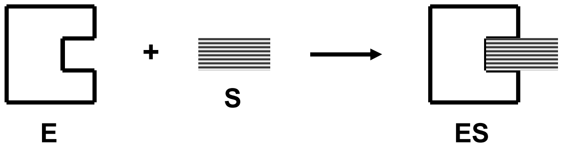
This is a short section. Phosphorescence is virtually never observed in liquid phase solutions.

This is because triplet state lifetimes are so long that deexcitation by collisions with solvent molecules will depopulate T_1 very efficiently, completely quenching the phosphorescence.

However, one does observe phosphorescence from molecules in the gas phase and in frozen glasses at 77 K.

Enzyme Kinetics: Introduction

- Enzymes are proteins
- Enzymes are highly efficient catalysts; up to 10^6 increase in rate
- Enzymes are highly specific catalysts; i.e. they have high selectivity
- The reactants are called "Substrates" [S]
- The rate of an enzyme catalyzed reaction is called the "velocity" [v]
- The "active site" of the enzyme (which binds the substrate) is only a few amino acid residues; the remainder of the protein provides the three dimensional structure



Observed Rate Law: $v = k'[E_o][S]$ at low [S]

$v = k''[E_o]$ at high [S] (independent of [S])

$[E_o]$ is the initial enzyme concentration.

Michaelis-Menten Mechanism (1913) Extended by Briggs-Haldane (1925)

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \qquad \text{followed by} \qquad ES \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} E + P$$

The k_{-2} step, which converts P back to the intermediate,, complicates the experimental kinetics and the derived rate law.

To avoid this complication, one measures only the initial rates, for the first 3%-5% of the reaction, in which case one may ignore the k_{-2} step.

$$v_o = (\Delta[P]/\Delta t)_{init}$$

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_2} E + P$$

$$\boxed{v_o = k_2[ES] = \frac{k_2[E]_o[S]}{K_M + [S]} \qquad K_M = \frac{k_{-1} + k_2}{k_1}}$$

SS on [ES]: $\Delta[ES]/\Delta t = 0 = + k_1[E][S] - k_{-1}[ES] - k_2[ES]$

$$0 = + k_1\{[E]_o - [ES]\}[S] - k_{-1}[ES] - k_2[ES]$$

$$0 = + k_1[E]_o[S] - \{k_{-1} + k_2 + k_1[S]\}[ES]$$

$$\{k_{-1} + k_2 + k_1[S]\}[ES] = + k_1[E]_o[S]$$

$$[ES] = \frac{k_1[E]_o[S]}{k_{-1} + k_2 + k_1[S]} = \frac{[E]_o[S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \boxed{\frac{[E]_o[S]}{K_M + [S]}}$$

Michaelis Constant

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

Better to determine [ES] in terms of $[E]_o$ than [E]

$$[E]_o = [E] + [ES] \longrightarrow [E] = [E]_o - [ES]$$

$$v_o = \frac{k_2[E]_o[S]}{K_M + [S]} \qquad K_M = \frac{k_{-1} + k_2}{k_1}$$

OR $v_o = \frac{V_m[S]}{K_M + [S]}$ $V_m = k_2[E]_o$ = maximum velocity

Limiting Cases

Low [S] $v_o = \frac{k_2}{K_M}[E]_o[S]$ For fixed $[E]_o$, $v_o \propto [S]$

High [S] $v_o = k_2[E]_o = V_m$ For fixed $[E]_o$, v_o is constant

V_m is the maximum velocity

[S] = K_M $v_o = \frac{V_m K_M}{K_M + K_M} = \frac{V_M}{2}$

Interpretation of Parameters

V_m: Maximum Velocity

$k_2 = V_m / [E]_o$ k_2 is the "turnover number".
This represents the moles of Product produced per unit time per mole of Enzyme.

Units: 1 / time; e.g. s^{-1}

K_M: Michaelis Constant

$$K_M = \frac{k_{-1} + k_2}{k_1} \approx \frac{k_{-1}}{k_1} \approx K_{Diss}$$

if $k_2 \ll k_{-1}$

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ES$$

$$K_M \approx K_{Diss} = \frac{k_{-1}}{k_1}$$

Units: $time^{-1} / time^{-1} \cdot M^{-1} = M$

Also: mM, μM, nM

Small K_M: Strong Binding

Large K_M: Weak Binding

“Practical” Interpretation of K_M

$$v_o = \frac{V_m[S]}{K_M + [S]}$$

[S]	v_o	
$0.5 \bullet K_M$	$0.33 \bullet V_m$	
$1 \bullet K_M$	$0.50 \bullet V_m$ ⟵	**50% of max. activity at [S] = K_M**
$5 \bullet K_M$	$0.83 \bullet V_m$	
$10 \bullet K_M$	$0.91 \bullet V_m$ ⟵	**90% of max. activity at [S] = $10 \bullet K_M$**
$50 \bullet K_M$	$0.98 \bullet V_m$	

Determination of the Michaelis-Menten Parameters

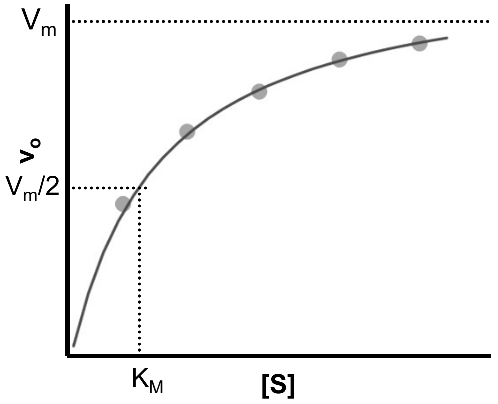
$$v_o = \frac{V_m[S]}{K_M + [S]}$$

As: $[S] \to 0$, $v_o \to 0$

$[S] \to \infty$, $v_o \to V_m$

At: $[S] = K_M$, $v_o = V_m/2$

[S]	v_o
0.10 μM	**33 μM/s**
0.20	**46**
0.30	**53**
0.40	**57**
0.50	**60**



This method is ***inaccurate !!***

The Lineweaver-Burk (Double Reciprocal) Plot

$$v_o = \frac{V_m[S]}{K_M + [S]}$$

$$\frac{1}{v_o} = \frac{K_M + [S]}{V_m[S]} = \frac{K_M}{V_m[S]} + \frac{[S]}{V_m[S]}$$

$$\boxed{\frac{1}{v_o} = \frac{K_M}{V_m}\frac{1}{[S]} + \frac{1}{V_m}}$$

Lineweaver-Burk
Equation

$$\underset{y}{\boxed{\frac{1}{v_o}}} = \underset{\uparrow}{\frac{K_M}{V_m}}\underset{x}{\boxed{\frac{1}{[S]}}} + \underset{\uparrow}{\frac{1}{V_m}}$$

$m = K_M/V_m$ $b = 1/V_m$

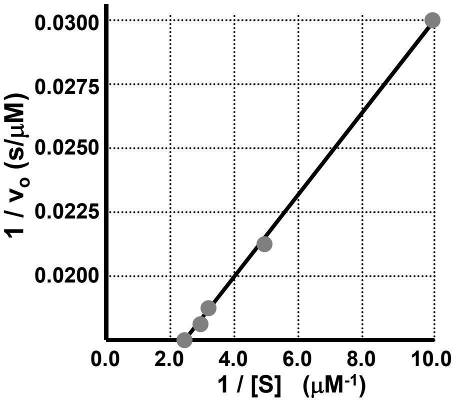
This is the equation of a straight line:
y = m•x + b

[S]	v_o
0.10 μM	**33 μM/s**
0.20	**46**
0.30	**53**
0.40	**57**
0.50	**60**

1/[S]	$1/v_o$
10.0 $(\mu M)^{-1}$	**0.030 s/μM**
5.00	**0.022**
3.33	**0.019**
2.50	**0.018**
2.00	**0.017**

$$\underset{y}{\boxed{\frac{1}{v_o}}} = \underset{\uparrow}{\frac{K_M}{V_m}}\underset{x}{\boxed{\frac{1}{[S]}}} + \underset{\uparrow}{\frac{1}{V_m}}$$

$m = K_M/V_m$ $b = 1/V_m$

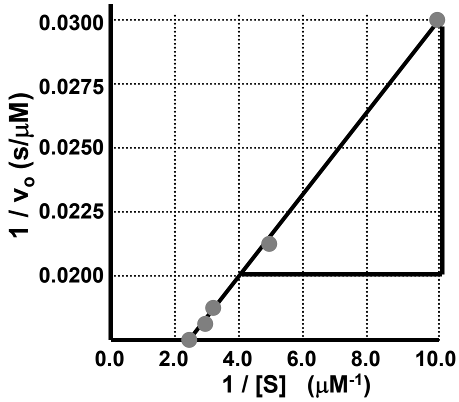


$$\underset{y}{\boxed{\frac{1}{v_o}}} = \underset{\uparrow}{\frac{K_M}{V_m}}\underset{x}{\boxed{\frac{1}{[S]}}} + \underset{\uparrow}{\frac{1}{V_m}}$$

m = K_M/V_m **b = $1/V_m$**

$$m = \frac{\Delta(1/v_o)}{\Delta(1/[S])} = \frac{(0.030-0.020)\text{s}/\mu\text{M}}{(10.0-4.0)\ \mu\text{M}^{-1}}$$

$= 1.67\text{x}10^{-3}$ s



b = $(1/v_o)_1$ - m•$(1/[S]_1)$
= 0.020 s/μM - $1.67\text{x}10^{-3}$ s•4.0 μM^{-1}
= 0.0133 s/μM

0.0133 s/μM = 1 / V_m

V_m = 1 / 0.0133 s/μM

$\boxed{V_m = 75\ \mu\text{M/s}}$

$1.67\text{x}10^{-3}$ s = K_M/V_m

K_M = 75 μM/s•$1.67\text{x}10^{-3}$ s

$\boxed{K_M = 0.125\ \mu\text{M}}$