Reaction Kinetics

An Introduction

- A condition of equilibrium is reached in a system when 2 opposing changes occur simultaneously at the same rate.

- The rate of a chemical reaction may be defined as the # of mols of a substance which **disappear** or **are formed** by the reaction per unit volume in a unit of time.

Example

$$I \rightarrow C$$

$$Rate_{forward} = \frac{[I]_2 - [I]_1}{t_2 - t_1} = \frac{\Delta [I]}{\Delta t}$$

- The previous rate is for the DISAPPEARANCE of I, therefore:

$$rate = -\frac{\Delta\,[I]}{\Delta\,t}$$

$$where\ the\ negative\ sign\ means\ disappearing\ or\ "loss\ of"$$

Backwards Example

$$Rate_{bkward} = \frac{[C]_2 - [C]_1}{t_2 - t_1} = \frac{\Delta [C]}{\Delta t} = + \frac{\Delta [C]}{\Delta t}$$

$$where\ the\ positive\ sign\ means\ for \min g$$

$$when\ both\ reaction\ rates\ study\ I$$

More Complex Reactions

$$X \rightarrow 3\,Z$$

$$Rate = -\frac{\Delta\,X}{\Delta\,t} \neq \frac{\Delta\,Z}{\Delta\,t}$$

this is due to Z appearing 3X as fast as X is disappearing

$$\therefore$$

$$Rate = -\frac{\Delta\,X}{\Delta\,t} = \frac{1}{3}\frac{\Delta\,Z}{\Delta\,t}$$

In General

For the Reaction:

$pP + qQ \rightarrow rR + sS$

$$Rate = -\frac{1}{p}\frac{\Delta P}{\Delta t} = -\frac{1}{q}\frac{\Delta Q}{\Delta t} = \frac{1}{r}\frac{\Delta R}{\Delta t} = \frac{1}{s}\frac{\Delta S}{\Delta t}$$

Reaction Order

In General

For the Reaction:

pP + qQ $\rightarrow$ rR + sS

$$Rate = -\frac{1}{p}\frac{\Delta P}{\Delta t} = -\frac{1}{q}\frac{\Delta Q}{\Delta t} = \frac{1}{r}\frac{\Delta R}{\Delta t} = \frac{1}{s}\frac{\Delta S}{\Delta t}$$

and is proportional to

$$[P]^n\ [Q]^m$$

or

$$Rate = k\ [P]^n\ [Q]^m$$

where

$$k = \text{proportionality constant or rate constant}$$

k

A reaction with an incredibly large rate constant is faster than a reaction with an incredibly small rate constant.

For the Reaction:

$pP + qQ \rightarrow rR + sS$

The reaction is “n” order in [P] and “m” order in [Q]

OR

Is OVERALL “(n + m)” order

KEY!!!!!!

"n" and "m" DO NOT necessarily equal "p", "q", "r" or "s"

Example

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

$$Rate = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta\ t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta\ t} = \frac{\Delta[O_2]}{\Delta\ t}$$

$$or$$

$$= k\ [N_2O_5]$$

- This reaction is FIRST order in N_2O_5, NOT SECOND order as one might intuit from the stoichiometry.

The Order of The Reaction

- = the specification of the empirical (experimentally-determined) dependence of the rate of the reaction on CONCENTRATIONS
- The order may = 0, a whole number or a non-whole number, e.g.,
  - 0
  - 1
  - 1½
  - 2
- We'll focus on whole numbers and 0 (zero) for reactions of the type:

$$fF + gG \rightarrow \text{Products}$$

- AND! The order of the reaction is defined in terms of REACTANTS not the products, therefore, products do not need to be specified

Zero-Order Reactions

$$Rate = -\frac{1}{f}\frac{\Delta[F]}{\Delta t} = k'[F]^0[G]^0$$

$$f \text{ is only a coefficient } \therefore -\frac{\Delta[F]}{\Delta t} = f\,k' = k$$

$$and$$

$$-\frac{\Delta[F]}{\Delta t} = k$$

$$\text{Rearrange}: \Delta[F] = -k\,\Delta t$$

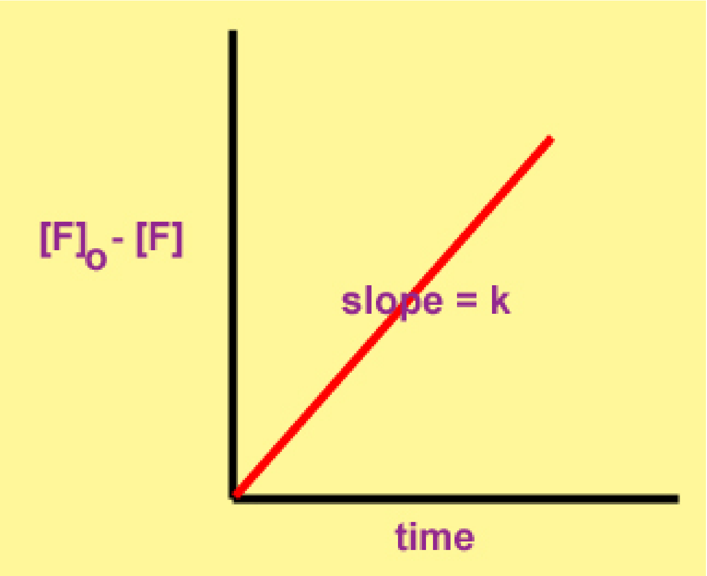
$$Integrate -- not\ here\ (P\ Chem): [F] = [F]_o - kt$$

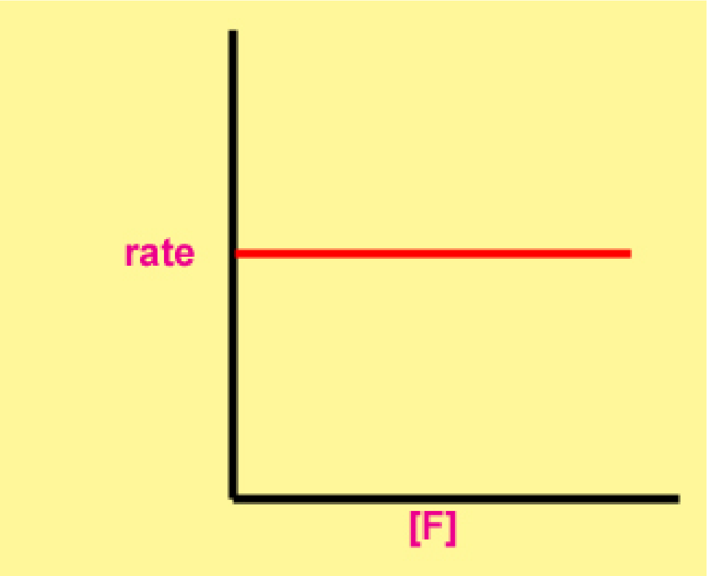
$$[F]\ at\ time = t; [F]_o = at\ t = 0$$

$$Straight\ line: y = mx + b\ form$$

For Zero-Order Reactions

- These reactions are relatively rare
- Occur on metal surfaces
- Reaction rate is INDEPENDENT of concentration of reactants





First Order Reactions

- Assume reaction is 1st order in F and zero order in G:

$$Rate = -\frac{1}{f}\frac{\Delta F}{\Delta t} = k'[F]^1 [G]^0$$

$$f\,k' = k \;\therefore\; \frac{\Delta F}{\Delta t} = k\,[F]$$

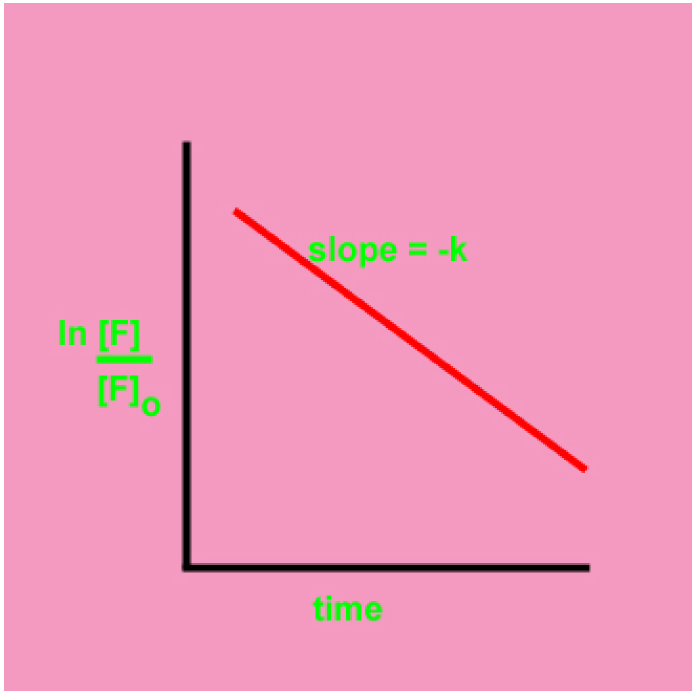
$$\mathrm{Re}\,arrange: \frac{\Delta F}{F} = k\,\Delta t \;\; and \;\; \mathrm{int}\,egrate:$$

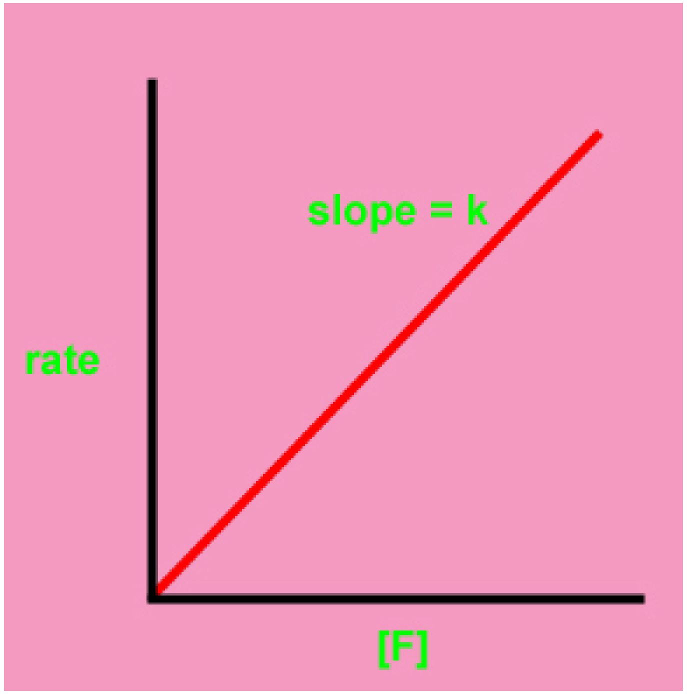
$$\ln\frac{[F]}{[F]_o} = -\,k\,t$$

$$OR$$

$$[F] = [F]_o\,e^{-k\,t}$$

- Many radioactive decays fit 1st order reactions:
  - $^{226}Ra_{88} \rightarrow {}^{222}Rn_{86} + {}^{4}He_{2}$
  - $^{238}U_{92} \rightarrow {}^{234}Th_{90} + {}^{4}He_{2}$
  - The rate is proportional to [F]





The Rate is Proportional to [F]

$$\frac{\Delta F}{\Delta t} = k[F]$$

Double [F]	k [F]	k $[F]^2$	k $[F]^3$
Rate Change	⇑ X 2	⇑ X 4	⇑ X 8

Second Order Reactions: Type 1

$$Rate = -\frac{1}{f}\frac{\Delta F}{\Delta t} = k'[F]^2[G]^0$$

$$f\ k' = k\ \ and$$

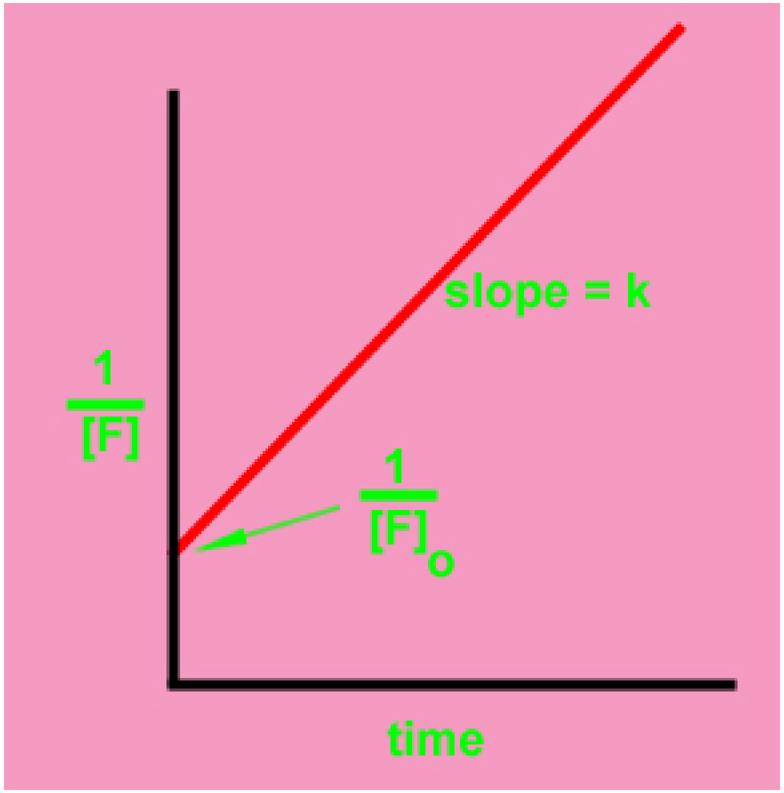
$$-\frac{\Delta F}{\Delta t} = k[F]^2$$

Second order with respect to F

Zero order with respect to G

Re*arrange and* int*egrate* :

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



Second Order Reactions: Type 2

$$Rate = -\frac{1}{f}\frac{\Delta F}{\Delta t} = -\frac{1}{g}\frac{\Delta G}{\Delta t} = k'[F][G]$$

$$f\ k' = k\ and,\ hence,$$

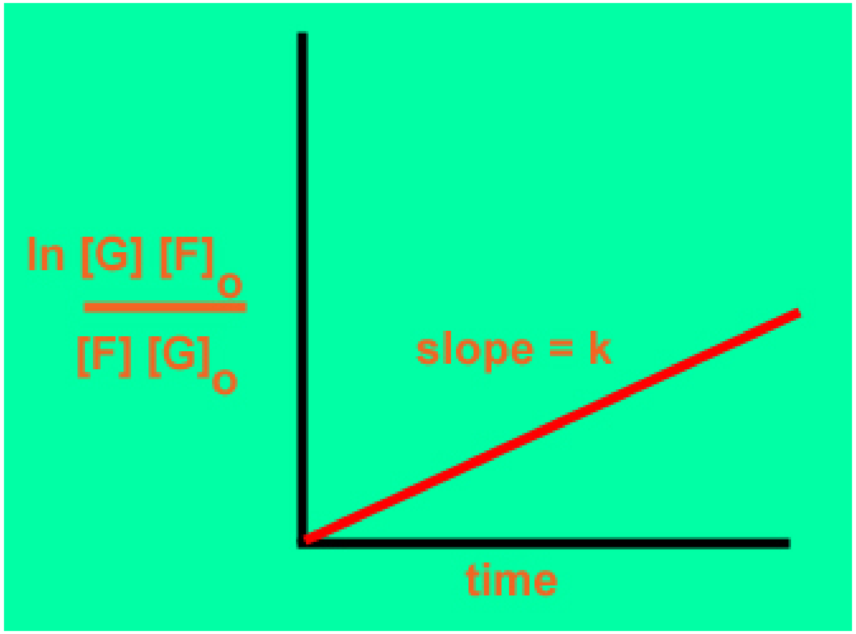
$$-\frac{\Delta F}{\Delta t} = k[F][G]$$

$$\text{Rearrange and integrate (by parts)}$$

$$\frac{1}{[G]_o - [F]_o}\ln\frac{[G][F]_o}{[F][G]_o} = k\,t$$

$$\text{Reaction is FIRST order in } F \text{ AND in } G,$$

$$\therefore \text{SECOND order overall}$$



Second order reactions are the most common reactions

The rate is proportional to [G], $[G]_o$, [F], $[F]_o$

Pseudo-First Order Reactions

- A special kind of 2^d order reaction:
- Example
- 1 M acetyl chloride (AcCl) reacted with 56 M water (XSSV amount) to for HOAC and HCl

$$AcCl + H_2O \rightarrow HOAc + HCl$$

$$Rate = -\frac{d[AcCl]}{dt} = k[AcCl][H_2O]$$

The change in $[H_2O]$ *is too small to detect, so*

$$k\,[H_2O] = k', \therefore$$

$$Rate = k'\,[AcCl]$$

Reaction "*APPEARS*" *to be first order,*

Hence: PSEUDO – First Order

Empirical Method in Determining Reaction Orders

$$First\ \ Step:$$

$$\frac{rate_1}{rate_2} = \frac{\Delta t_2}{\Delta t_1} = \left(\frac{[A]_1}{[A]_2}\right)^X$$

$$X\ = the\ unknown\ order\ \ for\ \ reaction\ "A"$$

$$Second\ \ Step:$$

$$X\ = \frac{\log\frac{\Delta t_2}{\Delta t_1}}{\log\frac{[A]_1}{[A]_2}}$$

Where 2 different reactions differing ONLY in [A] are being studied

Example

$$\text{Re}\,action\ 1:$$

$$A \rightarrow B\ and\ [A] = 0.3\ M;\ \Delta t_1 = 5'$$

$$\text{Re}\,action\ 2:$$

$$A \rightarrow B\ and\ [A] = 0.173\ M;\ \Delta t_2 = 15'$$

$$X = \left(\frac{\log \frac{\Delta t_2}{\Delta t_1}}{\log \frac{[A]_1}{[A]_2}} \right) = \left(\frac{\log \frac{15'}{5'}}{\log \frac{0.3M}{0.173M}} \right) = \frac{\log 3}{\log 1.734} = \frac{0.477}{0.239} = 2$$

$$\therefore reaction\ is\ \text{sec}\,ond\ order\ in\ A$$

Practical Application

- Reaction rates are proportional to some power of [reactant]
- Determined by using “initial reaction rate method”

E.g.,

$$Zn + 2HCl \rightarrow H_2(g) + ZnCl_2$$

Experiment	[Zn]	[HCl]	$+d[H_2]/dt$ (M/s)
1	0.05	0.1	0.055
2	0.05	0.2 ←	0.22
3	0.1 ←	0.1	0.11

Compare Reaction 2 with Reaction 1

$$\frac{Rate_2}{Rate_1} = \frac{0.220}{0.055} = 4$$

$$\therefore Rate\,2 = 4\,Rate\,1$$

2 fold ↑ in [HCl] = 4 fold ↑ in reaction rate 2° doubling of [HCl]

This is dependent on $[HCl]^2$

Compare Reaction 3 with Reaction 1

$$\frac{Rate_3}{Rate_1} = \frac{0.110}{0.055} = 2$$

$$\therefore \quad Rate_3 = 2\, Rate_1$$

2 fold ↑ in [Zn] = 2 fold ↑ in reaction rate 2° doubling of [Zn]
This is dependent on [Zn]

- Fuse both effects and the rate equation for this reaction =

$$\text{Rate} = k\,[\text{Zn}]\,[\text{HCl}]^2$$

- REMEMBER:
- The exponent in a rate equation generally does NOT match the chemical equation coefficients.
- The exponent MUST be determined experimentally.

Another way to do this

Experiment	[Zn]	[HCl]	$+d[H_2]/dt$ (M/s)
1	0.04	0.05	0.5
2	0.02	0.05	0.25
3	0.04	0.075	1.114

Compare Reaction 1 with Reaction 2

$$\frac{Rate_1}{Rate_2} = \frac{k\,(0.04)^x (0.05)^y}{k\,(0.02)^x (0.05)^y} = \left(\frac{0.04}{0.02}\right)^x$$

$$\frac{Rate_1}{Rate_2} = 2^x \qquad \log\left(\frac{Rate_1}{Rate_2}\right) = x \log 2$$

$$\frac{\log 2}{\log 2} = x = 1$$

$$\therefore \propto [Zn]^1$$

Compare Reaction 3 with Reaction 1

$$\frac{\text{Rate}_3}{\text{Rate}_1} = \frac{k\,(0.04)^x(0.075)^y}{k\,(0.04)^x(0.05)^y} = \left(\frac{0.075}{0.05}\right)^y$$

$$\log\left(\frac{1.114}{0.5}\right) = y \log 1.5$$

$$\frac{\log(2.228)}{\log 1.5} = y = \frac{0.348}{0.176} = 1.98 \sim 2$$

$$\therefore \propto [HCl]^2$$

Reaction Order Half-Lives

$$Zero\ Order:$$

$$t_{\frac{1}{2}} = \frac{[F]_o}{2k} = M\,s^{-1}$$

$$First\ Order:$$

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

$$First\ Order\ t_{\frac{1}{2}}\ is\ INDEPENDENT\ of\ CONCENTRATION$$

$$Second\ Order:$$

$$t_{\frac{1}{2}} = \frac{1}{[F]_o\,k} = M^{-1}\,s^{-1}$$

Example

- For the reaction:
- $C \rightarrow D + E$,
- Half of the C is used up in 60 seconds. Calculate the fraction of C used up after 10 minutes – reaction is first order in C.

Solution

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \; and \; k = \frac{0.693}{60} = 0.01155 \; \sec onds^{-1}$$

$$\ln\frac{[C]}{[C]_o} = -k\,t$$

$$Key : [C]_o = 1$$

$$\ln[C] - \ln[C]_o = -(0.01155)(600)$$

$$\ln[C] = -6.93$$

$$[C] = 0.000978 \; C \; LEFT$$

$$Hence : 1 - 0.000978 = 0.999022 \; C \; USED \; UP \; -- \; or \; 99.9\% \; C \; Used \; Up$$

Example

- ^{14}C is present at about $1.1*10^{-13}$ mol% naturally in living matter. A bone dug up showed $9*10^{-15}$ mol% ^{14}C. The half life of ^{14}C is 5720 years. How old is the bone?

Solution

$$k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{0.693}{5720} = 1.211 * 10^{-4} \ \ yrs^{-1}$$

$$\ln \frac{[^{14}C]}{[^{14}C]_o} = -k\,t$$

$$\ln \frac{9 * 10^{-15}}{1.1 * 10^{-13}} = -(1.2115 * 10^{-4})\,t$$

$$\frac{-2.503}{-1.2115 * 10^{-4}} = 20662.45 \ \ years\ old$$

Example

- A decomposition reaction occurs in a fixed-volume container at 460°C. Its rate constant is $4.5*10^{-3}$ seconds^{-1}. At t = 0, P = 0.75 atm. What is the pressure (P) after 8 minutes?

Solution

$$\ln\frac{P}{P_o} = -k\,t$$

$$\ln\frac{P}{0.75} = -(4.5*10^{-3})(480)$$

$$\ln P - \ln 0.75 = -(4.5*10^{-3})(480)$$

$$\ln P + 0.288 = -2.16$$

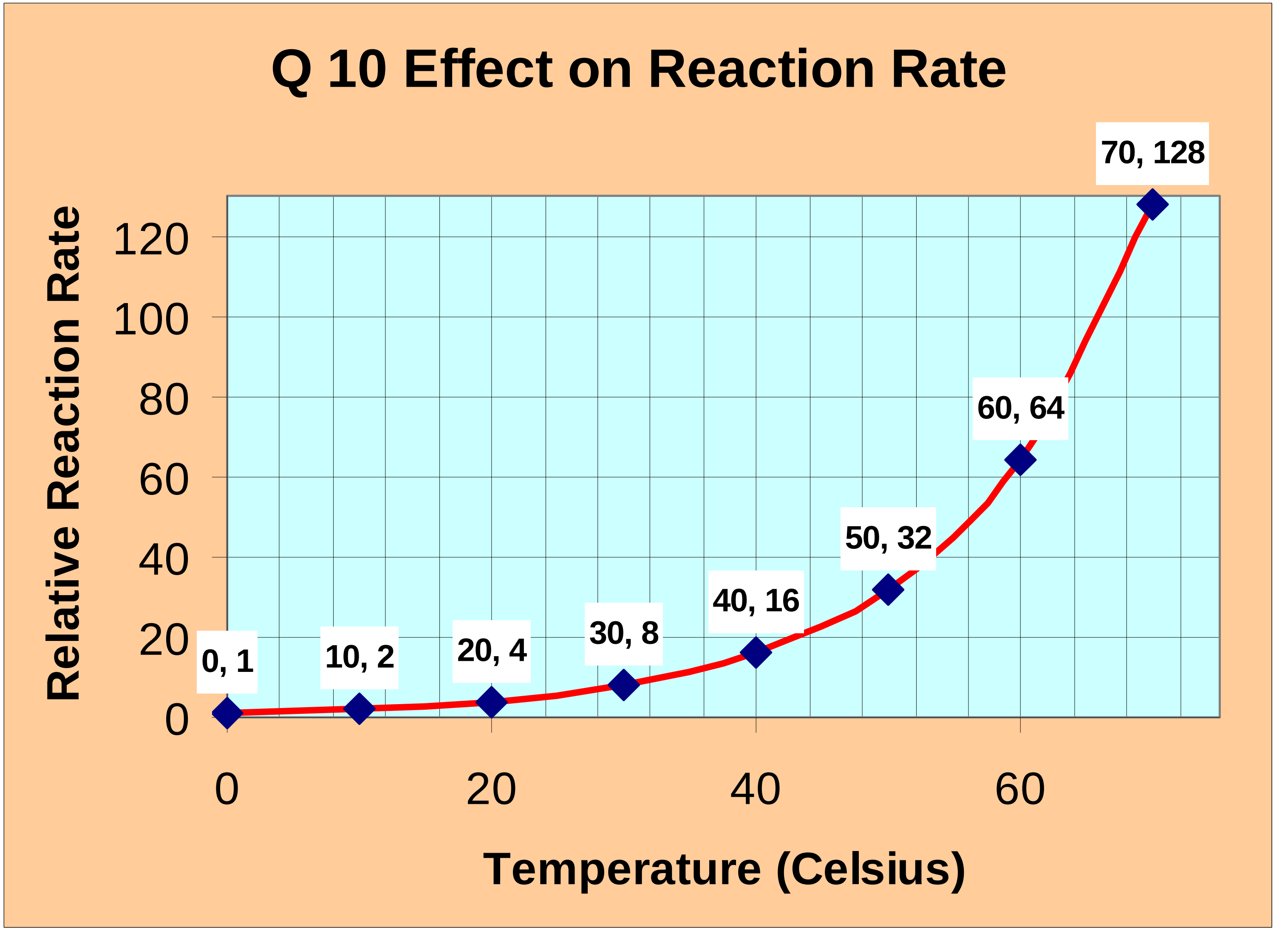
$$P = 0.0865\ atm$$

Q_{10} Effect

Example

- If the rate of a chemical reaction doubles for every 10°C rise in temperature, how much faster would the reaction proceed at 55°C than at 25°C?

Q 10 Effect


Q 10 Effect on Reaction Rate
Relative Reaction Rate
Temperature (Celsius)
0
20
40
60
80
100
120
0
20
40
60
0, 1
10, 2
20, 4
30, 8
40, 16
50, 32
60, 64
70, 128

Solution

- Temperature increased 30°C, therefore, reaction rate increases 8-fold

Example:

- What if the temperature was increased to 105°C from 25°C?
- Temperature increased 80°C, therefore reaction rate increases 256-fold

Example

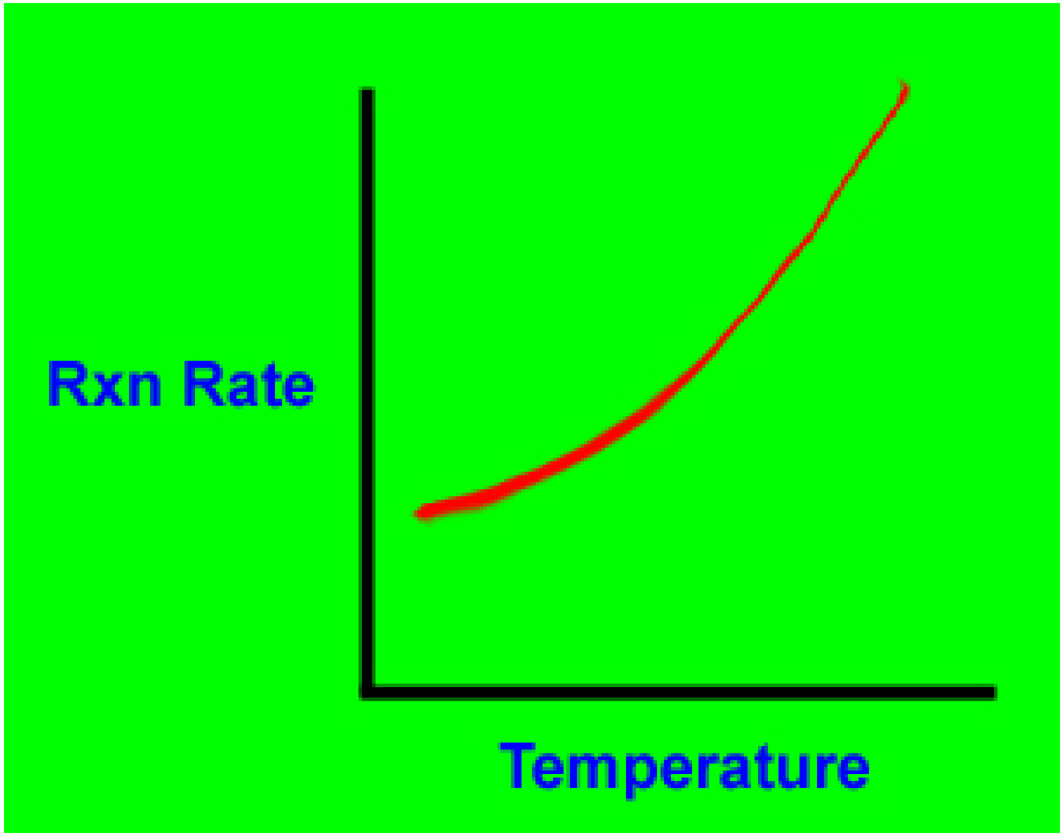
- How much faster would a reaction go at 100°C than at 25°C?
- For every 10°C increase in temperature, the reaction rate doubles. The change in temperature is 75°C. This is 7.5 10°C increases.
- Hence $2^{7.5}$ = 181 times faster

Example

- In an experiment, a sample of NaOCl was 85% decomposed in 64 minutes. How long would it have taken if the temperature was 50°C higher?
- For every 10°C increase, the reaction rate doubles. 50°C increase is 5 10°C increases.

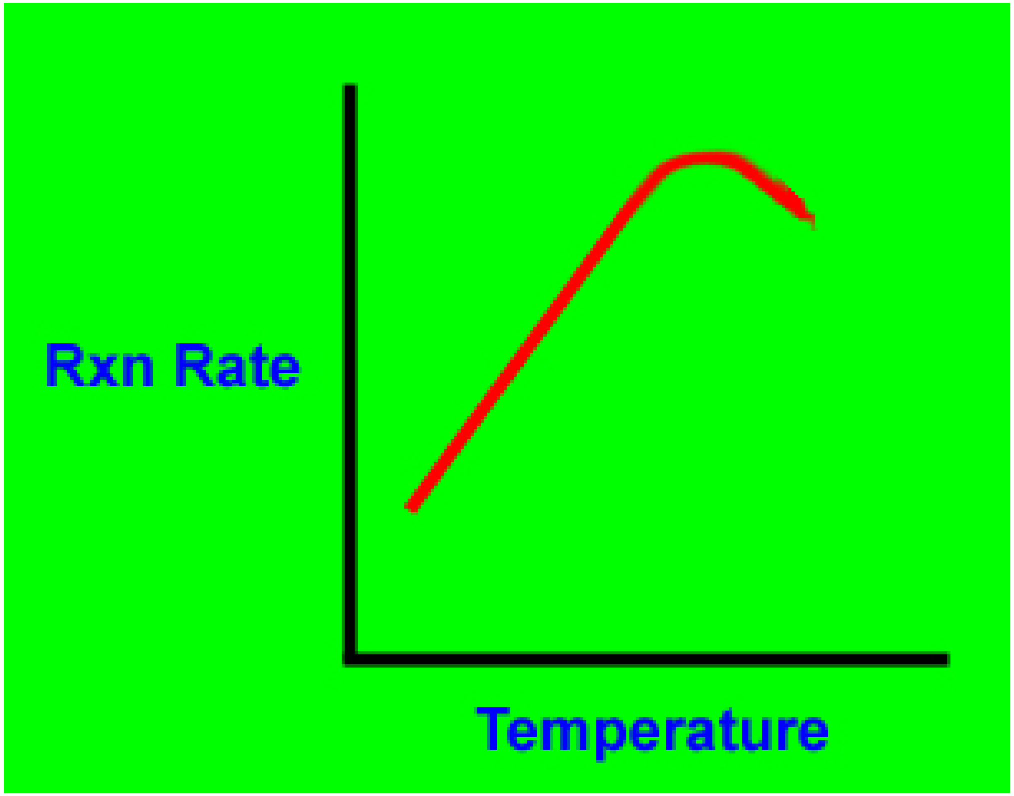
- Hence: $2^5 = 32$ times faster
- So: (64 minutes)/(32 times faster) = 2 minutes

There are 4 types of temperature dependence for reaction rates -- 1



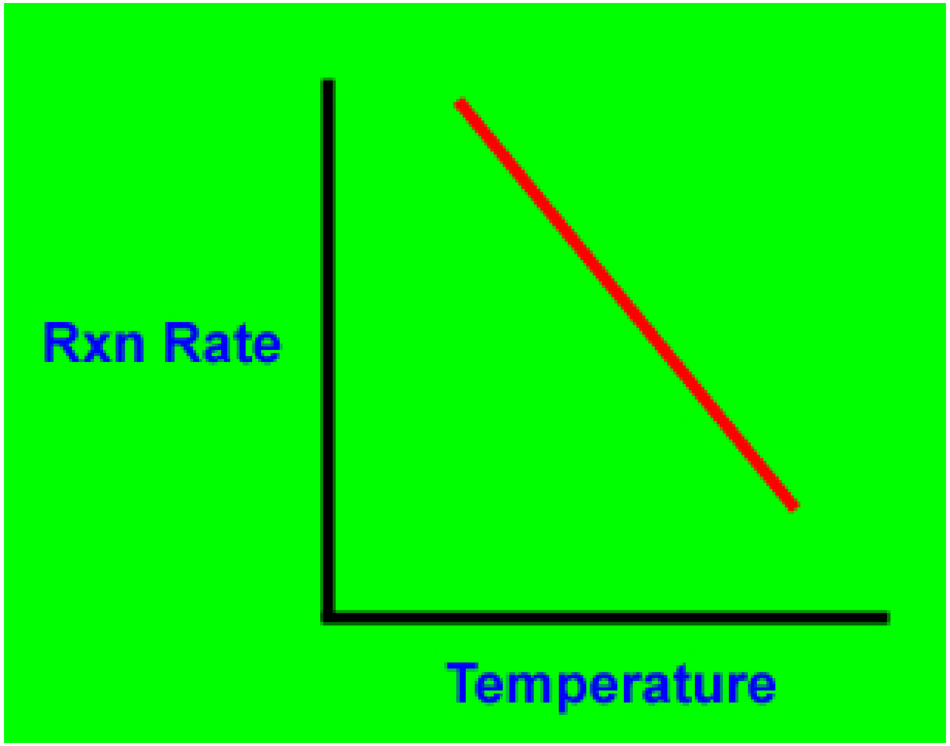
- Rate increases with increasing temperature
- NORMAL

There are 4 types of temperature dependence for reaction rates -- 2



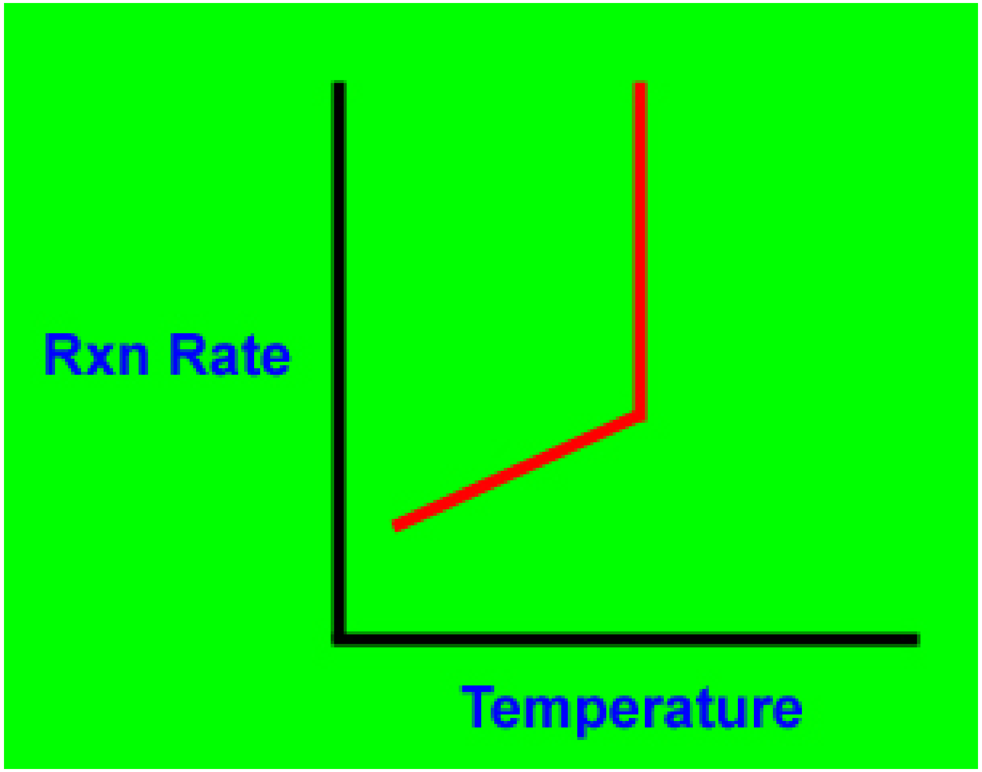
- Rate increases to a point, then reduces with increasing temperature
- E.g., enzymes being denatured

There are 4 types of temperature dependence for reaction rates -- 3



- Rate decreases with increasing temperature
- VERY RARE
- Known only for a few reactions that are multi-step reactions:
  - $A \rightarrow B$ Fast step
  - $B \rightarrow C$ Rate limiting step

There are 4 types of temperature dependence for reaction rates -- 4



- Rate increases with increasing temperature
- Odd behavior
- Explosive reaction when temperature shoots up
- Gradual rise in temperature due to chain reactions

- The Q 10 effect is “not entirely perfect”
- There is another way to study temperature dependence:
- Mathematically with Energy of Activation

$$k = Ae^{-E_a/RT}$$

k = rate constant

A = frequency factor (total frequency of collisions between reactant molecules)

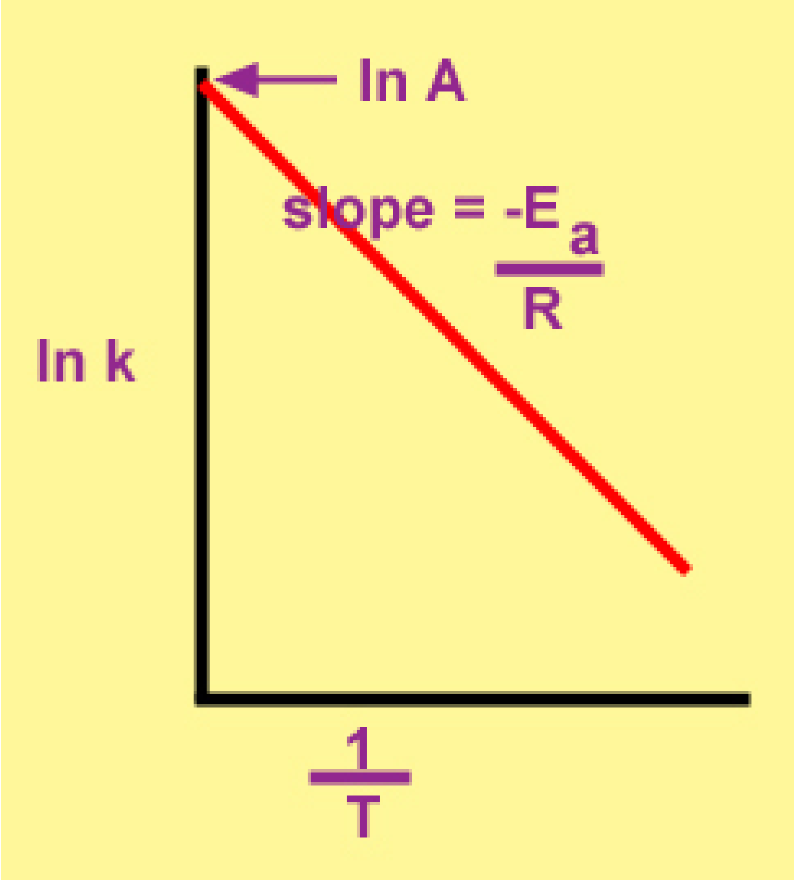
E_a = Energy of Activation

R = Gas constant

T = absolute temperature

Take Natural Log (ln) of Above Equation

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



Previous Equation Can Be Manipulated

- If you know the rate constants for reactions at 2 different temperatures you can calculate the E_a:

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

Example

- At T_1 of 308 K, k_1 = 0.326 s^{-1}; at T_2 of 318 K, k_2 = 1.15 s^{-1}. R = 8.314 J/mol-K. Determine E_a

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

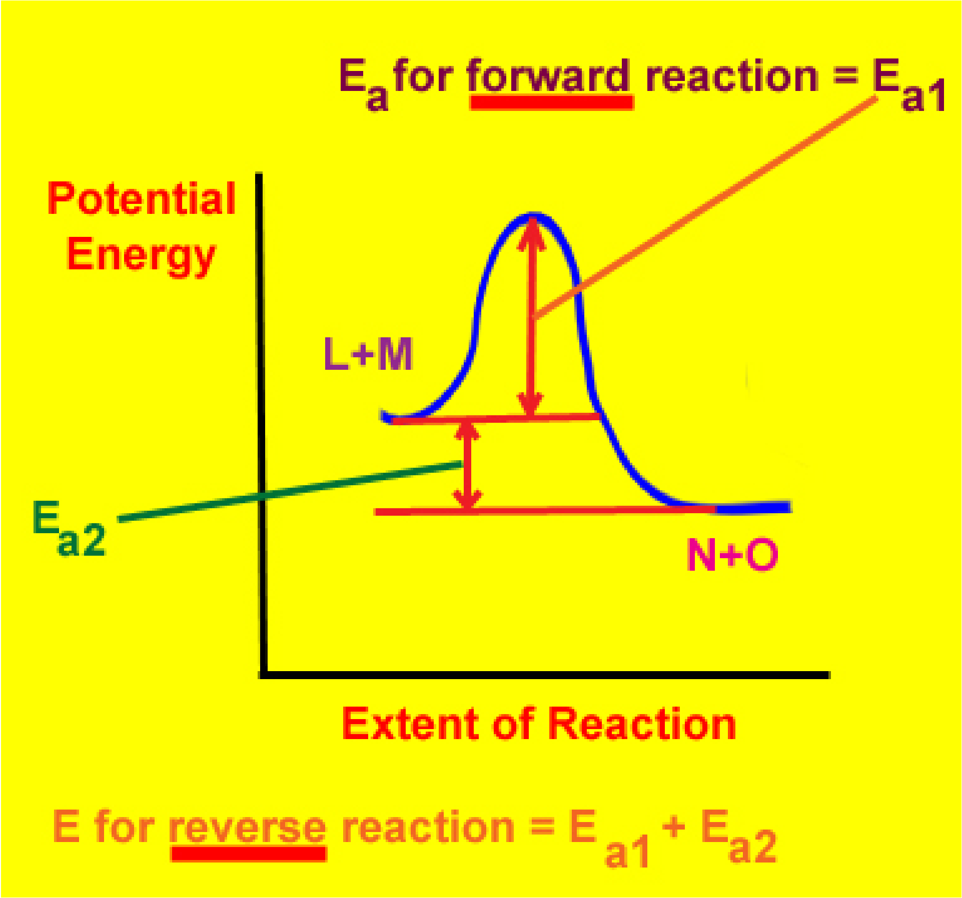
$$\ln\frac{1.15}{0.326} = -\frac{E_a}{8.314}\left(\frac{1}{318}-\frac{1}{308}\right)$$

$$1.26 = -\frac{E_a}{8.314}(-1.021*10^{-4})$$

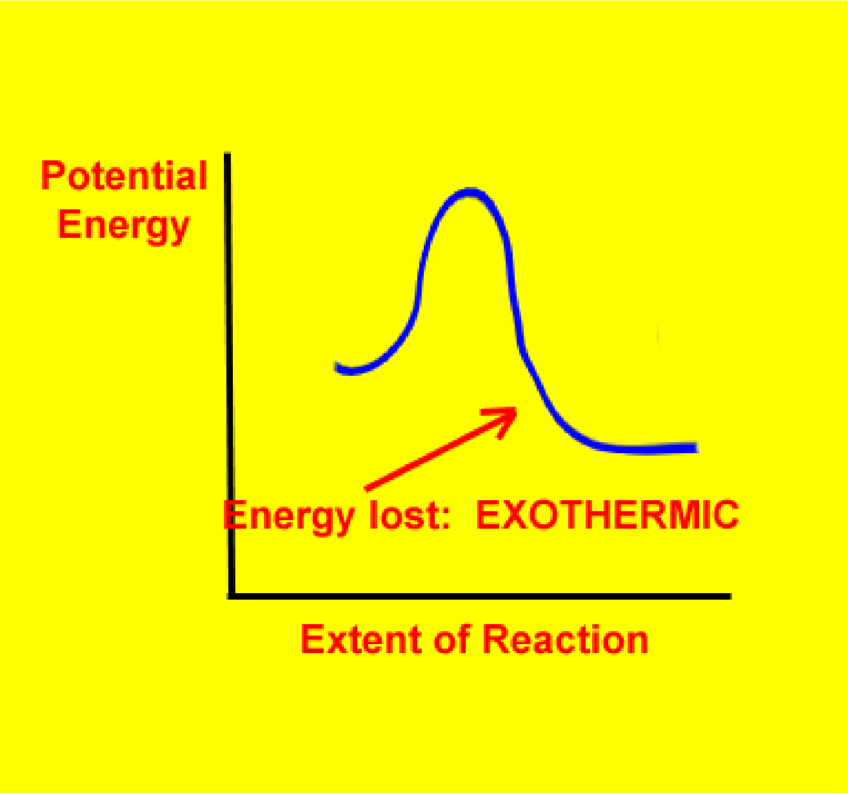
$$\frac{(-1.26)(8.314)}{-1.021*10^{-4}} = E_a = 102{,}601.8\frac{J}{mol} \Leftrightarrow 102.6\frac{kJ}{mol}$$

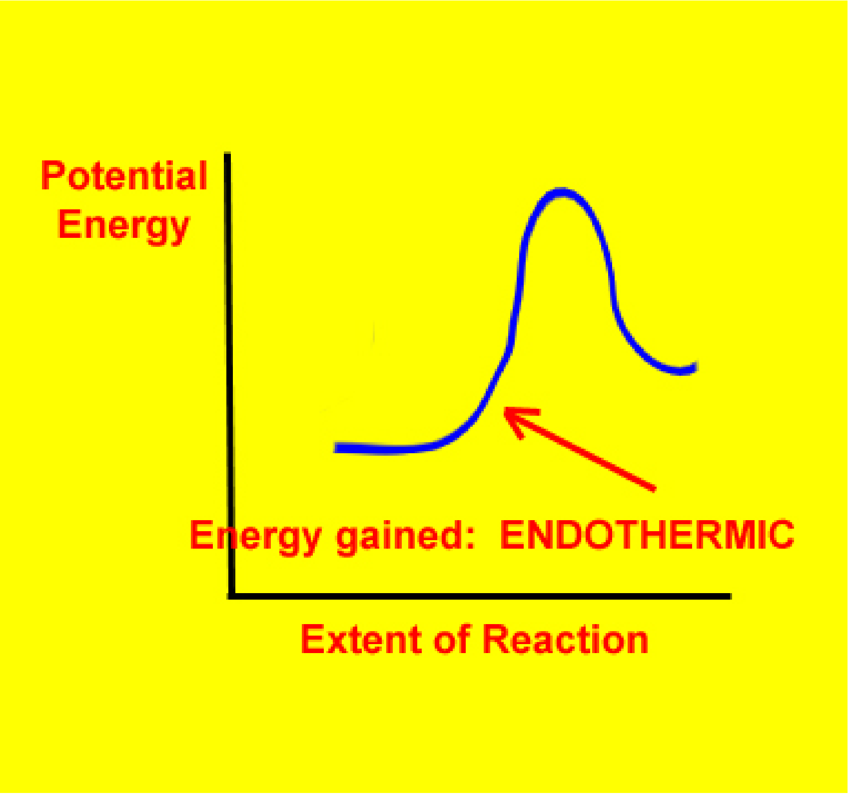
E_a -- Transition

- Top of Energy curve ("hump") = transition state
- The smaller the E_a, the easier it is for the reaction "to go"



E_a – “thermic”



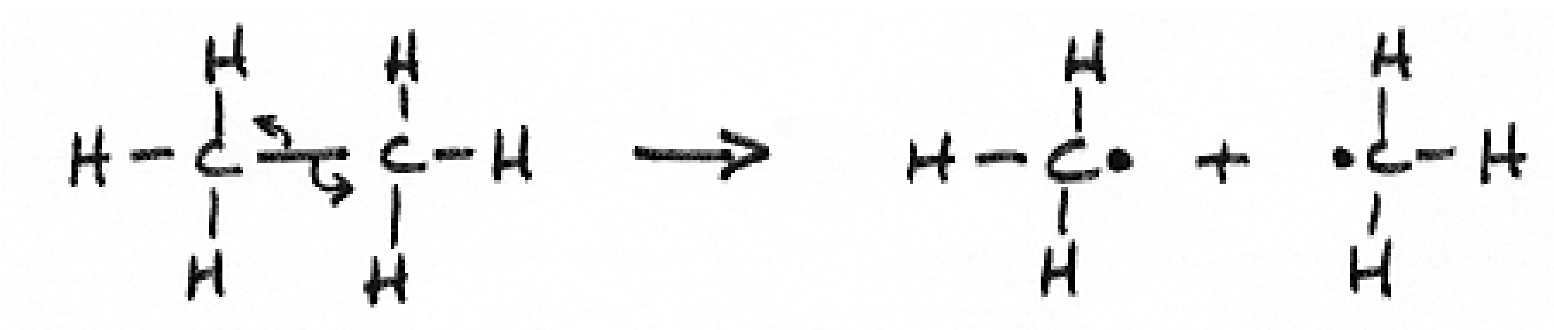


E_a is related to ΔG

Reaction Mechanisms

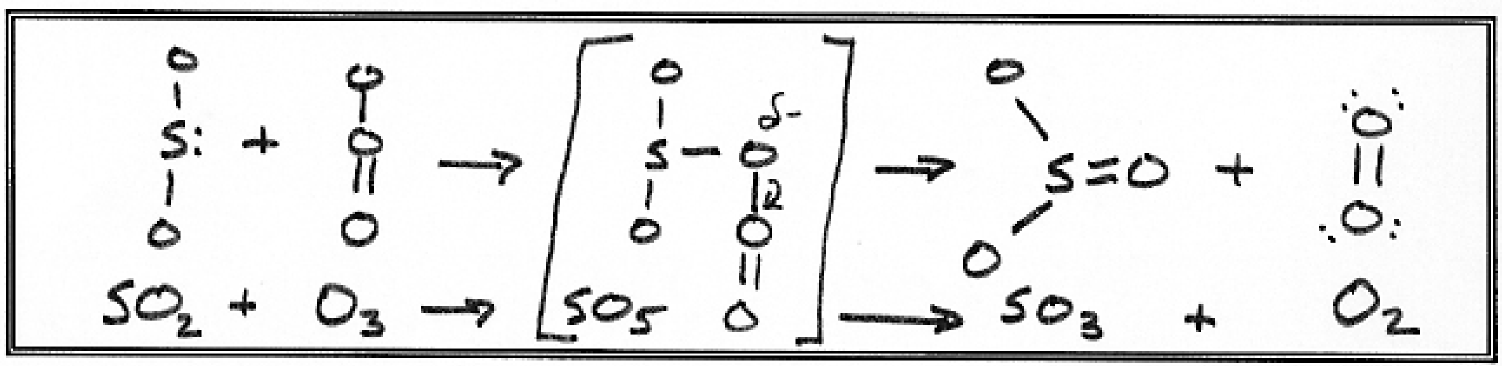
Unimolecular Steps

- A single molecule or atom breaks down or rearranges itself into another species.



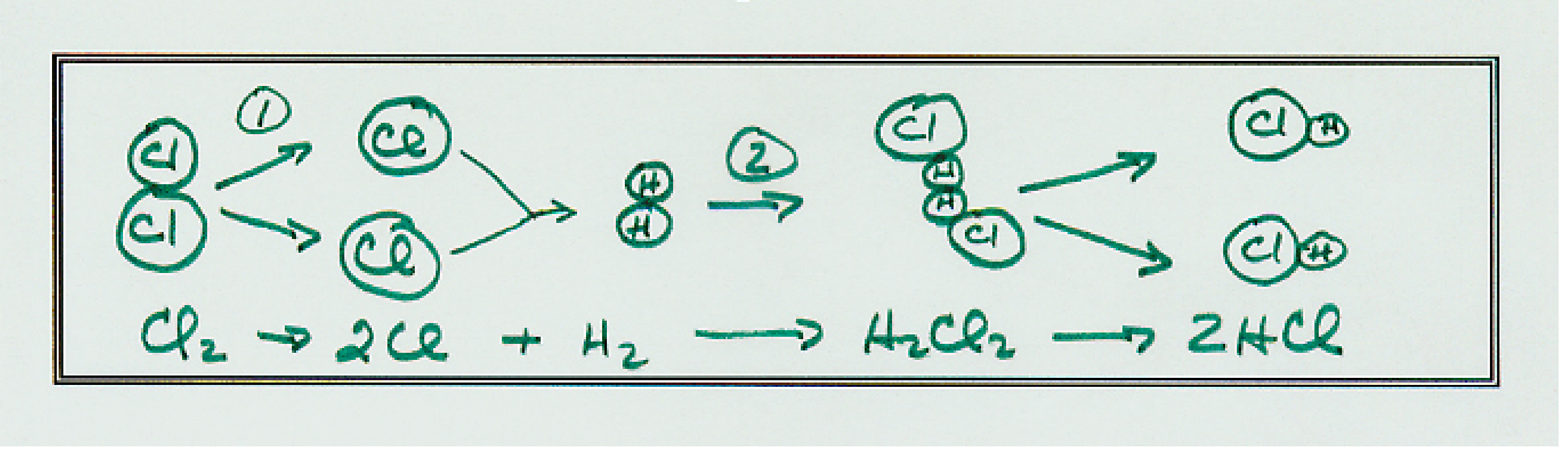
Bimolecular Steps

- Collision of two molecules or atoms; relatively common



Termolecular Steps

- 3 molecules or atoms collide simultaneously; relatively rare and SLOW



Elementary Steps

- = each step in a mechanism; a specific occurrence in the reaction sequence
  - The rate of elementary steps are proportional to the number of collisions per step
  - The number of collisions per step are proportional to every reactant concentration
  - Hence the rate of elementary steps are proportional to the concentration of every reactant

The exponents of an elementary step rate equation are equal to the coefficients in the step's equation

E.g., Bi Elementary Steps

$$SO_2 + O_3 \rightarrow SO_3 + O_2 \qquad Overall\ Rxn$$

$$SO_2 + O_3 \rightarrow SO_5 \qquad Step\ 1$$

$$SO_5 \rightarrow SO_3 + O_2 \qquad Step\ 2$$

$$Rate\ equation\ for\ Step\ 1:$$

$$k_1[SO_2][O_3] \qquad 2d\ Order$$

$$Rate\ equation\ for\ Step\ 2:$$

$$k_1[SO_5] \qquad 1st\ Order$$

E.g., Termolecular Elementary Steps

$$Cl_2 + H_2 \rightarrow 2HCl \qquad Overall\ Rxn$$

$$Cl_2 \rightarrow 2Cl^- \qquad Step\ 1$$

$$2Cl^- + H_2 \rightarrow H_2Cl_2 \qquad Step\ 2$$

$$H_2Cl_2 \rightarrow 2HCl \qquad Step\ 3$$

$$Rate\ equation\ for\ Step\ 1:$$

$$k_1 = [Cl_2] \qquad 1st\ Order$$

$$Rate\ equation\ for\ Step\ 2:$$

$$k_2 = [Cl^-]^2[H_2] \qquad 2d\ Order$$

$$Rate\ equation\ for\ Step\ 3:$$

$$k_3 = [H_2Cl_2] \qquad 1st\ Order$$

Reaction Mechanisms

TWO requirements of postulated mechanisms:

1) MUST account for the postulated mechanism
2) MUST explain the experimental rate equation
    1) – INHERENT in this is the assumption that
    2) 1 step is incredibly SLOWER than the others, hence, it determines the speed of the reaction.
    3) This step is called the rate limiting step.
    4) Therefore, the overall rate equation is determined by rate equations for the rate limiting step.
    5) ALSO: when a catalyst is present, there MUST BE at least 2 steps in the mechanism!

Example

- The empirically derived rate equation for:

$$2NO_2\ (g) + Cl_2\ (g) \rightarrow 2NO_2Cl \uparrow \text{ is}$$

$$k\ [NO_2]\ [Cl_2]$$

- Write a two-step mechanism with a slow first step

$$2\,NO_2 + Cl_2 \rightarrow 2NO_2Cl \qquad Overall\ Rxn$$

$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl \qquad Step\ 1$$

$$Rate\ Equation$$

$$k[NO_2][Cl_2]$$

$$NO_2Cl + Cl \rightarrow 2NO_2Cl \qquad Step\ 2$$

$$Rate\ Equation$$

$$k[NO_2Cl][Cl]$$

$$BUT$$

$$Rate\ Equation\ \ for\ Step\ 1 = Empirical\ Rate\ Equation$$

$$Hence,\ Step\ 1\ is\ the\ slow\ step$$

Comments

- Any steps after Step 1 will NOT effect the rate because step 1 is the rate limiting step
- Add up the 2 steps (just like in thermodynamics) and you get the overall reaction

Illustrative Example

$$2ICl + H_2 \rightarrow 2HCl + I_2 \qquad Overall\ Rxn$$

$$k[ICl][HI] \qquad Empirically\ Derived\ Rate\ Equation$$

$$ICl + H_2 \rightarrow HI + HCl \qquad Step\ 1$$

$$Rate\ Equation$$

$$k\ [ICl][H_2]$$

$$ICl + HI \rightarrow I_2 + HCl \qquad Step\ 2$$

$$Rate\ Equation$$

$$k[ICl][HI]$$

$$Note\ that\ Empirical\ Rate\ Equation\ Equals\ Step\ 2\ Equation$$

$$Step\ 2\ is\ Rate\ Limiting$$

$$(In\ \mathrm{Re}ality,\ is\ STEP\ 1 - this\ was\ for\ illustrative\ purposes)$$

Example

- The empirical rate equation for

$$2ClO_2 + F_2 \rightarrow 2FClO_2$$

Is: $k\,[ClO_2]\,[F_2]$

- Write the reaction mechanism (2-step) consistent with the rate equation.

$$2ClO_2 + F_2 \rightarrow 2FClO_2 \qquad Overall\ Rxn$$

$$ClO_2 + F_2 \rightarrow FClO_2 + F \qquad Step\ 1$$

$$Rate\ Equation$$

$$k[ClO_2][F_2]$$

$$ClO_2 + F \rightarrow FClO_2 \qquad Step\ 2$$

$$Rate\ Equation$$

$$k[ClO_2][F]$$

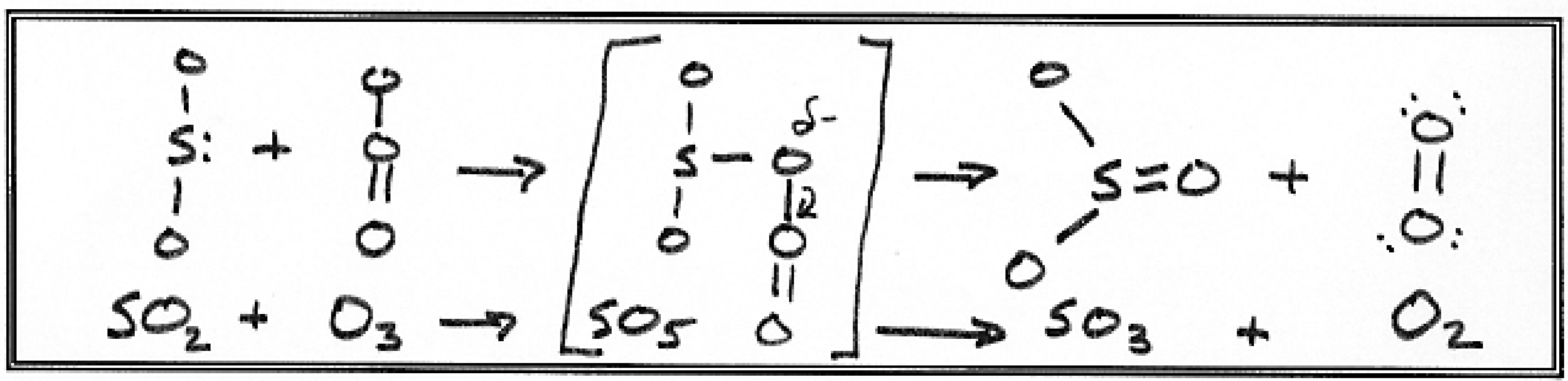
$$Step\ 1\ Rate\ Equation\ Matches$$

$$Empirically\ Dtn'd\ Rate\ Equation$$

$$Hence, Step\ 1\ is\ Rate\ Limiting$$

Steady State Approximation

- The majority of mechanisms are NOT as easy as previous examples.
- Let's return to our Bimolecular Reaction Step Example:



Focus

- SO_5
- This is an "intermediate" – a "transition"
- An intermediate (or transition) is a compound that is neither reactant nor product, rather in between the two.
- Intermediates are very difficult to isolate in many cases.
- They are highly reactive and, more often than not, are used up as quickly as they are formed. It is because of this characteristic that we have the Steady State Approximation

Steady State Approximation

- The concentration of intermediate is a constant
- I.e., the rate of formation of the intermediate is equal to the rate of disappearance of the intermediate:

$$\frac{d[intermediate]}{dt} = -\frac{d[intermediate]}{dt}$$

Example

- $2O_3 \rightarrow 3O_2$
- Empirically derived rate equation = k $[O_3]^2/[O_2]$

$$MECHANISM:$$

$$O_3 + catalyst \xrightarrow{k_1} O_2 + O + catalyst \qquad Step\ 1\ FAST$$

$$k_1 = rate\ k\ \ for\ \ forward\ \ reaction$$

$$O_2 + O + catalyst \ \xrightarrow{k_{-1}} O_3 + catalyst \qquad Step\ 2\ FAST$$

$$k_{-1} = rate\ k\ \ for\ backwards\ reaction\ (some\ sources\ call\ it\ k_2)$$

$$I\ \ prefer\ k_{-1}\ as\ it\ re\min ds\ you\ that\ it's\ \ for\ the\ backwards\ reaction\ clearly$$

$$O + O_3 \xrightarrow{k_3} 2O_2 \qquad Step\ 3\ SLOW$$

- The constant of a reverse reaction is indicated by (-), e.g., k_{-1}
- The intermediate in this mechanism is the oxygen ATOM, hence:

$$\frac{d\,[O]}{d\,t} = -\frac{d\,[O]}{d\,t}$$

- Knowing this, we need to show that the empirical rate equation and mechanism are consistent with each other.

$$\text{Rate of For'd Rxn} \qquad\qquad \text{Rate of Bckw'd Rxn}$$

$$\frac{d\,[O]}{d\,t} = k_1 [O_3][catalyst] \qquad\qquad -\frac{d\,[O]}{d\,t} = k_{-1} [O_2][O][catalyst]$$

$$Now\ Equate\ The\ Two$$

$$k_1\,[O_3][catalyst] = k_{-1}[O_2][O][catalyst]$$

$$Cancel\ out\ [catalyst]$$

$$k_1 [O_3] = k_{-1} [O_2][O]$$

$$Solve\ for\ [O]$$

$$\frac{k_1[O_3]}{k_{-1}[O_2]} = [O]$$

- Stop temporarily
- REMEMBER: the rate limiting step is #3; the rate equation for this step = k_3 [O] [O_3]
- So, substitute the solution for [O] from the first for'd and bkw'd reactions in to the rate equation for Step 3:

$$k_3 * \frac{k_1 [O_3]}{k_{-1} [O_2]} * [O_3]$$

$$Let\ k = \frac{k_3\, k_1}{k_{-1}}\ and\ substitute:$$

$$equation = k \frac{[O_3]^2}{[O_2]}$$

$$Is\ identical\ to\ empirically\ derived\ rate\ equation$$

- This series of kinetic equations fulfills the 2 requirements:

- 1) Accounts for the products, and,
- 2) Explains the observed rate law

Second Example

- For $2NO + O_2 \rightarrow 2NO_2$, the empirical rate equation is:

$$k\,[NO]^2\,[O_2]$$

- The postulated mechanism follows:

$$NO + O_2 \underset{k_{-1}}{\overset{k_1}{\Leftrightarrow}} NO_3 \qquad Step\ 1\ FAST$$

$$NO_3 + NO_2 \xrightarrow{k_2} 2NO_2 \qquad Step\ 2\ SLOW$$

- Show that the empirical rate equation and mechanism are consistent with each other.
- Use the methodology we used in the previous example.

$$NO + O_2 \xrightarrow{k_1} NO_3$$

$$NO_3 \xrightarrow{k_{-1}} NO + O_2$$

$$NO_3 + NO \xrightarrow{k_2} 2NO_2$$

and

$$\frac{d\,[NO_3]}{d\,t} = -\frac{d\,[NO_3]}{d\,t}$$

$$For'd \;\; Rate \;\; Equation \qquad Bkw'd \;\; Rate \;\; Equation$$

$$\frac{d[NO_3]}{d\;t} = k_1[NO][O_2] \qquad -\frac{d\;[NO_3]}{d\;t} = k_{-1}[NO_3]$$

$$Equate \;\; the \;\; two:$$

$$k_1[NO][O_2] = k_{-1}[NO_3]$$

$$Solve \;\; for \;\; [NO_3]:$$

$$k_1\frac{[NO][O_2]}{k_{-1}} = [NO_3]$$

$$Stop \;\; here \;\; temporarily$$

- The rate limiting step is step 3.
- The rate equation for step 3 is: k_2 [NO_3] [NO]
- Substitute the solution for [NO_3] into the rate equation for step 3.

$$\left(\frac{k_1\,k_2}{k_{-1}}\right)[NO][O_2][NO] = k\,[NO]^2\,[O_2]$$

Apply This to Enzymes

- Enzymes are, with a couple of exceptions, proteins
- Enzymes are biological catalysts
- Enzymes speed up biological reactions incredibly
- For this discussion:
  - E = enzyme,
  - S = substrate and
  - P = product

$$E + S \xrightarrow{k_1} ES \qquad FAST$$

$$ES \xrightarrow{k_{-1}} E + S \qquad FAST$$

$$ES \xrightarrow{k_2} E + P \qquad SLOW$$

$$AND$$

$$\frac{d\,[ES]}{d\,t} = -\frac{d\,[ES]}{d\,t}$$

$$Short\ \ Method$$

$$k_1[E][S] = k_{-1}[ES]$$

$$Solve\ \ for\ [ES]:$$

$$\frac{k_1}{k_{-1}}[E][S] = [ES]$$

$$Stop\ temporarily$$

- Rate limiting step is step 3
- Rate equation is: k_2 [ES]
- Substitute as before:

$$\left(\frac{k_1 k_2}{k_{-1}}\right)[E][S] = k[E][S]$$

$$Write\ the\ overall\ reaction:$$

$$E + S \Leftrightarrow ES \rightarrow E + P$$

$$This\ is\ a\ Uni-Uni\ Rxn$$

Uni-Uni Reaction – Cleland Plot

Bi-molecular Reactions

- An enzyme catalyzed reaction may utilize 2 substrates.
- This reaction is always SEQUENTIAL, however,
- May be
  - ORDERED or
  - RANDOM

E.g., Ordered Sequential Reaction

$$E + X + Y \rightarrow E + R + S$$

E is still enzyme

X and Y are substrates

R and S are products

Putative Mechanism

E + X $\rightarrow$ EX

EX + Y $\rightarrow$ EXY

EXY $\rightarrow$ ERS SLOW STEP

ERS $\rightarrow$ ER + S

ER $\rightarrow$ E + S

And:

$$\frac{d[ERS]}{d\,t} = -\frac{d\,[EXY]}{d\,t}$$

$$\frac{d[ERS]}{dt} = k_1[E][X]k_2[EX][Y] \qquad -\frac{d[EXY]}{dt} = k_3[EXY]$$

Equate

$$k_1[E][X]k_2[EX][Y] = k_3[EXY]$$

Solve for $[EXY]$

$$\left(\frac{k_1 k_2}{k_3}\right)[E][X][Y][EX] = [EXY]$$

Stop here temporarily

- Rate Limiting Step is: k_3 [EXY]
- Substitute:

$$k_3 \frac{k_1 k_2}{k_3}[E][X][Y][EX] = k_1 k_2 \; [E][X][Y][EX]$$

$$= k \; [E][X][Y][EX]$$

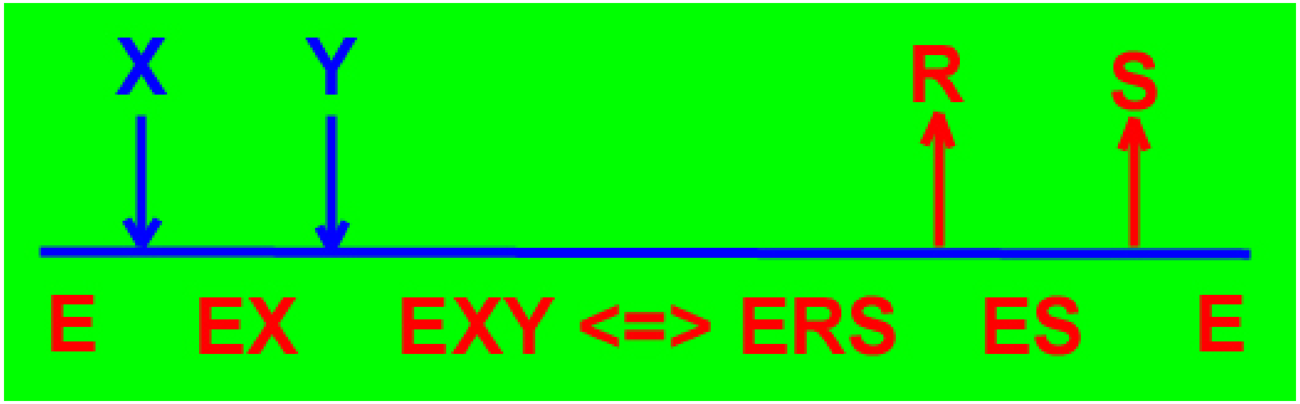
Kinetic Data Tells us:

- The following sequence MUST be taking place:

E + X + Y → EX (FIRST!) → EXY (SECOND!) → ERS → ES + R → E + S

- And is an Ordered Bi Bi Reaction

Ordered Bi Bi Reaction – Cleland Plot



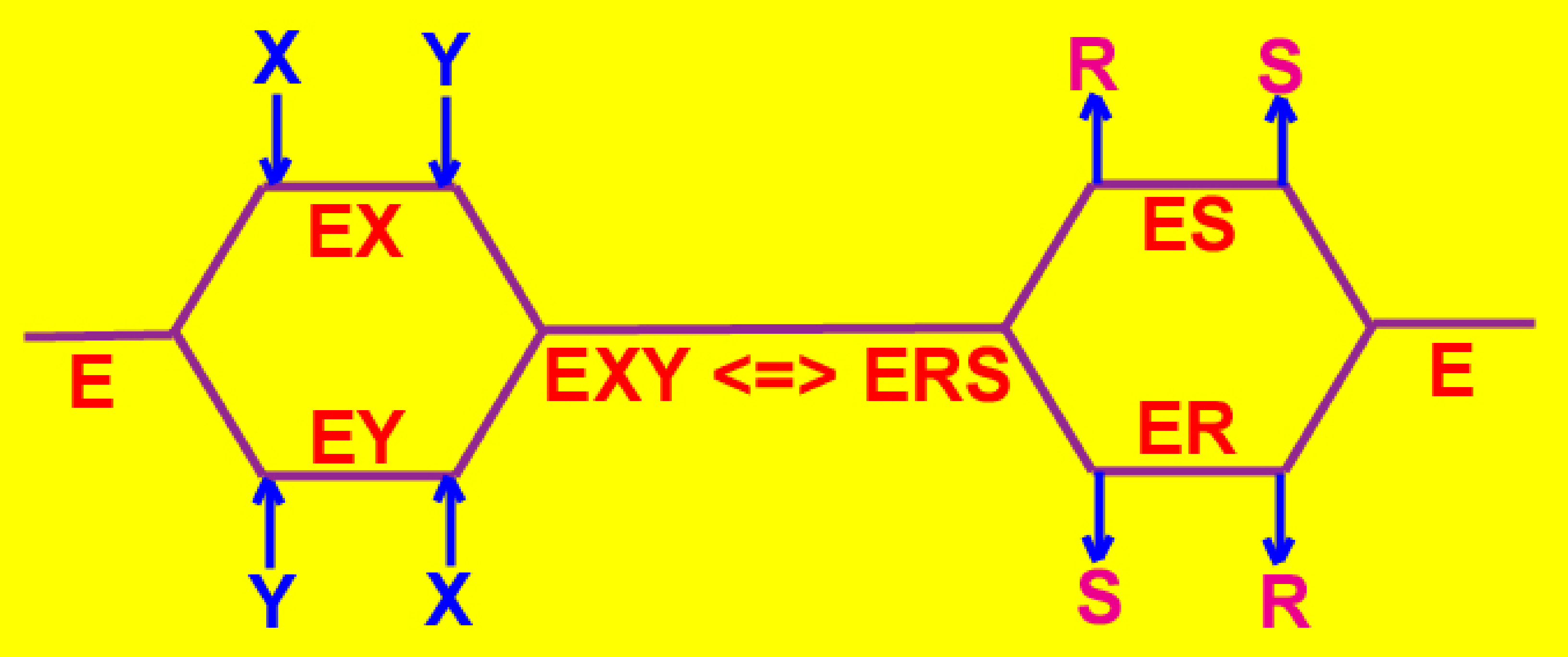
- In the case where separate experiments about the same system give 2 different rate equations, e.g.,

k [E] [X] [Y] [EX]

And

k [E] [X] [Y] [EY]

Mechanism = Random Sequential – Cleland Plot



- What, though, if an enzyme catalyzed a reaction that bound one substrate, released its product, then binds a SECOND substrate and releases ITS product?

Overall Reaction is: $E + X + Y \rightarrow E + R + S$

Mechanism

$E + X \rightarrow EX$

$EX \rightarrow ER$ 1st rate limiting step

$ER \rightarrow E + R$

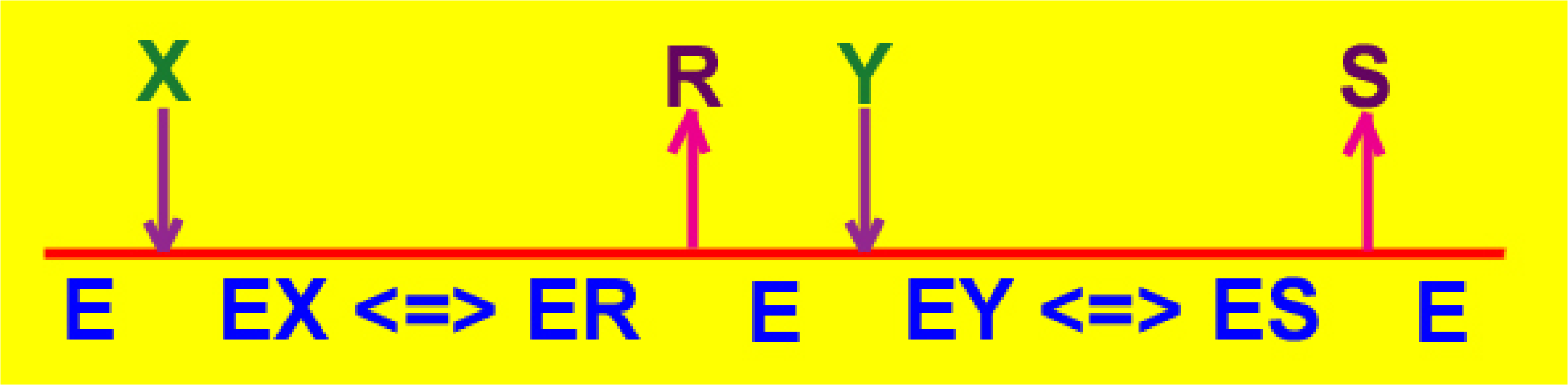
$E + Y \rightarrow EY$

$EY \rightarrow ES$ 2d rate limiting step

$ES \rightarrow E + S$

- Note: while written unidirectionally, in many cases the reactions are reversible
- With 2 rate limiting steps, this reaction and its kinetics get ugly fast.
- This sort of reaction between 2 substrates and the 1 enzyme act like a ping pong game.

Ping Pong Mechanism – Cleland Plot



Function of Kinetics

- To Determine Reaction Mechanisms