Chapter 16: Chemical Kinetics

Thermodynamics is used to predict whether a reaction will proceed under specified conditions – but it cannot be used to predict how fast the reaction will go or by what mechanism it will proceed.

Examples:

$2\,HCl(aq) + Mg(OH)_2(s) \rightarrow MgCl_2(aq) + 2\,H_2O(l)$ $\Delta G = -97\,kJ$ v. rapid

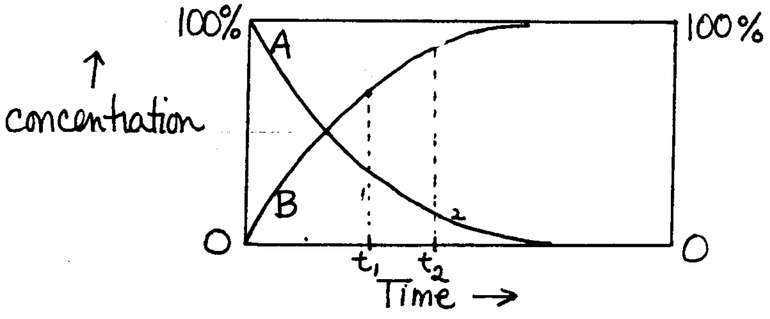
$C(diamond) + O_2(g) \longrightarrow CO_2(g)$ $\Delta G = -396\,kJ$ v. slow

Chemical kinetics is the study of rates of chemical reactions (i.e. determinatio of how fast reactions go) and the mechanisms by which they occur.

Let's consider what this means:

rate: change in the concentration of product or reactant per unit time. It is always a positive number. The reactant over time disappears and the product appears.

Consider a 1-step reaction: A → B



Note: for A → 2B,
Rate $= -\frac{\Delta A}{\Delta t} = +\frac{\Delta B}{2\Delta t}$

rate of reaction for any time interval $\Delta t = t_2 - t_1$ $= \underset{\uparrow}{-}\frac{\Delta A}{\Delta t} = \frac{-(A_2 - A_1)}{t_2 - t_1}$ rate of loss of A with time

since rate must be positive

$= \frac{\Delta B}{\Delta t} = \frac{B_2 - B_1}{t_2 - t_1}$ rate of production of B with time

For most purposes we are interested with the initial rate of reaction

which is the rate at $t=0$ when the reaction just begins
As time progresses, we see the rate of reaction slow down (slope of line → 0)

How do reactions occur? They occur via the reaction mechanism: the pathway (or series of steps) by which the reaction proceeds. The reaction rate is dependent on the rates of individual steps - as we shall see.

The rate of reaction depends on 4 factors:
(1) the nature of the reactants
(2) the concentration of reactants
(3) temperature
(4) catalysis

(1) Nature of Reactant

- chemical activity: eg some metals are more active than others in activity $K(s) > Na(s) > Li(s)$

- physical state (size of particles, phase, etc.)
  (a) a substance that is finely ground reacts faster than the same substance in chunks due to the much greater surface area exposed for reaction in the powdered sample.
  (b) reactions that occur between dissolved ions in solution are much more rapid than between solids or gases, since in the former case, no bonds need to be broken.

(2) Concentration of Reactants

In general, as the concentration of reactants increase
the probability of collisions increase
∴ the probability of reactions occurring increases.

For a simple one step reaction: $A \rightarrow B + 2C$ (decomposition reaction)

Rate of reaction = $\frac{-\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t} = \frac{\Delta C}{2\Delta t}$

∴ at any time, t

Rate $\propto [A]$ $\quad$ [ ] ≡ concentration in $\frac{mol}{L} = M$

$\boxed{\text{Rate Law Expression: Rate} = k[A]}$ for a specific temperature

where k is the rate constant

∴ if [A] is doubled, the rate of reaction doubles

* MOST reactions are NOT one step reactions!
The rate law expressions <u>must</u> be determined experimentally.

Consider the general reaction:

$$aA + bB + cC \rightarrow dD + eE + fF$$

General form of the rate law expression:

$$\text{Rate}\left(\frac{M}{\text{time}}\right) = k[A]^x[B]^y[C]^z$$

where
k is the specific rate constant
A, B, C are reactants (no products are involved)
x is the order of the reaction with respect to A
y is the order of the reaction with respect to B
z is the order of the reaction with respect to C
(in general, x, y, z have values of 0, 1, 2).
(x + y + z) is the overall order of the reaction.

*<u>Note</u>: x, y, z have NOTHING to do with the stoichiometric coefficients in the equation for the reaction – they must be obtained by experiment.

Example: The following rate data were obtained at 25°C for the following reaction. What is the rate law expression?

$$2A + B \rightarrow 3C$$

Experiment	[A] initial	[B] initial	Initial rate of formation of C
1	0.10 M	0.10 M	2.0×10^{-4} M·s^{-1}
2	0.30 M	0.30 M	6.0×10^{-4} M·s^{-1}
3	0.10 M	0.30 M	2.0×10^{-4} M·s^{-1}
4	0.20 M	0.40 M	4.0×10^{-4} M·s^{-1}

We know that the rate law expression will be: rate = $k[A]^x[B]^y$

By observation, we identify pairs of experiments where concentrations of reactants are all the same, except for one. We look to see what affect a change in its concentration has on the initial rate of reaction.

Aside: Consider Rate = $k[A]^x$

- if $x = 0$ (zero order w/r A) : Rate = $k\overset{=1}{[A]^0}$ Rate = constant, k
- if $x = 1$ (first order w/r A) : Rate = $k[A]^1$ Rate $\propto$ [A]
- if $x = 2$ (second order w/r A) : Rate = $k[A]^2$ Rate $\propto [A]^2$

Experiment 1 + 3: [A] is constant = 0.10 M
[B] increases by a factor of 3 $\left(= \frac{0.3\ M}{0.1\ M}\right)$
but the rate of reaction does NOT change
∴ [B] does not affect the rate
∴ order of reaction w/r (with respect to) B = y = 0

Experiments 2 + 3: [B] is constant = 0.30 M, [A] decreases by factor of 3
rate of reaction decreases by a factor of 3 $\left(= \frac{6\times10^{-4}}{2\times10^{-4}}\right)$
∴ rate $\propto$ [A]; order of reaction w/r A = 1 (first order)

Rate law expression: Rate = $k[A]^1[B]^0 = k[A]$

The overall order of rxn is (1 + 0) = 1

Example: What is the rate law expression for the following reaction, given the data below?

$$2A + B + 2C \rightarrow 3D + 2E$$

Experiment	[A]initial	[B]initial	[C]initial	Initial Rate of Formation of D
1	0.20 M	0.10 M	0.10 M	2×10^{-4} M/min
2	0.20 M	0.30 M	0.20 M	18×10^{-4} M/min
3	0.20 M	0.10 M	0.30 M	2×10^{-4} M/min
4	0.10 M	0.60 M	0.40 M	3.6×10^{-3} M/min

The rate law expression will have the form: $\text{Rate} = k\,[A]^x[B]^y\,[C]^z$
Now we must look at the data to derive the values of x, y, z.

Experiments 1 + 3: [A], [B] are constant, [C] increases by a factor of 3 $\left(= \frac{0.3}{0.1}\right)$
rate does NOT change
∴ reaction is zero order w/r to C and we can ignore this data

Experiments 1 + 2: [A] is constant, [B] increases by a factor of 3
rate increases by a factor of 9 $\left(= \frac{18\times10^{-4}}{2\times10^{-4}}\right)$
∴ rate $\propto [B]^2$, reaction is second order w/r B

There are no experiments where [A] varies and [B] remains constant, so we will have to evaluate the order of the reaction w/r A mathematically. Lets use Exp. 2 + 4 where [A] varies and write down the rate law expressions <u>with</u> the values plugged in, and solve 2 equations with 2 unknowns: x and k by dividing one equation by the other.

$$\text{Rate} = k\,[A]^x\,[B]^2\,\overset{\overset{1}{\shortparallel}}{\cancel{[C]}^0}$$

$$\begin{array}{l}\text{Expt 4}\\ \text{Expt 2}\end{array}\quad \frac{3.6\times10^{-3}}{1.8\times10^{-3}} = \frac{\cancel{k}(0.1)^x\,(0.6)^2}{\cancel{k}\,(0.2)^x\,(0.3)^2}$$

Note: Put the experiment with the larger rate on top - the numbers work out easier that way.

Simplifying, $2 = \left(\frac{0.1}{0.2}\right)^x \left(\frac{0.6}{0.3}\right)^2$

$= \left(\frac{1}{2}\right)^x (2)^2$

$\frac{1}{2} = \frac{2}{4} = \left(\frac{1}{2}\right)^x$

$x = 1$ ∴ reaction is first order w/r A

The rate law expression is $\text{Rate} = k[A][B]^2$ overall order is $1+2=3$

Example: Using the above rate law expression, if the concentration of A were halved and the concentration of B were tripled during a reaction, what would happen to the rate?

Assume the initial concentrations of A and B were both 1 M. Therefore

$\text{Rate} = k[A][B]^2 = k(1)(1)^2 = k$

After the change in the reaction,

$\text{Rate} = k\left(\frac{1}{2}\right)(3)^2 = \frac{9}{2}k$

∴ the rate of the reaction would ~~double~~. increase by a factor of 9/2

Specific Rate Constant, k

Reaction rate always has units of $\frac{\text{concentration}}{\text{time}}$ eg $\frac{M}{s}$, $\frac{M}{min}$ $\equiv M \cdot t^{-1}$

The units of k therefore depend on the overall order of the reaction ($\text{Rate} = k[A]^x$,

Overall Order of Reaction	Units of k	Example
0	$M \cdot t^{-1}$	$\text{Rate} = k$
1	t^{-1}	$\text{Rate} = k[A]$
2	$M^{-1} \cdot t^{-1}$	$\text{Rate} = k[A]^2$
3	$M^{-2} \cdot t^{-1}$	$\text{Rate} = k[A]^3$

In some examples, units of k are omitted - but you need to know them.

To determine value for k in an example, use the data from any experiment in that example, plug into the rate law expression and solve for k.

Example: Recall the second example for which we determined the rate-law expression:

$$\text{Rate} = k[A][B]^2$$

Using Expt 1 $$2\times10^{-4}\,\frac{M}{min} = k\,(0.20\,M)(0.10\,M)^2$$

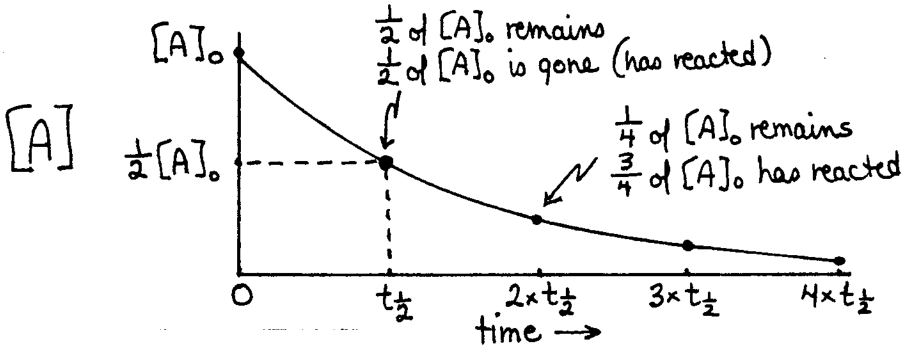
$$k = 0.1\ M^{-2}\cdot min^{-1}$$

Now we can write the complete rate law expression: $\text{Rate} = 0.1\ M^{-2}min^{-1}[A][B]^2$

Many times we wish to know the concentration of a reactant that would remain after a specified time, or how long it would take for some amount of the reactants to be used up. This leads us to the concepts of

Half-life and the Integrated Rate Equation (for first order reactions, only reactant has stoich. coeff. of 1)

The half-life of a reactant is the time required for half of the reactant to be consumed in the reaction



$[A]_0$ is the concentration of A at $t=0$ (the beginning of the reaction)

For reactions that are first order w/r A and first order overall (eg radioactive decay)

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = \frac{-d[A]}{dt} = k[A]$$

$$\int \frac{-d[A]}{[A]} = \int kt$$

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

where $[A]_t$ = amt or conc^n of A remaining at time, t

$[A]_0$ = initial amt or conc of A

$\frac{[A]_t}{[A]_0}$ = fraction remaining of A at time, t

k = rate constant

$$\boxed{\ln\frac{[A]_t}{[A]_0} = -kt \quad \text{or} \quad \log\frac{[A]_t}{[A]_0} = \frac{-kt}{2.303}} \quad \boxed{\text{(in book) or } \log\frac{[A]_0}{[A]} = \frac{kt}{2.303}}$$

↖ I prefer

Note: "log is exponent" $\log_{10} y = x \Leftrightarrow 10^x = y$ base 10
$\ln y = x \Leftrightarrow e^x = y$ base $e \equiv 2.7183\cdots$

example: $\log_{10} 100 = 2$
$10^2 = 100$

At time $t = t_{\frac{1}{2}}$, $[A]_t = \frac{1}{2}[A]_0$ by definition

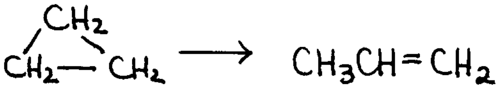
If we plug this into the previous equation (the one that I like), we have

$$\log \frac{\frac{1}{2}\cancel{[A]_0}}{\cancel{[A]_0}} = \frac{-kt_{\frac{1}{2}}}{2.303}$$

$$-0.301 = \frac{-kt_{\frac{1}{2}}}{2.303}$$

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

Example: Cyclopropane decomposes to propene by first order kinetics.



$t_{\frac{1}{2}} = 0.075\,s$

(a) calculate the rate constant, k:

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{0.075\,s} = 9.2\ s^{-1}$$

(b) How much of a 3.0 g sample remains after 0.20 s?

$$\log \frac{A_t}{A_0} = \frac{-kt}{2.303}$$

$$\log \frac{A_t}{3.0} = \frac{-9.2\ s^{-1} \times 0.20\,s}{2.303}$$

$$\log \frac{A_t}{3.0} = -0.799$$

Take the inverse log of both sides (on calculator: inv log or

$$\frac{A_t}{3.0} = 0.159 \qquad \therefore A_t = 0.48\,g$$

(c) How long does it take (in seconds) to have only 0.010 g remaining of a 3.0 g sample?

$$\log \frac{A_t}{A_o} = \frac{-kt}{2.303}$$

$$\log \frac{0.010}{3.0} = \frac{-9.2\,s^{-1} \times t}{2.303}$$

simply take log of $\frac{0.010}{3.0}$: $-2.48 = \frac{-9.2\,s^{-1} \times t}{2.303}$

$$t = 0.62\,s$$

(d) What fraction of the sample has been converted to propene after 0.50 s?

$$\log \frac{A_t}{A_o} = \frac{-kt}{2.303}$$

where $\frac{A_t}{A_o}$ is the fraction that <u>remains</u>!

and $\left(1 - \frac{A_t}{A_o}\right.$ is the fraction that has reacted.

$$\log \frac{A_t}{A_o} = \frac{-9.2\,s^{-1} \times 0.50\,s}{2.303}$$

$$\log \frac{A_t}{A_o} = -2.0$$

$$\frac{A_t}{A_o} = 0.01$$

∴ 0.01 (or 1%) is the fraction of cyclopropane remaining

<u>0.99</u> (or 99%) is the fraction that has reacted.

Two theories are used to explain why certain factors affect reaction rates.

I. <u>Collision Theory of Reaction Rates</u> (used for 1-step reactions)

premise: in order for a reaction to occur, the atoms, molecules or ions

(a) must collide (come into contact)

(b) must have an effective collision ie

- reacting species must have a minimum energy which will be transferred into breaking old bonds and making new ones.
- reacting species must have proper orientation

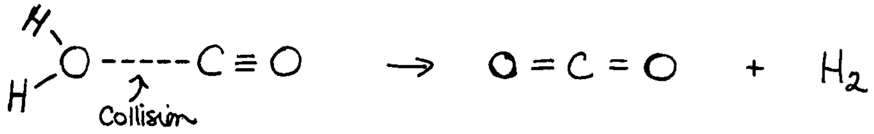
Consider the gas phase reaction: $CO + H_2O \rightarrow CO_2 + H_2$ $\quad \Delta G_{rxn} = \underset{\uparrow}{-}28.6$ kJ/mo

rxn is spontaneous

$$C{\equiv}O \;+\; H{-}O{-}H \;\rightarrow\; O{=}C{=}O \;+\; H{-}H$$

What kind of a collision do we need to get bond formation?

ANS. The O atom in H_2O must come into contact with the C atom in CO



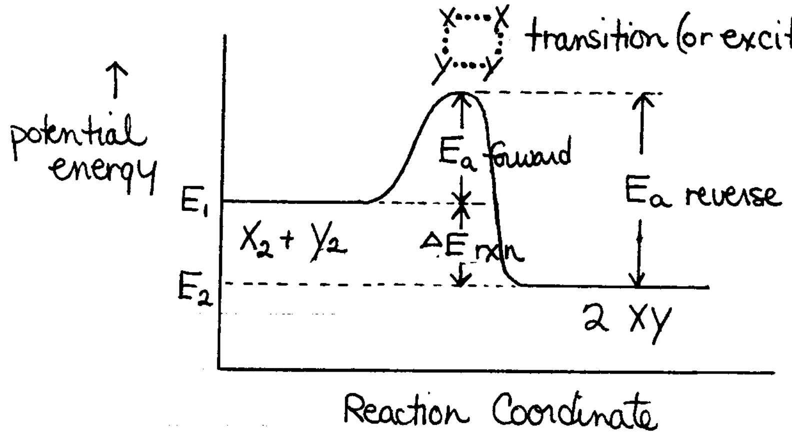
$$H_2O \cdots C{\equiv}O \rightarrow O{=}C{=}O + H_2$$

Effective collision (providing the energy of impact is great enough)

II Transition State Theory:

premise: in a 1-step reaction, the reactants are first converted into a high energy intermediate state, called a transition state, before forming products.

Consider $X_2 + Y_2 \rightarrow 2\,XY$



Ea forward is the activation energy for the forward reaction.

Ea reverse is the activation energy for the reverse reaction:

$2XY \rightarrow X_2 + Y_2$

reactants X_2 and Y_2 have to possess activation energy, E_a, in order to react.

If X_2 and Y_2 do react, the change in internal energy, ΔE_{rxn}, decreases $\therefore E_2 - E_1 < 0$ $\therefore$ there is a release of energy. If in the above reaction X_2, Y_2 + XY are gases, then $\Delta E = \Delta H$ and the reaction is exothermic.

$$\Delta E = \Delta H - P\Delta V = \Delta H - \underbrace{\Delta n RT}_{0}$$

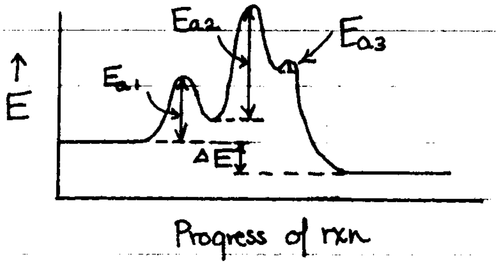
Reaction Mechanisms and the Rate-Law Expression

Most reactions occur in a series of steps called the mechanism of a reaction. These steps are thought to be primarily

(1) unimolecular decomposition steps eg. $A \rightarrow B + C$
(2) bimolecular collisions * eg. $A + B \rightarrow C$

* trimolecular collisions between 3 (or more) species are rare since it is very improbable that 3 (or more) species will be at the same place at exactly the same time to collide and react. ∴ We do not consider them.

- the SLOWEST step determines the rate of the overall reaction. It is called the "rate-determining step" and it is the step with the highest activation energy (Fig 16-12, p. 640).



Potential Energy Diagram for a 3-step reaction; the 2nd step is the rate determining step (has highest E_a)

The experimentally-derived rate-law expression eg Rate = $k[A]^x[B]^y$ is used to postulate a mechanism for the reaction. The values of x and y are related to the coefficients of the reactants in the SLOWEST step, influenced in some cases by earlier steps.

When the slow step in a mechanism is the first step, the order of a reaction w/r to a particular reactant (the exponent) indicates the number of molecules of that reactant that appear as reactants in that first, slow, rate-determining step. If there are fast, equilibrium steps prior (before) to the slow step, the situation is more complicated as we'll see.

To determine if a proposed mechanism is the correct one for a reaction, at least 2 criteria must be met:

(1) the sum of all the steps must be the same as the overall reaction when like terms are cancelled.

(2) the rate-law expression of the mechanism must match the true, experimentally-derived rate-law expression.

erion (1) self-explanatory

ion (2) (a) if the slow, rate-determining step is the first step, then the number of times each reactant appears as a reactant is the exponent in the rate law expression : $\text{Rate} = k\,[\text{each reactant}]^{\text{number of times it appears.}}$

Example: Consider the hypothetical reaction

$$2A + B + C \rightarrow AC + AB$$

with the experimentally-derived rate law expression:

$$\text{Rate} = k[A][B][C]$$

The rate law expression tells us that one molecule each of A, B and C are involved in determining the rate of the reaction.

Possible mechanism 1:

Step ①	$A + A \rightarrow A_2$	(slow)
Step ②	$A_2 + B \rightarrow AB + A$	(fast)
Step ③	$A + C \rightarrow AC$	(fast)
overall	$2A + B + C \rightarrow AC + AB$	

Note: A_2 is called an intermediate; it is both produced and consumed in the reactions.

Interpretation of this mechanism:

Step① two atoms of A collide together with enough energy to produce 1 molecule of A_2

Step② that molecule of A_2 (an intermediate, remember) collides with an atom of B to produce a molecule of AB and an atom of A.

Step③ the atom of A then collides with an atom of C; a chemical bond is formed between A and C and Voilá: a molecule of AC.

The overall reaction is the sum of the reactants and products – after crossing out like terms.

So, could Mechanism 1 be a possible mechanism for this reaction?

- criterion 1 is met – the overall reactions match
- the rate law expression, tho, for this mechanism is: Rate $= k[A]^2$

∴ Mechanism 1 <u>cannot</u> be the correct mechanism.

ion 2(b) If the slow step is preceeded by fast, equilibrium steps, then we have the following situation

<u>Possible Mechanism 2</u>: (for our same hypothetical reaction)

Step① $A + B \rightleftharpoons AB$ (fast equilibrium)

Step② $AB + C \rightarrow ABC$ (slow) ABC is intermediate

Step③ $\underline{ABC + A \rightarrow AC + AB}$ (fast)

overall $2A + B + C \rightarrow AC + AB$

- criterion 1 is met: overall reaction agrees with reaction under study
- criterion 2:

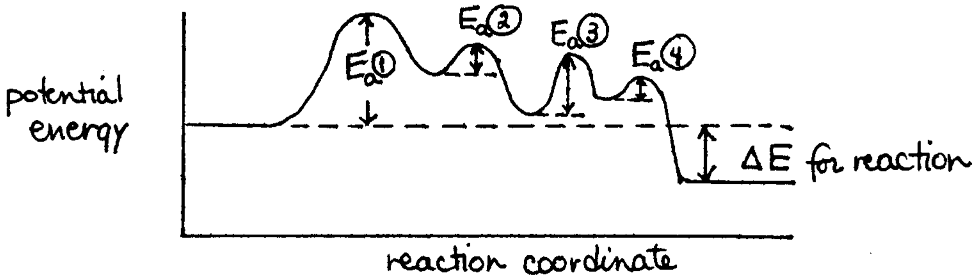
using the slow step, the rate law expression is:

$$\text{Rate} = k\,[AB][C]$$

Example: $2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$ Rate = $k[N_2O_5]$

Possible mechanism:
① $N_2O_5 \rightarrow NO_2 + NO_3$ (slow)
② $N_2O_5 + NO_2 \rightarrow N_2O_4 + NO_3$ (fast)
③ $NO_3 + N_2O_4 \rightarrow 2\,NO_2 + NO_3$ (fast)
④ $NO_3 + NO_3 \rightarrow 2\,NO_2 + O_2$ (fast)
overall $2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$

Recall the slower the step, the higher is the activation energy for that step.
∴ a possible potential energy diagram (Assuming Arrhenius frequency factor, A, is constant)



Is the following a potential mechanism?
Step ① $N_2O_5 \rightarrow N_2O + 2\,O_2$ (slow)
② $N_2O_5 + N_2O \rightarrow 2NO_2 + O_2 + N_2$ (fast)
③ $N_2 + 2O_2 \rightarrow 2\,NO_2$ (fast)
overall $2\,N_2O_5 \rightarrow 4NO_2 + O_2$

Ans. you might think so; step ① contains 1 molecule of N_2O_5 and it is the slow reaction. However step ③ is a trimolecular reaction which is not likely ∴ this is NOT a likely mechanism (TRICKY).

But AB is not a reactant; it is formed in Step ① and consumed in Step ②

For equilibrium reactions (e.g. Step ① in Mechanism 2) we can write

$$\text{equilibrium constant, } K = \frac{[\text{product 1}][\text{product 2}] \text{ etc.}}{[\text{reactant 1}][\text{reactant 2}] \text{ etc.}}$$ simplified (see Ch 17)

for Step ①: $A + B \rightleftarrows AB$ $\quad K = \frac{[AB]}{[A][B]} \Rightarrow [AB] = K[A][B]$ rearranging

Substituting into the rate law expression: $\text{Rate} = k[AB][C]$
we have,

$$\text{Rate} = k\,(K[A][B])\,[C] = k'\,[A][B][C]$$

where $k' = k \cdot K$

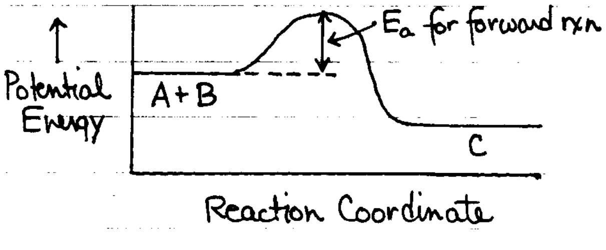
Therefore, this mechanism MAY be correct. To prove it, we must isolate the intermediate, ABC, in the laboratory.

Thus far, we have studied two factors that control the rate of the reaction:
(1) nature of reactants
(2) concentration of reactants.
Now we will address

(3) Effect of temperature changes on reaction rates. (Examples: 49, 53)

Consider the 1 step reaction: $A + B \rightarrow C$ $\quad \therefore \text{Rate} = k[A][B]$

A possible potential energy diagram:



As the temperature increases, more and more reactant molecules have the necessary energy, E_a (the activation energy) to react and form product molecules upon collision.
E_a does not change with the temperature; it only changes if mechanism change

Arrhenius developed the mathematical relationship between temperature, the rate constant, k (which does depend on T) and the activation energy, Ea (which does NOT depend on T).

$$k = A e^{\frac{-E_a}{RT}}$$

where k: specific rate constant
A: frequency factor - related to
(1) nature of reactants
(2) no. + effectiveness of collisions
E_a activation energy
R 8.314 J/mol.K
T absolute T (K)

$$\text{if } T \uparrow, \frac{E_a}{RT} \downarrow, \frac{-E_a}{RT} \uparrow, e^{\frac{-E_a}{RT}} \uparrow, k \uparrow, \text{rate} \uparrow$$

Taking natural log of both sides,

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

① at T_1: $\log k_1 = \log A - \frac{E_a}{2.303\, RT_1}$

② at T_2: $\log k_2 = \log A - \frac{E_a}{2.303\, RT_2}$

subtracting ① from ②, we have,

$$\log k_2 - \log k_1 = \cancel{\log A} - \cancel{\log A} - \left(\frac{E_a}{2.303\, RT_2} - \frac{E_a}{2.303\, RT_1}\right)$$

$$\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{E_a}{2.303\, R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

Example: What is the activation energy for the reaction: $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$?
where $k_1 = 2.6 \times 10^{-11}\ s^{-1}$ at 300°C (573 K)
$k_2 = 2.1 \times 10^{-10}\ s^{-1}$ at 330°C (603 K)

$$\log \frac{2.1 \times 10^{-10}\ s^{-1}}{2.6 \times 10^{-11}\ s^{-1}} = \frac{E_a}{2.303 \times 8.314\ J/mol \cdot K}\left(\frac{603 - 573}{603 \times 573}\right)$$

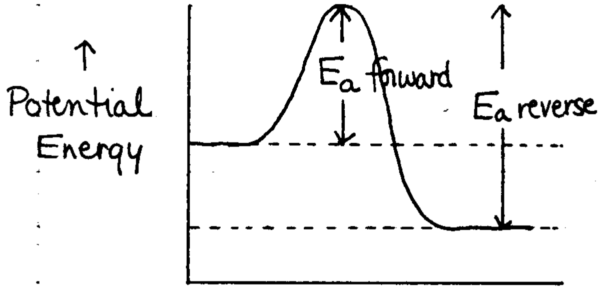
$$\log 8.1 = \frac{E_a}{19.15}\left(\frac{30}{345519}\right)$$

$$E_a = 2.00 \times 10^5\ J/mol \text{ or } 200.\ kJ/mol$$

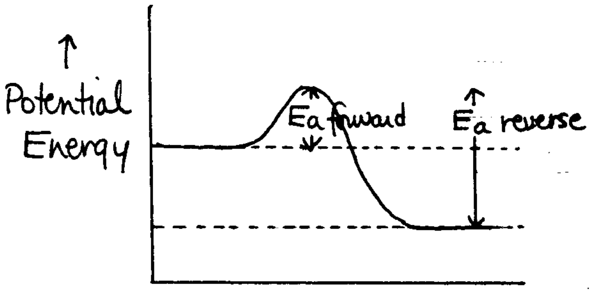
(4) Effect of Catalysts

Catalysts are substances that speed up reaction rates without being consumed. They can appear in an equation: A + B + catalyst → C + catalyst, or may only appear over the arrow $\xrightarrow{c}$.

Most catalysts appear to function by somehow <u>lowering</u> the activation energy of the original reaction by providing an alternate reaction pathway. (see Fig 16-15 p 645). ∴ $E_a \downarrow$ $\frac{E_a}{RT}\downarrow$ $-\frac{E_a}{RT}\uparrow$ $e^{-\frac{E_a}{RT}}\uparrow$ $k\uparrow$ rate ↑



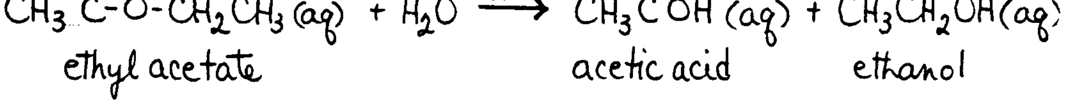
Reaction Coordinate
UNCATALYZED



Reaction Coordinate
CATALYZED

There are two categories of catalysts:

(1) homogeneous : the catalyst exists in same phase as reactants
example : strong acids



$$CH_3\overset{O}{\overset{\|}{C}}-O-CH_2CH_3(aq) + H_2O \xrightarrow{H^+} CH_3\overset{O}{\overset{\|}{C}}OH(aq) + CH_3CH_2OH(aq)$$

ethyl acetate — acetic acid — ethanol

(2) heterogeneous : the catalyst exists in a different phase than reactants. It is usually a solid – which lowers the activation energy by providing a surface upon which the reactions can occur.

example: $2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$ $\Delta G = -474$ kJ

this reaction does not go appreciably at room temperature but in the presence of Pt which is finely divided, the reaction is explosive.