Chemical Kinetics

Branch of chemistry that studies the rate of chemical reactions, the factors affecting them and the mechanism by which they proceed.

Rate of a Reaction

Change in concentration of reactant or product per unit time.

$$\boxed{r\_av = -\triangle[R] \;/\; \triangle t = +\triangle[P]}$$ <- average rate <-(over interval)

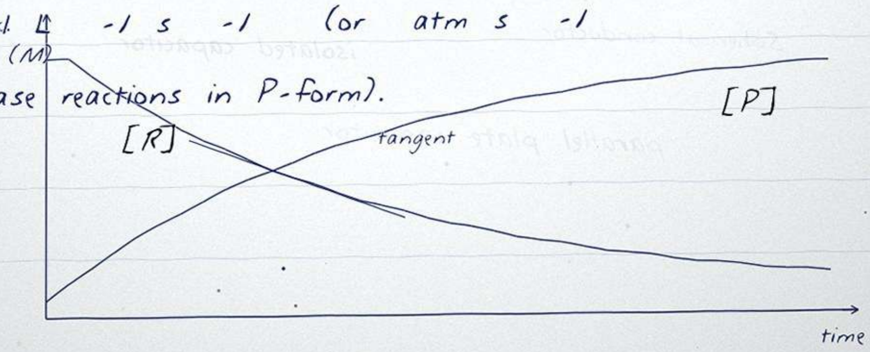
-ve sign: [R] decreases, so ~~delR~~ D[R] < 0.

Instantaneous Rate

Rate at a given instant of time, found by shrinking Dt -> 0 (i.e., slope of tangent).

$$\boxed{r\_inst = -d[R]/dt = +d[P]/dt}$$ <- tangent slope <- on c-vs-t graph

Units : ~~mol~~ L -1 s -1 (or atm s -1 for gas-phase reactions in P-form).



Rate in Terms of Stoichiometry

For $aA + bB \rightarrow cC + dD$,

we divide each rate by its coefficient :

$$\boxed{\text{rate} = -(1/a)\, d[A]/dt = -(1/b)\, d[B]/dt}$$

$$\boxed{= +(1/c)\, d[C]/dt = +(1/d)\, d[D]/dt}$$

<- unique rate
<- of the rxn

Example : $2\, N_2O_5 \rightarrow 4\, NO_2 + O_2$

rate $= -(1/2)\, d[N_2O_5]/dt$

$= +(1/4)\, d[NO_2]/dt$

$= +d[O_2]/dt$

Worked Example - 1

$[N_2O_5]$ falls $2.33 \rightarrow 2.08$ mol/L in 184 min.

Find avg rate & rate of NO_2 formation.

rate $= -(1/2)(2.08 - 2.33)/184$

$= -(1/2)(-0.25 / 184)$

$= 6.79 \times 10^{-4}$ mol L^{-1} min^{-1}

$= 1.13 \times 10^{-5}$ mol L^{-1} s^{-1}

$d[NO_2]/dt = 4 \times$ rate

$= 4 \times 6.79 \times 10^{-4}$

$= 2.72 \times 10^{-3}$ mol L^{-1} min^{-1}

Factors Affecting Rate

(1) Concentration of reactants

More molecules -> more collisions -> faster.

(2) Temperature

Rate roughly doubles for every 10 K rise.

(3) Surface area (for heterogeneous rxn)

Powder reacts faster than lumps.

(4) Catalyst

Lowers activation energy.

(5) Pressure (for gas phase)

Higher P -> higher conc. -> faster.

(6) Nature of reactants & light (photochem).

Rate Law

For a A + b B -> products :

$$\boxed{\text{rate} = k\,[A] \quad x \quad [B]}$$

<- x, y found
y <- experimentally

x, y are NOT always = a, b (only sometimes).

Order of a Reaction

Order = sum of powers of conc. terms in the rate law. For rate = $\kappa [A]^x \times [B]^y$,

$$\boxed{\text{order} = x + y.}$$

<- overall order
<- of reaction

Can be 0, 1, 2, 3, or even fractional.
Negative order rare; ~~alaways~~ always experimental.

Units of κ

From rate = $\kappa [\text{conc}]^n$,

$$\boxed{\kappa \text{ units} = (\text{mol/L})^{(1-n)}\ s^{-1}}$$

<- n = order

0 order : $mol\ L^{-1}\ s^{-1}$

1 order : s^{-1}

2 order : $L\ mol^{-1}\ s^{-1}$

3 order : $L^2\ mol^{-2}\ s^{-1}$

Molecularity

No. of reacting species (atoms / ions / molecules) that collide simultaneously.

Order vs. Molecularity

Molecularity is defined only for an elementary (single-step) reaction.

Comparison

Order	Molecularity
experimental	theoretical
from rate law	from balanced eqn
0, 1, 2, 3, frac.	1, 2, 3 (whole)
can be zero	never zero
for any rxn	only elementary
may differ from M	for one step

Worked Example - 2

Find order, units of k for :

(a) 3 NO -> N2O ; rate = k[NO] 2

(b) CH3CHO -> CH4 + CO ;

rate = k [CH3CHO] (3/2)

Ans (a) : order = 2 ;

k in L mol -1 s -1

Ans (b) : order = 3/2 ;

k in L (1/2) mol (-1/2) s -1

Elementary & Complex Reactions

Elementary : goes in one step. Order = molecularity for such reactions.

Complex : proceeds by 2 or more steps (a mechanism). Slowest step is the rate-determining step.

Example : $KClO_3$ decomp.

$4\,KClO_3 \rightarrow 3\,KClO_4 + KCl$

Molecularity = 4 (theoretical),

but ~~4-body~~ 4 molecules colliding at once → impossible.

Hence actually goes by a multi-step path.

Why integrate the rate law ?

Differential form $-d[R]/dt = k\,[R]^n$ tells rate at any moment, but to get $[R]$ as a function of t we must INTEGRATE.

$$\boxed{[R] = f(t) \quad \& \quad k = (\text{something})/t}$$

<- directly usable

<- experimental form

Now we tackle zero and first order integrated rate equations.

Zero Order Reaction

Rate does NOT depend on conc. of reactant.

$$\boxed{\text{rate} = -d[R]/dt = k\,[R]\quad 0} = k$$ <-constant rate

Derivation

Step 1 : $d[R] = -k\,dt$

Step 2 : integrate both sides

$$[R] = -k\,t + I$$

Step 3 : at $t = 0$, $[R] = [R]0$

$$\Rightarrow \quad I = [R]0$$

Step 4 : integrated rate law

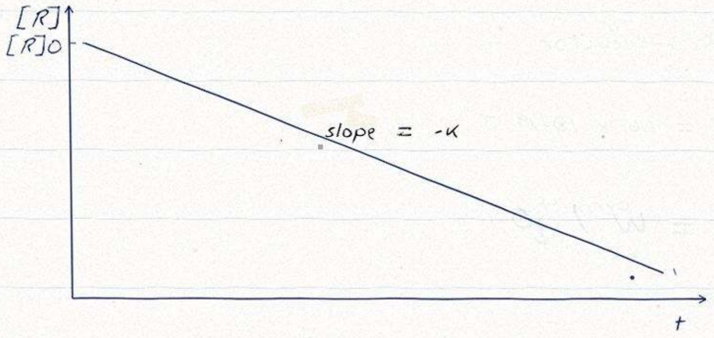
$$\boxed{[R] = [R]0 - k\,t}$$

<- linear in t
<- slope $= -k$

$$\boxed{k = ([R]0 - [R]) / t}$$

Examples : decomp. of NH_3 / HI on Pt surface ; photochemical rxns.

Zero Order : Graphs & t1/2



Plot of [R] vs t :

STRAIGHT LINE,

slope = -k,

intercept = [R]0.

Half-Life (t1/2)

Time required for [R] to drop to [R]0 / 2.

Put $[R] = [R]_0/2$ in $[R] = [R]_0 - k t$:

$$[R]_0/2 = [R]_0 - k\, t_{1/2}$$

$$k\, t_{1/2} = [R]_0/2$$

$$\boxed{t_{1/2} = [R]_0 / 2k}$$

<- DEPENDS on
<- [R]0 (zero order)

i.e. t1/2 is proportional to [R]0.

First Order Reaction

Rate is proportional to [R] to the first power.

$$\boxed{\text{rate} = -d[R]/dt = \kappa\ [R]}$$ <- linear in [R]

Derivation

Step 1 : separate variables

$$d[R]/[R] = -\kappa\ dt$$

Step 2 : integrate

$$\ln\ [R] = -\kappa\ t + I$$

Step 3 : at $t = 0$, $[R] = [R]0$

$$I = \ln\ [R]0$$

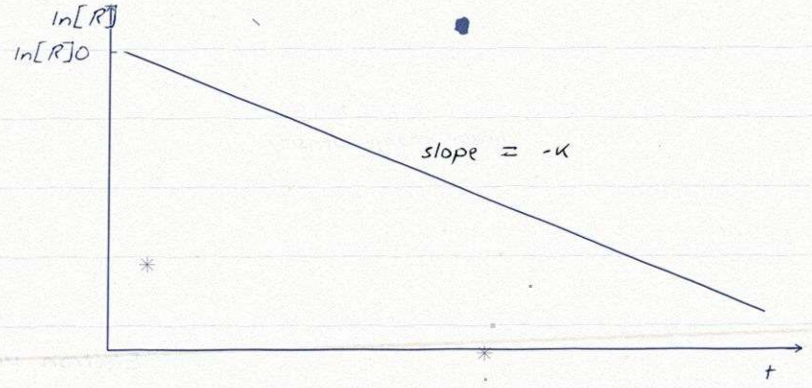
Step 4 : final form

$$\boxed{\ln\ (\ [R]\ /\ [R]0\ ) = -\kappa\ t}$$ <- integrated <- form (natural log)

$$\boxed{\kappa = (2.303\ /\ t)\ \log\ ([R]0\ /\ [R])}$$ <- base-10 <- form

Also : $[R] = [R]0\ e\ (-\kappa\ t)$.

First Order : ln[R] vs t plot



$\ln [R] = \ln [R]_0 - k \cdot t$ (rearranged).

Plot of $\ln [R]$ vs t : STRAIGHT LINE

slope = $-k$

intercept = $\ln [R]_0$

Equivalently : $\log [R]$ vs t :

- slope = $-k / 2.303$

Examples

(i) $N_2O_5 \rightarrow 2\ NO_2 + (1/2)\ O_2$

(ii) $CH_2{=}CH_2 + H_2 \rightarrow C_2H_6$ (hydrog.)

(iii) all radioactive decays.

First Order : Half-Life

Put $[R] = [R]0 / 2$ in

$k = (2.303 / t) \log ([R]0 / [R])$:

$k = (2.303 / t1/2) \log ([R]0 / ([R]0/2))$

$= (2.303 / t1/2) \log 2$

$= (2.303 \times 0.301) / t1/2$

$= 0.693 / t1/2$

*

$\boxed{t1/2 = 0.693 / k}$ <- INDEPENDENT *
<- of [R]O (?)

Big idea : for a 1st order rxn, t1/2 is the same NO MATTER how much you start with - this is unique to first order.

Quick comparison

0 order : $t1/2 = [R]0 / 2k$ (prop to [R]O)
1 order : $t1/2 = 0.693 / k$ (independent)
2 order : $t1/2 = 1 / (k [R]0)$ (inversely ~~dependent~~

n order : t1/2 prop. to [R]O (1-n).

Scanned with CamScanner

Worked Example - 3

Initial $[N_2O_5] = 1.24 \times 10^{-2}$ mol/L; after 60 min, $[N_2O_5] = 0.20 \times 10^{-2}$ mol/L. Find rate constant (1st order rxn).

$$k = (2.303 / t) \log ([R]_0 / [R])$$

$$= (2.303 / 60) \log (1.24/0.20)$$

$$= (2.303 / 60) \log 6.20$$

$$= (2.303 / 60) \times 0.7924$$

$$= 0.0304 \text{ min}^{-1}$$

$$\boxed{k = 3.04 \times 10^{-2} \text{ min}^{-1}}$$

Worked Example - 4

1st order rxn, $k = 5.5 \times 10^{-14}$ s^{-1}. Find half-life.

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

$$= 0.693 / (5.5 \times 10^{-14})$$

$$= 0.126 \times 10^{14} \text{ s}$$

$$\boxed{t_{1/2} = 1.26 \times 10^{13} \text{ s}}$$

Worked Example - 5

Show that for a 1st order rxn, time for 99.9 % completion is 10 t1/2.

Solution

Let [R]0 = 100. At 99.9 % done, [R] = 0.1.

$k = (2.303 / t) \log([R]_0 / [R])$

$k = (2.303 / t) \log(100 / 0.1)$
$= (2.303 / t) \log 1000$
$= (2.303 / t) \times 3$

$\Rightarrow t = 6.909 / k$

Now $t_{1/2} = 0.693 / k$

$t / t_{1/2} = 6.909 / 0.693 = 10$

$$\boxed{t\,(99.9\,\%) = 10\, t_{1/2}}$$

<- ten half-
<- lives to 99.9%

(After n half-lives : $[R] = [R]_0 / 2^n$.)

Summary - Rate Laws

Order	Diff. form	Integ. form	Linear plot	
0	$-d[R]/dt = \kappa$	$[R] = [R]_0 - \kappa t$	$[R]$ vs t slope $= -\kappa$	
1	$-d[R]/dt = \kappa [R]$	$\ln([R]_0/[R]) = \kappa t$	$\ln[R]$ vs t slope $= -\kappa$	
2	$-d[R]/dt = \kappa [R]^2$	$1/[R] - 1/[R]_0 = \kappa t$	$1/[R]$ vs t slope $= +\kappa$	
$t_{1/2}$	$[R]_0/(2\kappa)$	$0.693/\kappa$	$1/(\kappa[R]_0)$	
κ units	$mol\ L^{-1}\ s^{-1}$	s^{-1}	$L\ mol^{-1}\ s^{-1}$	

Memorise this table - shows all of the kinetics calculations on one page.

Note : for nth order ($n \neq 1$),
$t_{1/2}$ prop. $[R]_0^{(1-n)}$.

Pseudo First Order Reactions

A reaction whose TRUE order is higher, but behaves as first order because conc. of one reactant is taken in LARGE EXCESS (so it stays effectively constant).

Example 1 : Acid hydrolysis of ester

$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$

Real rate : $k\,[\text{ester}]\,[H_2O]$ (2nd order)

Water is in great excess => $[H_2O] = \text{const.}$

$$\boxed{\text{rate} = k'\,[\text{ester}] \quad \text{where} \quad k' = k\,[H_2O]}$$ <- absorbed <- into k'

Behaves as a 1st order reaction.

Example 2 : Inversion of cane sugar

$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

(sucrose) glucose fructose

$\text{rate} = k\,[\text{sucrose}]\,[H_2O]$

=> $\text{rate} = k'\,[\text{sucrose}]$ (~~2nd~~ 1st order, pseudo)

Useful when one species is solvent.

Effect of Temperature on Rate

Rough rule (temp. coefficient) :

$\boxed{\left(k_{(T+10)} \right) / k_T}$ 2 to 3 <- rate doubles
<- for every 10 K rise

Why ? Two reasons :

(a) more KE means more collisions per second (small effect).

(b) bigger fraction of molecules have enough energy to cross the activation barrier (LARGE exponential effect).

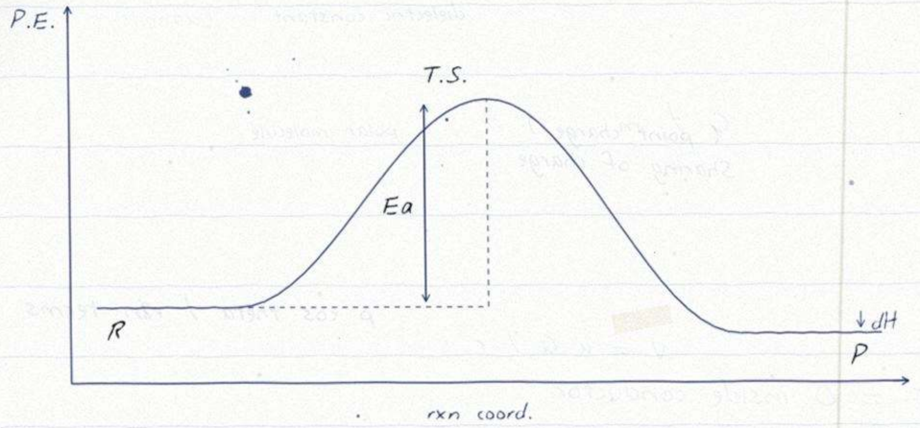
Activation Energy (Ea)

Min. energy that colliding molecules must have for the collision to LEAD to reaction.

Threshold energy = Ea + avg KE of reacting species.

Activated complex / ~~transmission~~ transition state : high-energy unstable intermediate at peak.

Potential Energy Profile



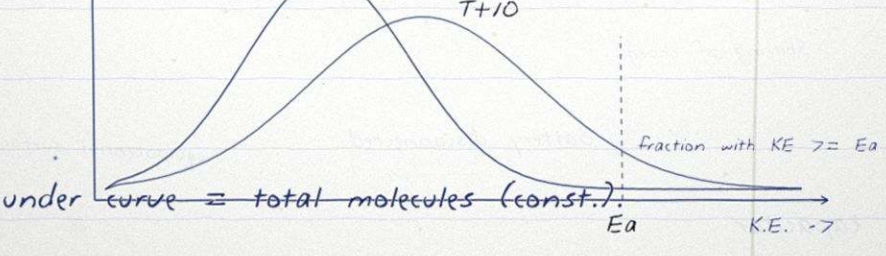
$E_a = E(T.S.) - E(\text{reactants})$.

$dH = E(P) - E(R)$ (the reaction enthalpy).

Lower Ea => faster reaction at given T.

Catalysts work by lowering Ea.

Maxwell - Boltzmann Distribution



Area under ~~curve = total molecules (const.)~~

Arrhenius Equation

Quantitative relation between k & T :

$$\boxed{k = A \; e \; (-Ea / R} \; T$$

<- exponential
<- form

where :

A = Arrhenius / pre-exponential factor
collision frequency (units of k).

Ea = activation energy (J mol -1).

R = 8.314 J K -1 mol -1 (gas const.).

T = temperature in K.

Physical meaning of e (-Ea/RT)

= fraction of molecules whose KE >= Ea.

As T rises -> exponent less negative ->
fraction grows -> k grows EXPONENTIALLY.

Two limits

T -> infinity : e (-Ea/RT) -> 1, so k -> A.

T -> 0 : e (-Ea/RT) -> 0, k -> 0
(reaction frozen).

Higher Ea -> more sensitive to T.

Logarithmic Form & Arrhenius Plot

Take natural log of $\kappa = A\ e\ (-Ea/RT)$:

$$\boxed{\ln \kappa = \ln A - Ea / (}\ R <\!\!- T\ \text{linear in} <\!\!- 1/T$$

$$\boxed{\log \kappa = \log A - Ea / (2.303\ R\ T)}$$

Plot :

$\ln \kappa$ vs $1/T$

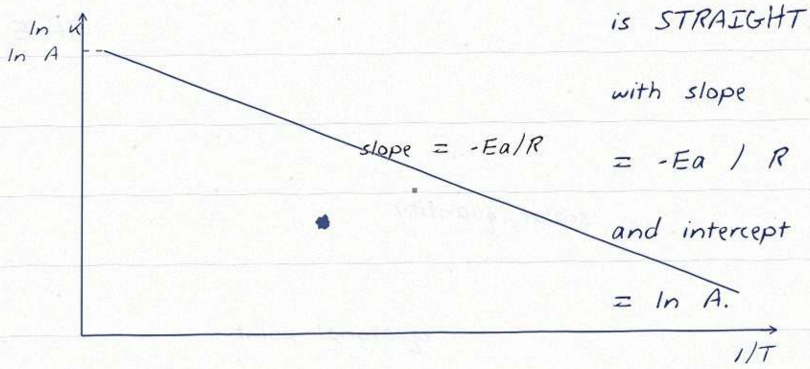
is STRAIGHT

with slope

$= -Ea / R$

and intercept

$= \ln A$.



From slope : find Ea

$$\boxed{Ea = -R \times slope}$$

<- Ea > 0

<- (slope is neg.)

From intercept : $A = \exp(\text{intercept})$.

So one plot gives BOTH Ea and A.

Two-Temperature Form

At T1 : $\ln K1 = \ln A - Ea / (R\, T1)$

At T2 : $\ln K2 = \ln A - Ea / (R\, T2)$

Subtract (eq.1) from (eq.2) :

$$\ln (K2 / K1) = (Ea / R) \left[1/T1 - 1/T2 \right]$$

$$\boxed{\log (K2/K1) = (Ea / 2.303\, R)(T2 - T1)/(T1\, T2)}$$

<-VERY
<-usef

Use this when you have K at two temps and want Ea - or vice versa.

Sign / sanity check

If $T2 > T1 \Rightarrow K2 > K1 \Rightarrow$ log positive.

Right side is also positive ($T2 - T1 > 0$, $Ea > 0$) - consistent.

Special case : rate doubles for $DT = 10$

near $T = 298$ K $\Rightarrow$ Ea 50 - 60 KJ/mol.

(this is the empirical 'rule of thumb' source.)

Worked Example - 6

$k_1 = 0.02\ s^{-1}$ at $T_1 = 500\ K$,

$k_2 = 0.07\ s^{-1}$ at $T_2 = 700\ K$.

Find Ea and A.

Solution

$\log (k_2/k_1) = (E_a / 2.303\ R)\ (T_2 - T_1)/(T_1\ T_2)$

$\log (0.07 / 0.02) = \log 3.5 = 0.544$

$(T_2 - T_1)/(T_1\ T_2) = 200 / (500 \times 700)$

$= 5.714 \times 10^{-4}\ K^{-1}$

$\Rightarrow E_a = (0.544 \times 2.303 \times 8.314) / (5.714 \times 10^{-4})$

$\boxed{E_a \quad 18\ 230\ J\ mol^{-1} = 18.23}$ kJ/mol

Now find A using $k = A\ e^{(-E_a/RT)}$:

$0.02 = A\ e^{(-18230 / (8.314 \times 500))}$

$0.02 = A\ e^{(-4.385)}$

$0.02 = A \times 0.01243$

$\boxed{A \quad 1.61\ s^{-1}}$

Worked Example - 7

1st order rxn $C_2H_5I \rightarrow C_2H_4 + HI$ has $k = 1.60 \times 10^{-5}\ s^{-1}$ at 600 K and $E_a = 209$ kJ/mol. Find k at 700 K.

Solution

$$\log k_2 - \log k_1 = (E_a / 2.303 R)(1/T_1 - 1/T_2)$$

$$\log k_1 = \log (1.60 \times 10^{-5})$$
$$= -4.796$$

$$1/T_1 - 1/T_2 = 1/600 - 1/700$$
$$= (700 - 600)/(600 \times 700)$$
$$= 100 / 420000$$
$$= 2.381 \times 10^{-4}\ K^{-1}$$

$$E_a / (2.303 R) = 209000 / (2.303 \times 8.314)$$
$$= 10920\ K$$

$$\log k_2 = -4.796 + 10920 \times 2.381 \times 10^{-4}$$
$$= -4.796 + 2.599 = -2.197$$

$$\boxed{k_2 \qquad 6.36 \times 10^{-3}}$$

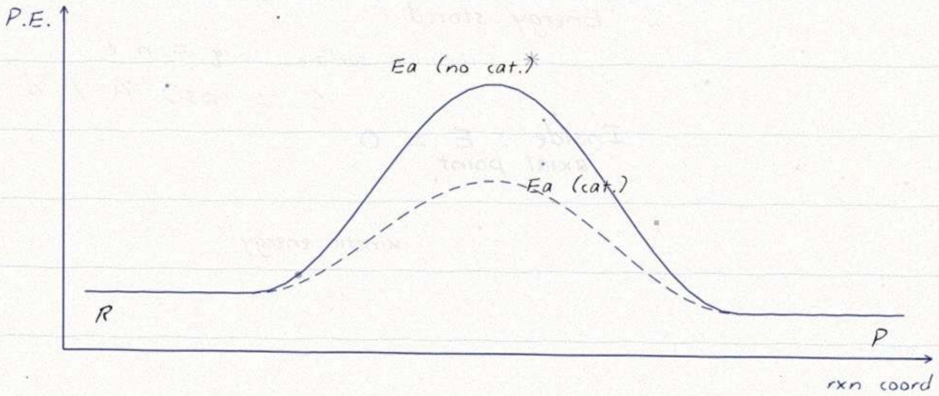
rate up

<- 400 x

Effect of a Catalyst

A substance that increases reaction rate without itself being permanently changed.

Action explained by INTERMEDIATE COMPLEX theory : catalyst forms a temporary complex with reactant, decomposing later to give products + free catalyst.



Key facts

- * Catalyst provides an alternate path of LOWER Ea.
- * Does NOT change dG, dH, K_eq.
- * Speeds BOTH forward & backward rxns equally => equilibrium reached faster.
- * A small amount catalyses a ~~small~~ LARGE amount of reactants (regenerated each cycle).

Collision Theory

Trautz & Lewis, 1916 - 18. Based on kinetic theory of gases. Idea : reactant molecules are hard spheres that REACT when they collide.

Collision frequency (Z)

Number of collisions per unit time per unit volume of the reaction mixture.

For bimolecular $A + B \rightarrow$ products

$$\boxed{\text{rate} = Z_{AB}\ e^{(-E_a/RT)}}$$

<- compare with Arrhenius

where Z_{AB} = collision frequency of A,B

$e^{(-E_a/RT)}$ = fraction with KE $\geq E_a$.

Comparing with $k = A\, e^{(-E_a/RT)}$:

A is essentially Z_{AB}.

Problem : not all collisions react

For complex molecules - prediction by Z alone overestimates k. Reason : ORIENTATION of molecules also matters.

Effective Collisions & Steric Factor

Effective collision : has BOTH

(i) energy >= Ea (threshold) ;
(ii) proper ORIENTATION of molecules.

Introduce steric factor P

Fraction of energetic collisions with the RIGHT orientation. $0 < P < 1$.

$\boxed{\text{rate} = P\ Z\_AB\ e\ (\ -Ea\ /\ R}$ T <- modified
<- collision form

Three criteria for a successful reaction :

(1) Collision must take place.
(2) Energy of collision >= Ea.
(3) Molecules must be properly oriented.

Limitations of collision theory

- * Treats molecules as hard spheres
  - ignores internal structure.
- * Cannot predict P from first principles.
- * Refined later by Transition State theory (Eyring, higher classes).

Worked Example - 8

Pseudo 1st order rxn in water :

t (s)	0	30	60	90
[A] (M)	0.55	0.31	0.17	0.085

Find k using last point (t = 90, A = 0.085).

$k = (2.303 / t) \log ([A]_0 / [A])$

$= (2.303 / 90) \log (0.55 / 0.085)$

$= (0.02559) \log 6.47$

$= (0.02559) (0.811)$

$\boxed{k \qquad 2.075 \times 10^{-2}} \quad s^{-1}$

Also : avg rate from t = 30 to 60 :

$\text{rate} = -(\Delta[A]/\Delta t) = -(0.17 - 0.31)/(60 - 30)$

$= 0.14 / 30 = 4.67 \times 10^{-3} \text{ mol } L^{-1} s^{-1}$

Half-life : $t_{1/2} = 0.693 / k$

$= 0.693 / 0.02075 = 33.4 \text{ s}$

Key Formulas - Last Look

Rate

$$\boxed{\text{rate} = -(1/a)\ d[A]/dt = +(1/c)\ d[C]/dt}$$

Rate law

$$\boxed{\text{rate} = k\ [A]\ x\ [B]}\ y$$

Integrated forms

0 order : $\boxed{[R] = [R]0 - k\,t}$

1 order : $\boxed{k = (2.303/t)\ \log([R]0/[R])}$

Half-life

0 order : $t1/2 = [R]0\ /\ 2\,k$

1 order : $t1/2 = 0.693\ /\ k$

Arrhenius

$$\boxed{k = A\ e\ \ (-Ea/RT)}$$

$$\boxed{\log(k2/k1) = (Ea/2.303R)(T2 - T1)/(T1\ T2)}$$

Exam Tips & Tricks

(1) Always quote the rate law - it must come from experiment, never from balanced equation.

(2) Units of k : use (mol/L) (1-n) s -1 to spot the order if it's not given.

(3) For 1st order - t1/2 is independent of [R]0. Big examiner favourite.

(4) After n half-lives : [R] = [R]0/2 n. Use this for 'time for X % completion'.

(5) Arrhenius eqn : pick the form you need
- one T -> use k = A e (-Ea/RT).
- two T -> use the log (k2/k1) form.
- graph -> use ln k vs 1/T.

(6) Pseudo 1st order : ester hydrolysis, inversion of cane sugar. Water in large excess => effective 1st order.

(7) Catalyst : ~~changes K_eq~~ lowers Ea only. K_eq, dG, dH UNCHANGED.

Common Pitfalls

X Confusing order with molecularity.

Order = experimental ;

Molecularity = theoretical (elementary).

X Assuming rate law follows stoich.

It ~~does~~ may or may not - always check.

X Forgetting -ve sign for reactant rate.

-(d[R]/dt) ALWAYS positive number.

X Using log vs ln incorrectly.

log10 = (1 / 2.303) ln. Mind the 2.303.

X Saying catalyst changes K_eq. Wrong.

Catalyst only changes the rate, not

the position of equilibrium.

X Mixing up Ea / R with Ea / RT in

Arrhenius plot. Slope = -Ea / R only.

X Pseudo 1st order - units of κ.

κ' is in s -1 ; original κ in L mol -1 s -

Don't quote the wrong constant.

Chapter Summary

- Rate of rxn : D[concentration] / Dt, instantaneous or average.

- Rate law : rate = k [A] x [B] y , x + y = order, found experimentally.

- Order vs molecularity : order is exp, molecularity is whole-number, elementary.

- Integrated rate laws give k from data ; half-life for 1st order is independent of [R]0 (unique property).

- Arrhenius k = A e (-Ea/RT) links rate constant to temperature ; ln k vs 1/T linear, slope = -Ea / R.

- Collision theory : rate = P Z_AB e (-Ea/RT) accounts for energy + orientation.

- Catalyst lowers Ea -> alternate path ; doesn't shift equilibrium.

\- end