Kinetics

- Study of rate of chemical processes
- Study of speed w/ which reactants convert to products.

College Board Reference Sheet:

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

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

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

- A chemical rxn = Molecules colliding!
- If collisions happen in right spots = rxn occurs
- If frequent, amt of rxt ↓ & amt of product ↑

Thermodynamics - Does a rxn take place?
Kinetics - How fast does a rxn proceed
How molecular collisions effect rxn rates

__Factors affecting rate of rxn:__ (Increase one = ↑ rate)

1. __Physical State of Rxt__ (to react, molecules must contact)
   = ↑ homogenous mixture = ↑ speed of rxn
   ... Also ↑ surface area of particles & Bond strength
2. __Concentration of Rxt__ = ↑ [Rxt] = ↑ collisions
3. __Temperature__ = ↑ Temp = ↑ KE = ↑ collisions
4. __Presence of Catalyst__ = ↑ rate by Δ Mechanism of Rxn
   (Not consumed in rxn)

(A) Reaction Rates "How we measure rates"

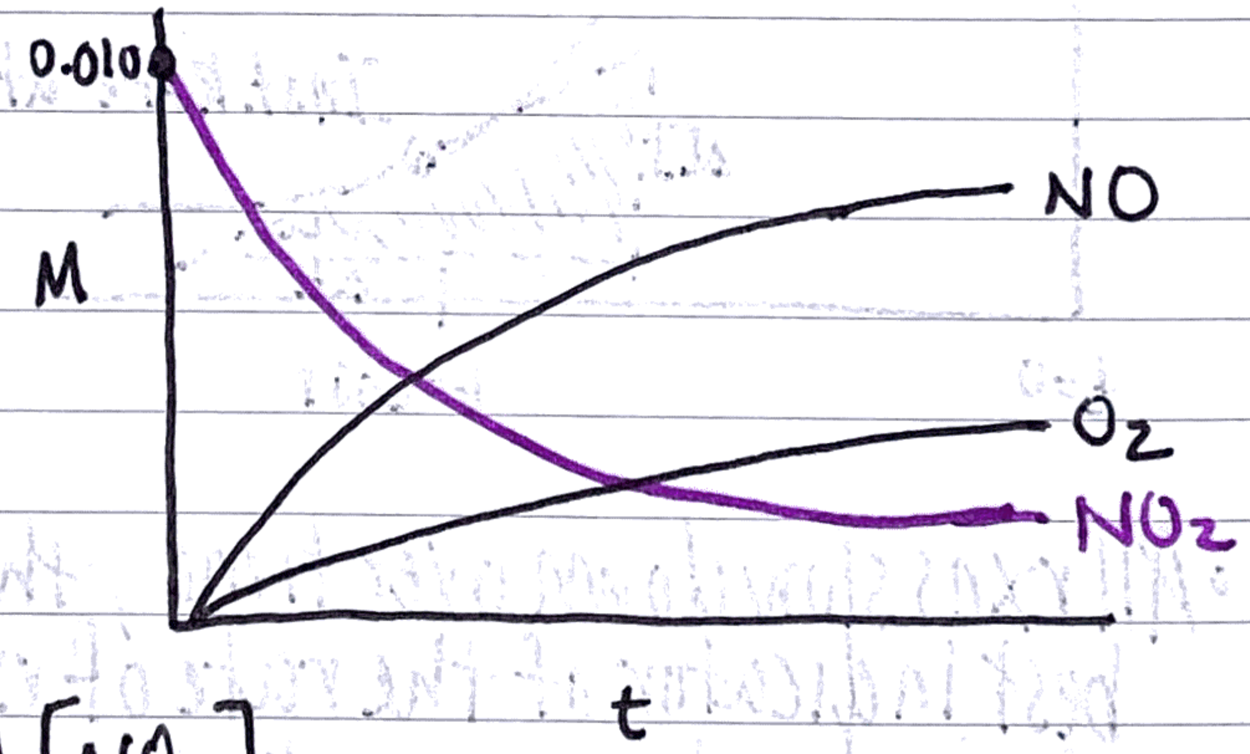
- Change in concentration of a reactant or product per unit of time
- Units = $M/s = M \cdot s^{-1} = mol \cdot L^{-1} \cdot s^{-1}$

→ $Rate = \frac{\Delta[A]}{\Delta t}$ $\frac{\text{(change in concentration)}}{\text{(Change in time)}}$ $\left(\frac{M}{s}\right)$

Graph of Conc. vs. Time from Data Table

Ex: Decomposition of NO_2 ($2NO_2 \rightarrow 2NO + O_2$)

Notice the speeds vary

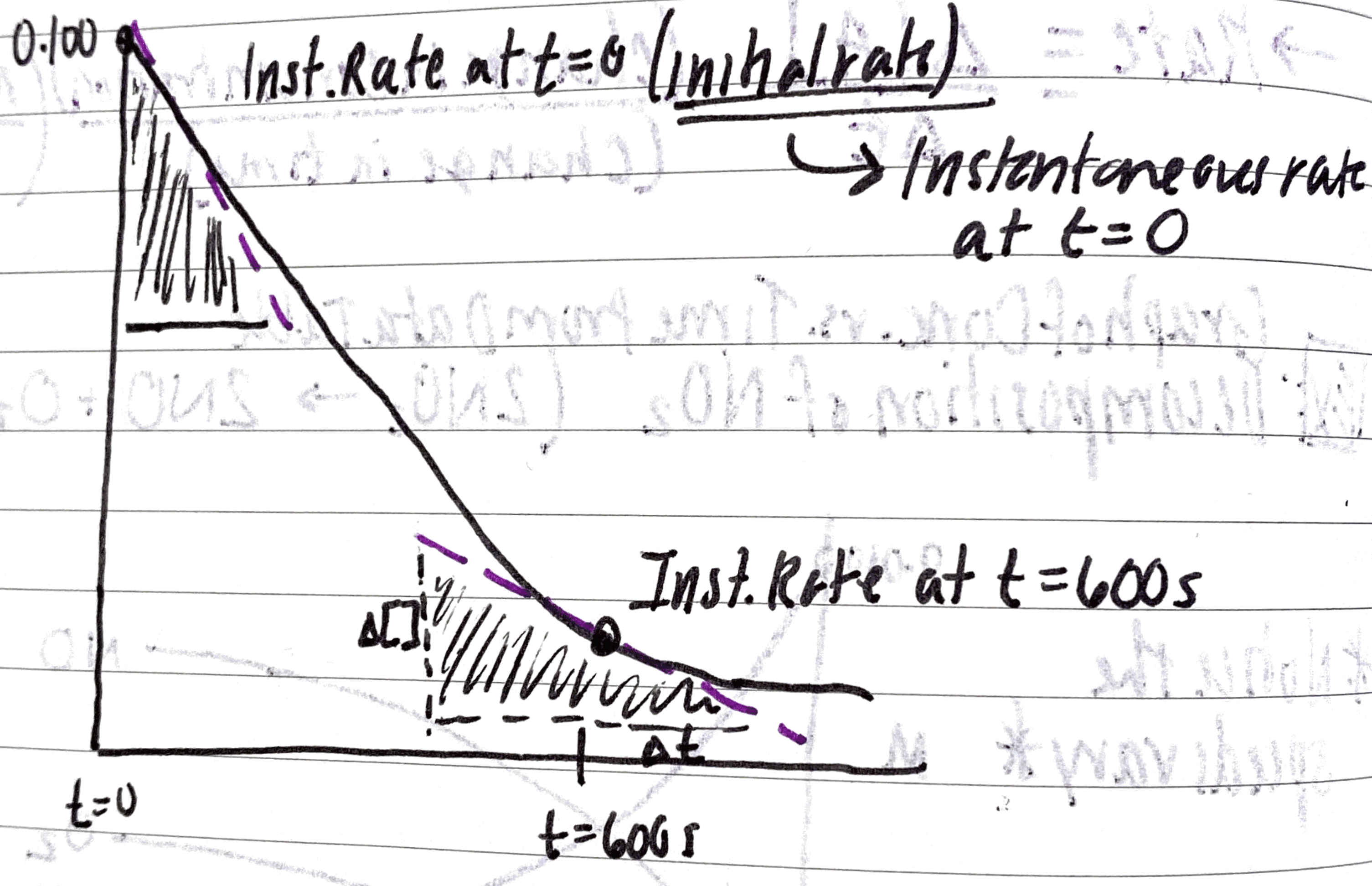


$rate = \frac{-\Delta[NO_2]}{\Delta t}$ → Reactant decreases (−) with time

$rate = \frac{\Delta[NO]}{\Delta t}$ → Product increases (+) with time

- Notice that the rxn Avg rate decreases as the rxn proceeds. = Fewer collisions between rxn molecules. = NOT CONSTANT
- Can determine rate at various points in time (instantaneous rate)

- find the instantaneous rate by finding the slope of a line tangent to a point representing a particular time.



- All rxns slow down over time, therefore the best indicator of the rate of rxn is the instantaneous rate near the beginning

- Relative Reaction Rates → What can the equation tell us?

Ex1: $C_4H_9Cl + H_2O \longrightarrow C_4H_9OH + HCl$

Ratio of C_4H_9Cl to C_4H_9OH is 1:1

∴ Rate of disappearance of C_4H_9Cl is the same as the rate of creation of C_4H_9OH

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = \frac{\Delta[C_4H_9OH]}{\Delta t}$$

Ex2: $\underline{2}HI \rightarrow \underline{\ }H_2 + \underline{\ }I_2$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

→ We can generalize by using:

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

(B) RATE LAWS

→ How the rate depends on amounts of reactants

→ General Form of Rate Law
= $rate = K[A]^m[B]^n$

(i) Differential Rate Law

- m and n = Rxn Orders = Must be determined experimentally ★
  NOT = to Coefficients!

- Will be given experimental data
  - Compare 2 experiments to determin rxn order
  - Concentrations of products not used in rate laws

- K = Rate Constant = Temperature dependent
  Units vary
  Accounts for activation E

→ For a given rxn, rate law describes dependence of intial rate on the [rxt].
"Double reactant, A = Effect on rate?

(Differential)
★ Determining the Rate Law of a Reaction

→ Experimentally vary the initial concentrations of reactants & measuring the effect on the initial rate
= Rate is directly proportional to concentration

→ Goal = Determine the exponents by doubling the reactants & observing change to rate
~> ↑ exponent = more effect concentration has on rate.

→

Hypothetical Rxn → $A + 2B + C \rightarrow D$

Experiment	$[A]_i$	$[B]_i$	$[C]_i$	Rate (M/s)
1	0.10M	0.10M	0.10M	0.01
2	0.10M	0.10M	0.20M	0.01
3	0.10M	0.20M	0.10M	0.02
4	0.20M	0.20M	0.10M	0.08

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

[A] → Exp 3 to 4 = [A] doubles
others constant
→ Rate quadruples (4x) = 0.02 to 0.08
→ What exponent relates doubling [A] to quadrupling rate?
$(2)^x = 4 \quad x = 2$

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

= Rxn is Second order w/ respect to reactant A.

[B] → Exp 1 to 3 = [B] doubles
→ Rate doubles (2x) = 0.01 to 0.02
$(2)^y = 2 \quad y = 1$

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

= Rxn is First Order w/ respect to reactant B

[C] → Exp 1 to 2 = [C] doubles
→ Rate remains @ 0.01M
→ $(2)^z = 1 \quad z = \varnothing$

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

= Rxn is Zero order w/ respect to reactant C

= Rate Law is $\text{Rate} = k[A]^2[B]$
Overall Order of Rxn = sum of exponents
$= (2+1) = 3$
(b) = THIRD ORDER RXN

(c)
Now... Calculate rate constant (w/ units)

Use any line of data + rate law

Exp #3 $\quad \text{rate} = k[A]^2[B]$

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

$$\frac{0.02\ \text{M/s}}{(0.10\text{M})^2(0.20\text{M})} = 10\ \frac{\text{M}}{(\text{M}^3)(\text{s})} = 10\ \text{M}^{-2}\cdot\text{sec}^{-1}$$

(d) Relate to balanced equation

$A + 2B + C \rightarrow D$

Rate of appearance of D = rate of disappearance of A & C (coefficients 1:1)

= Coefficient of D is 1/2 of B, so rate that D appears is 1/2 the rate that B disappears

- So what do orders mean?

Zero Order = Δ[rxt] = no effect on rate
not very common
rate = K

First Order = Rate directly proportional to reactant concentration
(double rxt = double rate)
Very common; Effect rate how rxt effected
$Rate = k[A]^1 = k[A]$

Second Order = Rate is quadrupled when rxt is doubled & factor of 9 when rxt is tripled
$Rate = k[A]^2$ or $k[A]^1[B]^1$

If $Rate = k[NO]^2[Br_2]$

NO × 4 = Rate × 16

NO × 2 (2M to 4M) ... 4x rate

Example Task #2: Determine overall rxn order & the units for k

(a) $2N_2O_5 \rightarrow 4NO_2 + O_2$

$Rate = k[N_2O_5]$ → First Order

$K = \frac{Rate}{[N_2O_5]} = \frac{M/s}{M} = \frac{1}{sec} = sec^{-1}$

(b) $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

$Rate = k[CHCl_3][Cl_2]^{1/2}$ → 1 1/2 Order

$K = \frac{Rate}{[CHCl_3][Cl_2]^{1/2}} = \frac{M/s}{(M)(M)^{1/2}} \rightarrow M^{-1/2}sec^{-1}$

(c) $H_2 + I_2 \rightarrow 2HI$

$Rate = k[H_2]^2[I_2]$ → Third Order

$K = \frac{Rate}{[H_2]^2[I_2]} = \frac{M/s}{(M^2)(M)} = \rightarrow M^{-2}sec^{-1}$

* Each order corresponds to specific units for k & tells how rate will Δ

Example: Determine Rate Law from given data

Exp	[A]	[B]	Initial Rate
1	0.100M	0.100M	4.0×10^{-5} M/s
2	0.100M	0.200M	4.0×10^{-5} M/s
3	0.200M	0.100M	16.0×10^{-5} M/s

Using the data, determine:

(A) Rate Law for the Reaction Rate = $K[A]^2[B]^0$

Exp 1 & 2 = [A] held constant; [B] is doubled
Rate = No change = [B] is Zero order

Exp 1 & 3 = [B] held constant; [A] is doubled
Rate = quadruples (x4)
$(2)^x = 4 \quad x = 2$ = Second Order

= rate = $K[A]^2$

(B) Magnitude of Rate Constant

$K = \frac{Rate}{[A]^2}$ Pick experiment #1 = $K = \frac{4.0 \times 10^{-5} M/s}{(0.100M)^2}$
$= 0.004\ M^{-1} sec^{-1}$

(C) Rate of Rxn when [A] = 0.050M [B] = 0.100M

[A] = 0.050M [B] = 0.100M

Rate = $K[A]^2 = (0.004\ M^{-1} sec^{-1})(0.050\ M^2)$
$= 0.00001$
$= 1.0 \times 10^{-5}$ M/s

*B = zero order
no effect