CHEMICAL KINETICS
CHAPTER 14

14.1 Factors Affecting Reaction Rates

14.2 Reaction Rates

14.3 Concentration & Rate (Rate Laws)

14.4 Concentration & Time

14.5 Temperature & Rate

Factors Affecting Reaction Rates

1. **Physical State of Reactants**
   rate increases with increasing number of collisions between reacting molecules.
2. **Reactant Concentrations**
   rate mostly increases with increasing temperature.
3. **Reaction Temperature**
   rate generally increases with temperature.
4. **Presence of a Catalyst**
   catalysts usually increase reaction rates.

Chemical Kinetics

Deals with speeds (rates) of reactions
How fast a reaction will go?

Reaction Rate:

A $\rightarrow$ B

Rate: change in concentration (Δ conc.) with change in time (Δt)

Rate of either: disappearance of reactants
or appearance of products

Reaction Rate:

A $\rightarrow$ B

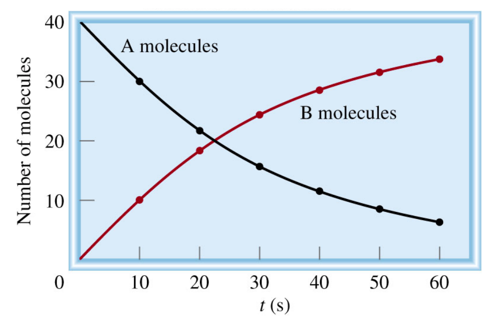
$\Delta[A] = [A]_f - [A]_i$ $\quad \Delta[A] = -$ **decreasing**

$\Delta[B] = [B]_f - [B]_i$ $\quad \Delta[B] = +$ **increasing**

$$\text{rate} = \frac{-\Delta[A]}{\Delta t}$$

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$$\text{Units} = \frac{M}{s}$$



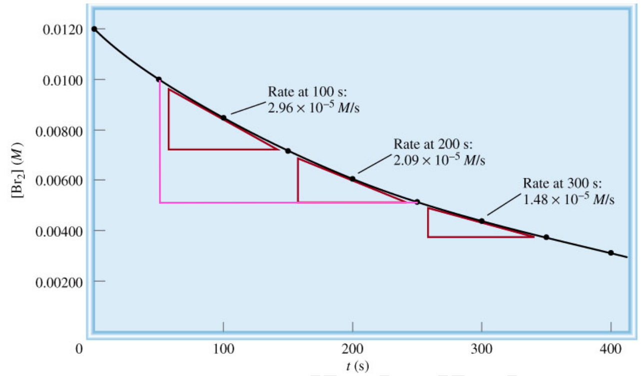
$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

brown **colorless**

time →

$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

Time (s)	$[Br_2]$ (*M*)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$$\textit{average rate} = \frac{-\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_f - [Br_2]_i}{t_f - t_i}$$

$$\textit{average rate} = -\frac{0.00500 - 0.0101}{250.0 - 50.0} = 2.55 \times 10^{-5}\ M.s^{-1}$$

$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

Time (s)	$[Br_2]$ (*M*)
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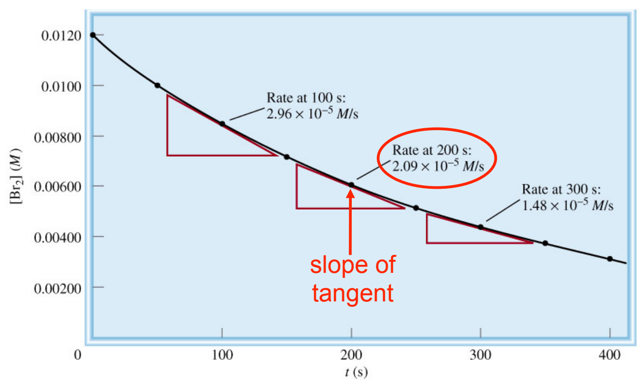


***instantaneous rate*: rate at specific instance in time**

***instantaneous rate* at 200s = 2.09×10^{-5} M/s**

***initial rate*: rate at $t = 0$**

Reaction Rates & Stoichiometry

$$2A \rightarrow B$$

$$\text{Rate} = \frac{\Delta[B]}{\Delta t}$$

rate of disappearance of A =

2 x rate of appearance of B

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = 2 \times \frac{\Delta[B]}{\Delta t}$$

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Reaction Rates & Stoichiometry

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

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t}$$

$$= \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

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

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

Rate Law

How the rate of the reaction changes with concentration of REACTANTS

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

rate $\propto [A]^x$ rate $\propto [B]^y$

rate = $k\,[A]^x[B]^y$ <u>RATE LAW</u>

Rate Law

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

rate = $k[A]^x[B]^y$ <u>RATE LAW</u>

k **= rate constant**

depends on: Specific reaction
Temperature
Presence of catalyst

larger *k*: faster reaction

Units: depend on *x* & *y*

Rate Law

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

rate = $k\,[A]^x[B]^y$ <u>RATE LAW</u>

<u>*x* and *y*:</u>

Not related to stoichiometric coefficients in the balanced equation

Mostly positive small integers (0, 1, 2)

Rate Law

aA + bB → cC + dD

rate = k [A]^x[B]^y **RATE LAW**

x and y: reaction order:

Reaction is xth order in A
If x = 2 2nd order in A

Reaction is yth order in B
If y = 1 1st order in B

Reaction is $(x + y)^{th}$ order overall
Reaction is 3rd order overall

Rate Law From Initial Rates

$F_2\ (g) + 2ClO_2\ (g) \longrightarrow 2FClO_2\ (g)$

rate = $k\,[F_2]^x[ClO_2]^y$

Rate Data for the Reaction Between F_2 and ClO_2

	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

rate = $k\,[F_2]^x[ClO_2]^y$

	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

$$\frac{rate_2}{rate_1} = \frac{4.8 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k\,[F_2]_2^x[ClO_2]_2^y}{k\,[F_2]_1^x[ClO_2]_1^y}$$

$$4 = \frac{(0.10)^x(0.040)^y}{(0.10)^x(0.010)^y} = \frac{(0.040)^y}{(0.010)^y} = (4)^y$$

$y = 1$ 1st order in ClO_2

$F_2\ (g) + 2ClO_2\ (g) \rightarrow 2FClO_2\ (g)$

	$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	2.4×10^{-3}

$$\frac{rate_3}{rate_1} = \frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k\,[F_2]_3^x[ClO_2]_3^y}{k\,[F_2]_1^x[ClO_2]_1^y}$$

$$2 = \frac{(0.20)^x(0.010)^y}{(0.10)^x(0.010)^y} = \frac{(0.20)^x}{(0.10)^x} = (2)^x$$

$x = 1$ 1st order in F_2

rate = $k\,[F_2]^1[ClO_2]^1$

[A]	Rate =		x	Order in A
1.0	$k(1.0)^x$	$= k$	1	
2.0	$k(2.0)^x$	$= 2k$	1	1st
2.0	$k(2.0)^x$	$= 4k$	2	2nd
2.0	$k(2.0)^x$	$= 8k$	3	3rd
3.0	$k(3.0)^x$	$= 3k$		
3.0	$k(3.0)^x$	$= 9k$		2nd
3.0	$k(3.0)^x$	$= 27k$		3rd

$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$

	[NO] (*M*)	[Br_2] (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	12
2	0.10	0.20	24
3	0.30	0.10	108

Determine the rate law rate = $k\,[NO]^x\,[Br_2]^y$

$$\frac{rate_2}{rate_1} = \frac{24}{12} = \frac{k\,(0.10)^x\,(0.20)^y}{k\,(0.10)^x\,(0.10)^y} = (2)^y$$

$$2 = (2)^y$$

$y = 1$ 1st order in Br_2

$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$

	[NO] (*M*)	[Br_2] (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	12
2	0.10	0.20	24
3	0.30	0.10	108

Determine the rate law rate = $k\,[NO]^x\,[Br_2]^y$

$$\frac{rate_3}{rate_1} = \frac{108}{12} = \frac{k\,(0.30)^x\,(0.10)^x}{k\,(0.10)^x\,(0.10)^x} = (3)^x$$

$9 = (3)^x$ $x = 2$ 2nd order in NO

rate = $k\,[NO]^2\,[Br_2]$

$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$

	[NO] (*M*)	[Br_2] (*M*)	Initial Rate (*M*/s)
1	0.10	0.10	12
2	0.10	0.20	24
3	0.30	0.10	108

Calculate the rate constant for the reaction

rate = $k[NO]^2[Br_2]$

$$k = \frac{rate}{[NO]^2\,[Br_2]} = \frac{108\ M.s^{-1}}{(0.30\ M)^2\,(0.10\ M)}$$

$k = 1.2 \times 10^4\ M^{-2}.s^{-1}$

$$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$$

What is the rate of the reaction when [NO] = 0.15 *M* and [Br_2] = 0.25 *M*

$$\text{rate} = k[NO]^2[Br_2]$$

$$\text{rate} = (1.2 \times 10^4\ M^{-2}.s^{-1})(0.15\ M)^2(0.25\ M)$$

$$\text{rate} = 67.5\ M.s^{-1}$$

$$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$$

How is the appearance of NOBr related to the rate of disappearance Br_2 and NO

$$\frac{1}{2}\frac{\Delta[NOBr]}{\Delta t} = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = -\frac{\Delta[Br_2]}{\Delta t}$$

therefore

$$\frac{\Delta[NOBr]}{\Delta t} = -\frac{\Delta[NO]}{\Delta t} = -\frac{2\ \Delta[Br_2]}{\Delta t}$$

Change of Concentration with Time

Rate law:

Tells how the reaction rate depends on reactant concentration

How the concentrations of reactants and products change with time?

Change of Concentration with Time

The Integrated Rate Law:

1. First-Order Reactions

A → product

$$\text{rate} = k\,[A]^1$$

$$k = \frac{\text{rate}}{[A]} = \frac{M.s^{-1}}{M} = s^{-1}$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

1. First-Order Reactions

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k\int_0^t dt$$

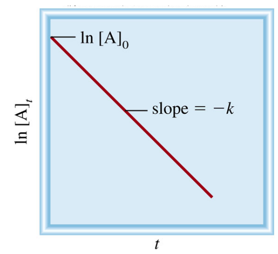
$$\ln\frac{[A]_t}{[A]_0} = -kt$$

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

1. First-Order Reactions

$$\underset{y}{\ln[A]_t} = \underset{mx}{-kt} + \underset{b}{\ln[A]_0}$$

linear



For gas-phase reactions:

$$\ln P_t = -kt + \ln P_0$$

The reaction 2A → B is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 80°C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M* ?

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

$[A]_0 = 0.88$

$[A]_t = 0.14$

$$t = \frac{\ln[A]_0 - \ln[A]_t}{k}$$

$$t = \frac{\ln\frac{[A]_0}{[A]_t}}{k} = \frac{\ln\frac{0.88\ M}{0.14\ M}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ s$$

Reaction Half-Life $t_{1/2}$

The time required for the concentration of a reactant to decrease to half of its initial concentration

$$t = \frac{\ln\frac{[A]_0}{[A]_t}}{k}$$

at $t_{1/2}$: $[A]_t = \frac{[A]_0}{2}$

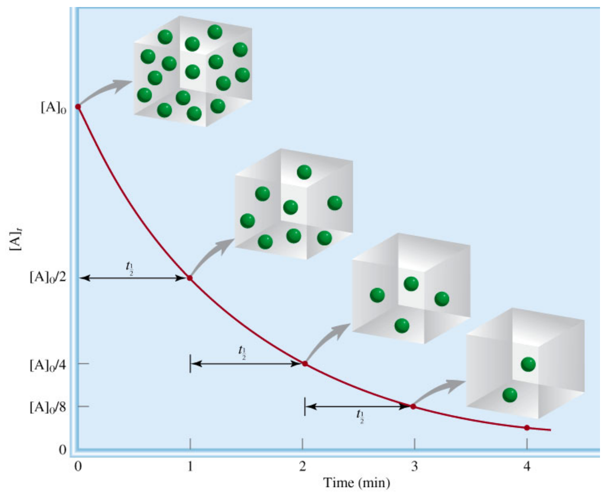
$$t_{1/2} = \frac{\ln 2}{k}$$

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

constant

independent of $[A]_0$

half life for a first order reaction is constant



Change of Concentration with Time

The Integrated Rate Law:

2. Second-Order Reactions

A → product

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

$$k = \frac{\text{rate}}{[A]^2} = \frac{M.s^{-1}}{M^2} = M^{-1}.s^{-1}$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

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

2. Second-Order Reactions

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

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k\int_0^t dt$$

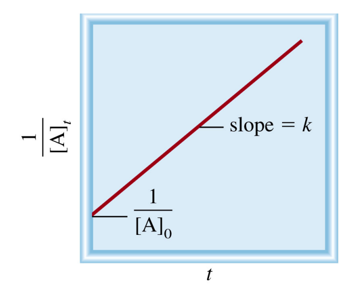
$$\frac{1}{[A]_0} - \frac{1}{[A]_t} = -kt$$

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

2. Second-Order Reactions

$$\underset{y}{\frac{1}{[A]_t}} = \underset{m\,x}{kt} + \underset{b}{\frac{1}{[A]_0}}$$

linear



For gas-phase reactions:

$$\frac{1}{P_t} = kt + \frac{1}{P_0}$$

2. Second-Order Reactions

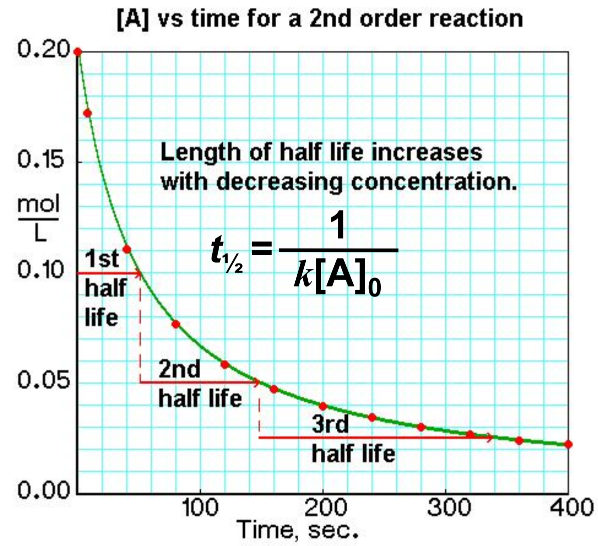
Reaction Half-Life Time $t_{½}$

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

$$\frac{1}{[A]_0/2} = kt_{½} + \frac{1}{[A]_0}$$

$$t_{½} = \frac{1}{k[A]_0}$$

Depends on initial concentration and *k*



Change of Concentration with Time

The Integrated Rate Law:

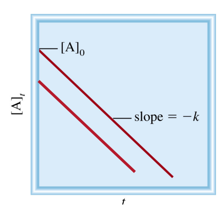
3. Zero-Order Reactions

A → product

rate = k [A]^0 = k = <u>constant</u> k: $M.s^{-1}$

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

$$d[A] = -k\,dt$$

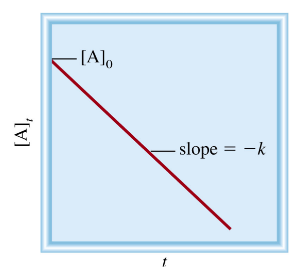


3. Zero-Order Reactions

$$\int_{[A]_0}^{[A]_t} d[A] = -k\int_0^t dt$$

$$[A]_t = -kt + [A]_0$$

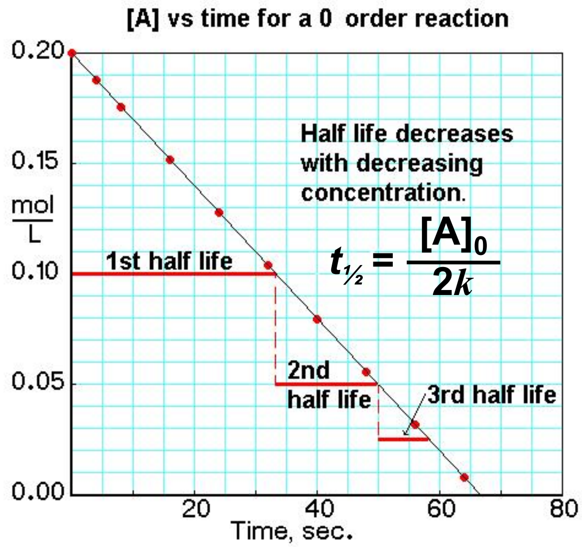
y mx b



Reaction Half-Life Time

$$\frac{[A]_t}{2} = -kt_{½} + [A]_0$$

$$t_{½} = \frac{[A]_0}{2k}$$



$$t_{1/2} = \frac{[A]_0}{2k}$$

Order	Rate Law	$\int$ Rate Law	Slope	Intercept	$t_{1/2}$
0th	Rate = k	$[A]_t = -kt + [A]_0$	$-k$	$[A]_0$	$\frac{[A]_0}{2k}$
1st	Rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_0$	$-k$	$\ln[A]_0$	$\frac{0.693}{k}$
2nd	Rate = $k[A]^2$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	k	$\frac{1}{[A]_0}$	$\frac{1}{k[A]_0}$

The following initial rate data were obtained for the stoichiometric reaction: 3A + B → 2P

Exp.	$[A]_0$, M	$[B]_0$, M	Initial rate = -d[A]/dt
1	0.20	0.20	1.2×10^{-8}
2	0.20	0.60	1.2×10^{-8}

For a third experiment, a plot of 1/[A] versus time was found to be linear. What is the order of the reaction with respect to the concentration of A and B?

	Order with Respect to [A]	Order with Respect to [B]
A)	1	0
B)	2	1
C)	2	0 ←
D)	0	2

Temperature and Rate

Reaction rates increase with:

1. **concentration**
2. **temperature**
3. **catalyst**

All explained by the collision model theory

Collision Model:

Molecules must collide to react

rate ∝ number of collision per second

higher conc. → **more collisions** → **faster reaction**

higher temp. → **faster molecules** → **more collisions** → **faster reaction**

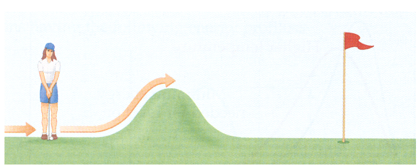
Only small fraction of collisions produce reaction. Why?

1. Colliding molecules should have a total kinetic energy equal to or greater than a minimum value (threshold) called the activation energy, E_a.

2. The relative orientation of the reactants must allow the formation of any new bonds necessary to produce products (steric effect)

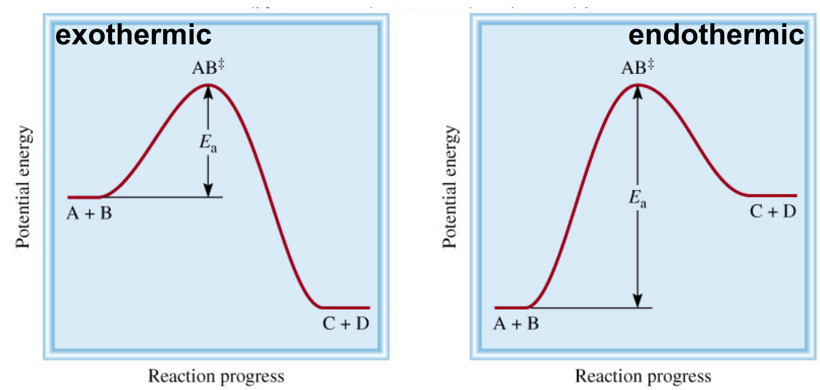
Activation Energy (E_a)

The minimum amount of energy required to initiate a chemical reaction



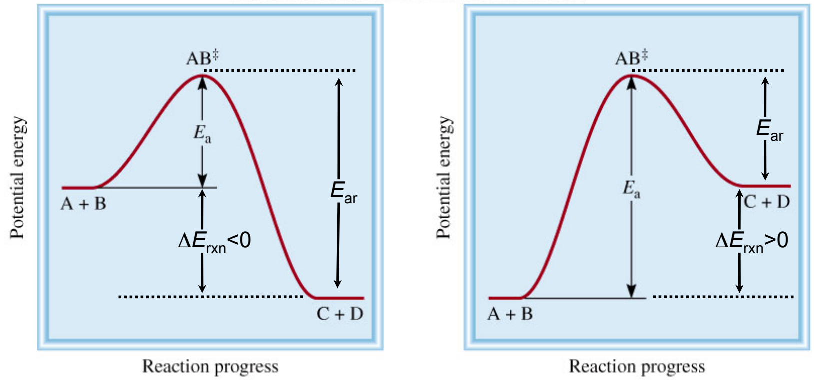
$A + B \rightarrow C + D$

$AB^{\ddagger}$: activated complex or transition state



Lower E_a, faster reaction

What about the activation energy for the reverse reaction, E_{ar}

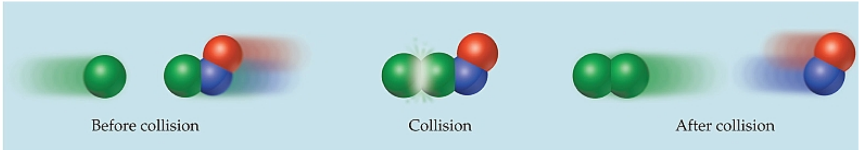


$E_{ar} = E_a + |\Delta E_{rxn}|$ $E_{ar} = E_a - \Delta E_{rxn}$

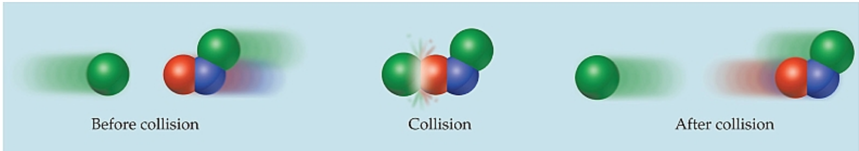
ΔE_{rxn} has no effect on the rate of a reaction

Relative Orientation:

$Cl + NOCl \rightarrow NO + Cl_2$



Effective collision: reaction occurs



Ineffective collision: no reaction

Arrhenius Equation

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

k = rate constant

E_a = activation energy

R = the gas constant (8.314 J/mol.K)

T = absolute temperature (K)

A = constant; frequency factor (frequency of properly oriented collisions)

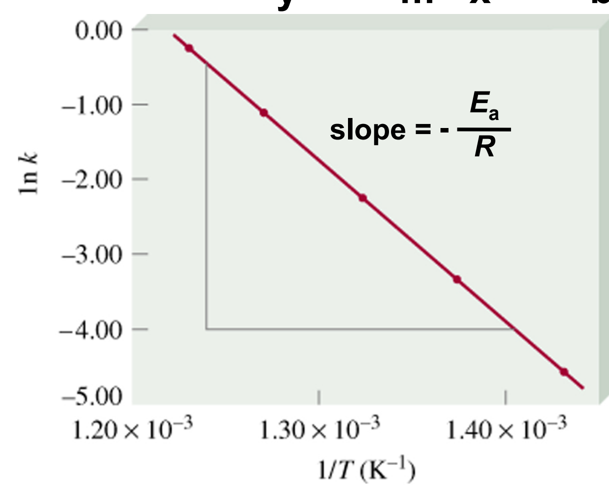
$e^{-E_a/RT}$ = fraction of collisions with sufficient energy

rate $\propto T$ rate $\propto A$ rate $\propto \frac{1}{E_a}$

Arrhenius Equation

$k = Ae^{-E_a/RT}$ $\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$

y m x b



Arrhenius Equation

At two different temperatures:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \qquad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

Subtract & rearrange

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}$$

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

The rate law for this reaction is first order in each of the two reactants and has a k = 0.0028/*M.s* at 200°C measured for - $d[H_2]/dt$. E_a for the reaction is 170. kJ/mol. What is the rate of HI formation at 300°C when both H_2 and I_2 are at a concentration of 0.0150 *M*?

At 300°C (573 K):

$$\frac{\Delta[HI]}{\Delta t} = 2\,\frac{-\Delta[H_2]}{\Delta t} = 2\,k_{573}[H_2][I_2]$$

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

$$\ln \frac{k_{473}}{k_{573}} = \frac{E_a}{R}\left(\frac{473-573}{473 \times 573}\right)$$

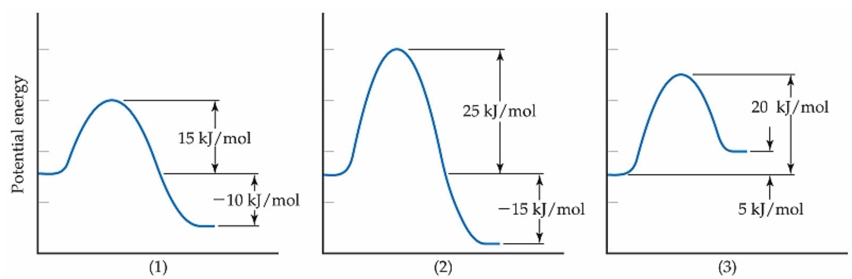
$$\ln \frac{0.0028\ M^{-1}.s^{-1}}{k_{573}} = \frac{1.70 \times 10^5\ J/mol}{8.314\ J.mol^{-1}.K^{-1}}(-3.69 \times 10^{-4}\ K^{-1})$$

$$k_{573} = 5.29\ M^{-1}.s^{-1}$$

$$\frac{\Delta[HI]}{\Delta t} = 2k_{573}[H_2][I_2] = (2)\underset{M^{-1}.s^{-1}}{(5.29)}\underset{M^2}{(0.0150)^2}$$

$$= 0.00238\ M.s^{-1}$$

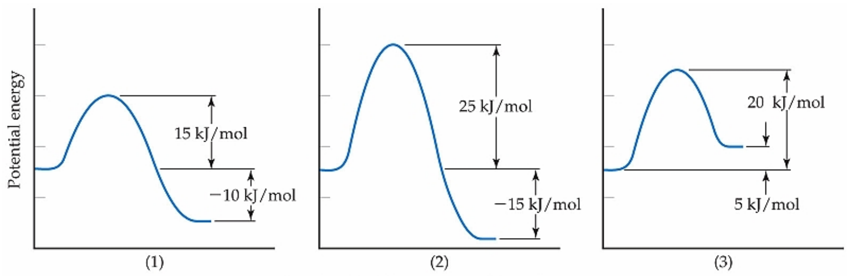
Consider a series of reactions having these energy profiles. Rank the reactions from slowest to fastest assuming that they have nearly the same value for the frequency factor *A*.



E_a = 15 kJ/mol 25 kJ/mol 20 kJ/mol

2 < 3 < 1

Consider a series of reactions having these energy profiles. Rank the reverse reactions from slowest to fastest assuming that they have nearly the same value for the frequency factor *A*.



E_a = 25 kJ/mol   40 kJ/mol   20 kJ/mol

2 < 1 < 3

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