1412 - E1
CH 12 - Kinetics
Notes

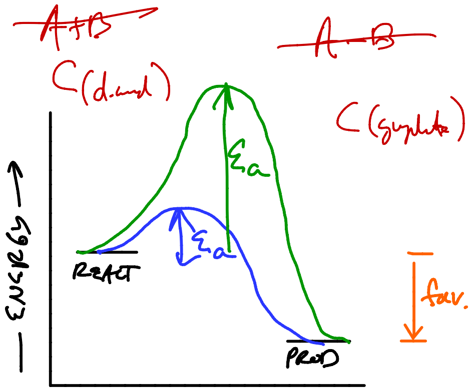
12

CHAPTER 12: KINETICS

Introduction

Sam Rayburn Dam Analogy

- Energy Potential is favorable — but there is a BARRIER ... a "hump"
- Flow can be regulated by lowering /raising the gate.
- In human body, ENZYMES "regulate the gate"



NOTE: Thermo = CH 16
BUT: ΔH covered extensively = CH 5

Chemical Reaction Rates [12.1]

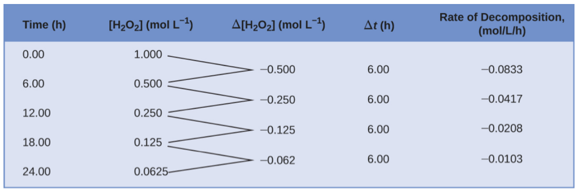
$$aA + bB \rightarrow cC + dD$$

$$-\underbrace{\frac{d[A]}{dt}}_{ROC}, \quad -\underbrace{\frac{d[B]}{dt}}_{ROC}, \quad +\underbrace{\frac{d[C]}{dt}}_{ROC}, \quad +\underbrace{\frac{d[D]}{dt}}_{ROC}$$

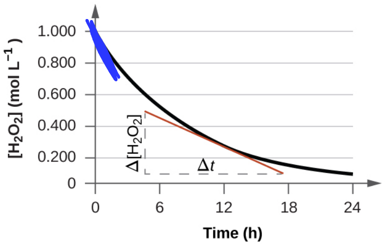
… for example…

$$2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$$

Focusing on H_2O_2…

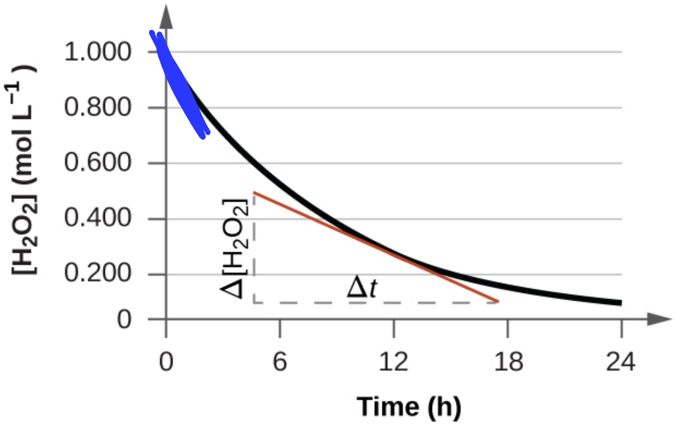


Time (h)	$[H_2O_2]$ (mol L^{-1})	$\Delta[H_2O_2]$ (mol L^{-1})	Δt (h)	Rate of Decomposition, (mol/L/h)
0.00	1.000			
		−0.500	6.00	−0.0833
6.00	0.500			
		−0.250	6.00	−0.0417
12.00	0.250			
		−0.125	6.00	−0.0208
18.00	0.125			
		−0.062	6.00	−0.0103
24.00	0.0625			



Terms

(i) Initial Rate
(ii) Instantaneous rate – any point on curve
(iii) Average rate – above: 0→6hr rate = 0.0833 M/h
6→24hr " = 0.0104 M/h



Rates of Reaction vs. Rates of Change

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

$$rate = \underbrace{-\frac{1}{a}\underbrace{\frac{d[A]}{dt}}_{ROC}}_{ROR} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

… for example…

$$2NH_3(g) \rightarrow 2N_2(g) + 3H_2(g)$$

- All 3 species appear/disappear at different rates, but there is only one rate of reaction (after all, we are talking about a single reaction)

There may be several ROC's for any given reaction, but always on one ROR

Analogy

$$\underbrace{2\,bread + 1\,slice\,meat + \overset{9}{3}\,pickles}_{\text{kitchen area}} \rightarrow \underbrace{\overset{3}{1}\,sandwich}_{\text{dining area}}$$

- Can monitor what is happening in the kitchen by merely observing what is happening in the dining area…
- can monitor what is happening with the entire reaction by merely observing what is happening with any one of the reagents

- Like H_2O_2 on previous page, each reactant/product has its own ROC curve...
- ... but multiplication of each ROC by "1/coeff" gives the same value: the ROR.

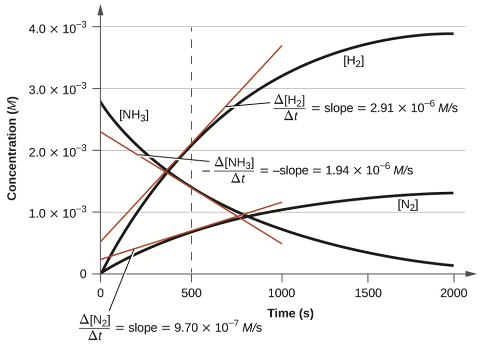
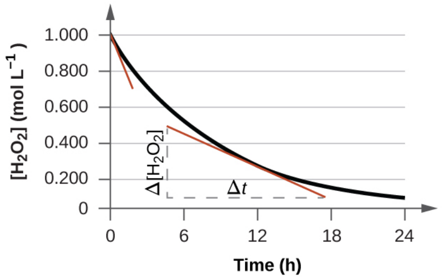


FIG. 12.5

(EX) Calculate Rate of Reaction from Rate of Change [12.2, modified]
¿Based on the following reaction (associated with FIG 12.3), the instantaneous reate of decomposition of H2O2 @ t = 11.1 hr is determined to be 3.20E-2 M/hr. What is the rate of reaction?



$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

$$ROR = \frac{ROC}{a} \quad \text{for any specie}$$

$$= \frac{1}{2}\left|\frac{3.20\times10^{-2}\ M}{h}\right. = \boxed{1.60\times10^{-2}\ M/h}$$

NOTE: ⓐ $-\frac{1}{2}\,ROC_{H_2O_2} = +\frac{1}{2}\,ROC_{H_2O} = ROC_{O_2}$

ⓑ The ROC for any specie with $a=1$ necessarily equals the ROR.

Five Factors Affecting Reaction Rates [12.2]

↳ Chemical nature
↳ Physical state
↳ Temperature
↳ Concentration
↳ Catalyst

Factor affecting "gate" raising/lowering

The Chemical Nature of the Reacting Substances

- Fe much less reactive than same amount of Na

- Ca reacts with water to produce H2 at much slower rate than Na
  (actually, Na reacts explosively

The State of Subdivision of the Reactants

- Physical state which affect surface area, effectively the concentration

(EX) Affect on Rxn Rate: Qualitative
¿Arrange the following in order of decreasing reaction rate, assuming an equal mass for each?
course-ground Zn vs. Zn chunks vs. powdered Zn

↙ 1st - add decreasing chevrons

powdered Zn > course-ground Zn > Zn chunks

Temperature of the Reactants

TREND: ↑ Temp ↑ Reaction Rate

RULE OF THUMB: Reaction rate doubles for about every increase in 10 °C

Concentrations of the Reactants

General Trend: $\uparrow$ [conc], $\underbrace{\uparrow \text{Rxn Rate}}_{\text{often varies for diff rxn. components}}$

<u>Ex</u>: phosphorus burns more rapidly in pure O_2 (100 % O_2) than it does in air (~20 % O_2)

The Presence of a Catalyst

<u>def</u>: Catalyst is substance which lowers the E_{act} without being consumed, thus <u>↑ Rxn Rate</u>

- Catalyst works by providing alternate pathway or mechanism (one w/ lower E_{act}) for the rxn to follow.

Mon 9/16

Rate Laws [12.3]

Rate Law Expression (RLE)

- Determined experimentally

$aA + bB \rightarrow \text{prod}$

reaction order

$$rate = k[A]^x[B]^y$$

RoR

concentration

rate law constant

$aA \rightarrow \text{prod}$

$$rate = -\frac{1}{a}\frac{d[A]}{dt}$$

- overall Reaction Order = sum of the individual reaction orders

- recall earlier,

(EX) Determination of ROR and ROC
¿For the following reaction, answer the following:

“ROR”
“rate”

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

(a) What is ROR in terms of ROC for each reactant

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

(b) What is the equation for the general RLE?

$$\text{rate} = \overset{\text{exp}}{k}\,[N_2O_5]^{\overset{\text{exp}}{x}}$$

(c) If the RLE is known to be: rate = K[N2O5], what is the Order wrt [N2O5]?

$x = 1$, ∴ 1st Order

(d) If the RLE is known to be: rate = K[N2O5], what is the Overall Order?

Sum of all superscripts = 1, therefor, 1st Order overall

(EX) cont'd

$$2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$$

(e) If we observed NO2 forming at a rate of 0.0072 M/s …what is the ROC for N2O5?

$$\frac{\square\ M\,(N_2O_5)}{s} = \frac{0.0072\ M\,(N_2O)}{s}\Bigg|\frac{-2\text{ mol }N_2O_5}{4\text{ mol }NO_2} = \frac{-0.0036\ M\,(N_2O_5)}{s}$$

(e) …what is the rate of reaction, as calculated from [N2O5]?

$$\text{rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta T} = \frac{-1}{2}\Bigg|\frac{-0.0036\ M}{s} = \boxed{0.0018\ M/s}$$

Part of RoR, not RoC

(f) …what is the rate of reaction, as calculated from [NO2]?

$$\text{rate} = \frac{1}{4}\Bigg|\frac{0.0072\ M}{s} = \boxed{0.0018\ M/s}$$

same (1 RoR)

(EX) Write Rate Law Formula from Eq [12.3]

¿For the following equation and associated rate law, what are the Orders for each component, and the overall Order?

$$H_2(g) + 2NO(g) \rightarrow N_2O(g) + H_2O(g)$$

$$rate = k[N\cancel{_2}O]^2[H_2]$$

[redacted]

Determining Rate Law from Initial Rates

$aA + bB \longrightarrow$

$$rate = k[A]^x[B]^y$$ ← how to det'n "k, x, y"?

- 3 unknowns, ∴ need 3 equations
- here, we will teach by example ...

(EX) Method of Initial Rates

¿For the reation: A + B → C

write the “full” rate law expression, including correct values and units for “x”, “y”, and “k”, given the data:

EXP	[A]	[B]	[C] ← {initial rate of formation of "C"}
1	0.10	0.10	2.0 E-4
2	0.10	0.20	8.0 E-4
3	0.20	0.40	2.56 E-2 (= 256 E-4)

ⓐ know generally: $\text{rate} = k\,[A]^x\,[B]^y$

ⓑ $$\frac{\text{rate }2}{\text{rate }1} = \underbrace{\frac{8.0E{-}4}{2.0E{-}4}}_{4} = \frac{k[A]^x[B]^y}{\cancel{k}\,\cancel{[A]^x}\,[B]^y} = \frac{[2.0]^y}{[1.0]^y}$$

$$= 2^y \rightarrow \boxed{y = 2}$$

ⓒ $$\frac{\text{rate }3}{\text{rate }2} = \frac{256E{-}4}{8E{-}4} = \frac{\cancel{k}\,[0.2]^x\,(0.4)^2}{\cancel{k}\,[0.1]^x\,(0.2)^2} \rightarrow 32 = 2^x\left(\frac{0.16}{0.04}\right)$$

$$32 = 2^x \cdot 4$$

$$8 = 2^x$$

$$\boxed{x = 3}$$

Cont'd next page ⇩

ⓓ Using any of the three experiment's data (here, choose Row 2), only 'k" is unknown.

$$\overset{\checkmark}{rate} = \overset{\boxed{?}}{k}\,\overset{\checkmark}{[A]}^{\overset{\checkmark}{x}}\,\overset{\checkmark}{[B]}^{\overset{\checkmark}{y}}$$

$$rate\ 2 = \frac{8.0E-4\ M}{s} = k\,(0.01)^3 M^3 \cdot (0.02)^2 M^2$$

$$8.0E-4\ M/s = k\ 0.0010\ M^3 \times 0.040\ M^2$$

$$8.0E-4\ M/s = \underset{\downarrow}{k} \cdot 4.0E-5\ M^5$$

$$k = \frac{8.0E - 4\ M}{s} \times \frac{1}{4.0E - 5\ M^5} = \frac{20.}{s\ M^4} = 20\ M^{-}4s^{-}1$$

$$rate = k\,[A]^x\,[B]^y$$

$$\boxed{rate = \frac{20}{M \cdot s}\,[A]^3\,[B]^2}$$

Reaction Order and Rate Constant Units

(I would know this, if I were you)

$$rate = \frac{M}{s} = \frac{\square}{\square}\,\frac{M^{overall}}{}$$

Order	Eq	Unit of k
0	$\frac{M^1}{s^1} = \frac{\boxed{\frac{M}{}}\ \cancel{M^0}}{\boxed{s}}$ $=1$	$\frac{M}{s}$
1	$\frac{M^1}{s^1} = \frac{\boxed{1}\ M^1}{\boxed{s}}$	$\frac{1}{s}$
5	$\frac{M^1}{s^1} = \frac{\boxed{}\ M^5}{\boxed{M^4 \cdot s}}$	$\frac{1}{M^4 s}$

$rate = k\, M^{ORDER}$

Integrated Rate Laws [12.4]

Integrated Rate Law (IRL) expressions will only be considered for one-significant-reactant-only reactions in this course… reactions with two or more significant reactants are too math intensive

$$aA \rightarrow bB$$

$$rate = \overbrace{-\frac{1}{a}\overbrace{\frac{d[A]}{dt}}^{ROC}}^{ROR} = \overbrace{k[A]^x}^{RLE}$$

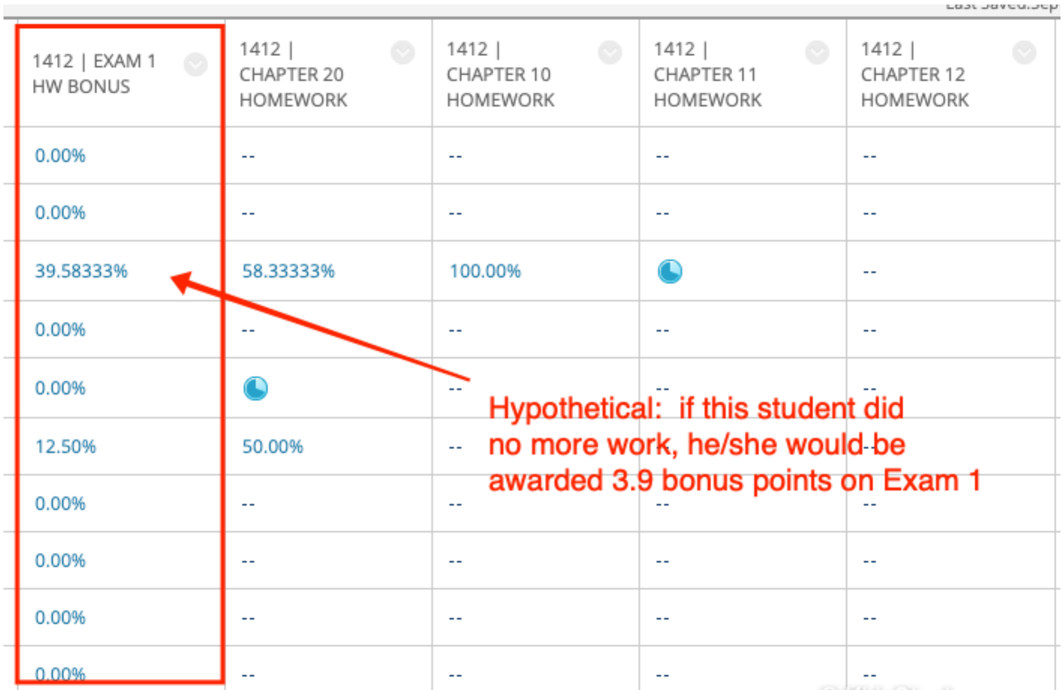
$\downarrow$ three solutions provided: x=0, x=1, x=2

	IRLE	$t_{1/2}$
$x=0$	$[A] = -k \cdot t + [A]_0$	$[A]_0 / 2ka$
$x=1$	$\ln[A] = -k \cdot t + \ln[A]_0$	$\ln 2 / ka$ $\left(= \frac{0.693}{ka}\right)$
$x=2$	$1/[A] = +k \cdot t + 1/[A]_0$	$1/[A]_0\, ka$

$y = m x + b$

← linear forms of eqs presented. (text presents in different form)

wed 9/18



1412 | EXAM 1 HW BONUS	1412 | CHAPTER 20 HOMEWORK	1412 | CHAPTER 10 HOMEWORK	1412 | CHAPTER 11 HOMEWORK	1412 | CHAPTER 12 HOMEWORK
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Hypothetical: if this student did no more work, he/she would be awarded 3.9 bonus points on Exam 1

$[A]$ = conc. of "A" at time "t"
$[A_0]$ = " " " " time = 0.

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]^x$$

$\downarrow$ {show your work}

if $x = 1$: $\ln[A] = -kt + \ln[A_0]$

$\int \frac{1}{x}dx = +\ln x + c$ integrated rate law

$$\frac{d[A]}{dt} = -K[A]^x \Longrightarrow \frac{d[A]}{dt} = -K[A]$$

seperable Differential equation

$d[A] = -K[A]dt$

divide by $[A]$

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

then integrate from 0 to t

Assume $x=1$

$$\int_{[A_0]}^{[A]} \frac{d[A]}{[A]}dt = \int_0^t -K\,dt$$

$$\ln([A])\Big]_{[A_0]}^{[A]} = -Kt\Big]_0^t$$ ← Definite Integral

$$\ln[A] - \ln[A_0] = -Kt + K(0)$$ Fundamental theorem of Calculus

$$\ln[A] = -Kt + \ln[A_0]$$ add $+\ln[A_0]$ & Simplify

Equations and Their Actions

- IRLE ························· conc-to-time
- RLE ·························· conc-to-rate
- Arrhenius ···················· temp-to-rate

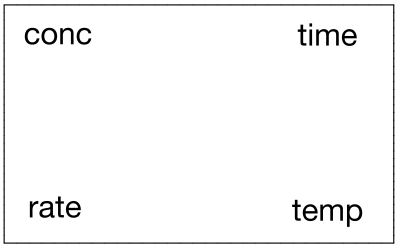
$$aA \rightarrow ?$$

$$\begin{aligned} A &= -kat + A_o && \longmapsto \quad 0th\ order \\ lnA &= -kat + lnA_o && \longmapsto \quad 1st\ order \\ 1/A &= +kat + 1/A_o && \longmapsto \quad 2nd\ order \end{aligned}$$

IRLE

RLE

$$rate = k[A]^x[B]^y = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$



conc

time

rate

temp

Arrhenius

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

Determine Reaction Order via Graphing

NOTE: determination of Reaction Order by graphing will be taught in the lab

(EX) Calculate Decay Time from IRLE

¿Iodine-131 is a radioactive isotope that is used to diagnose and treat some forms of thyroid cancer. Iodine-131 decays to xenon-131 according to the equation below.

The decay is first-order with a rate constant of 0.138 d–1 . All radioactive decay is first order. How many days will it take for 90% of the iodine–131 in a 0.500 M solution of this substance to decay to Xe-131?

Ratio

ⓘ Relating [conc] to time → IRLE

ⓘⓘ 1st order

$${}^{131}\mathrm{1\,I} \rightarrow \mathrm{1}\,{}^{131}\mathrm{Xe}$$

a=1

$$\underbrace{}$$

$$\ln[I] = -kt + \ln[I]_0$$

✓ ✓

$$\ln\frac{[I]_0}{[I]} = +k\cdot t \longrightarrow \ln\left(\frac{100}{10}\right) = \frac{0.138}{} \Big| \frac{1}{} \cdot k$$

$$\ln 10 = 0.138/d \cdot k$$

$$2.30 = 0.138/d \cdot k$$

$$\boxed{16.7\,d = k}$$

(EX) The Integrated Rate Law for a Second-Order Reaction

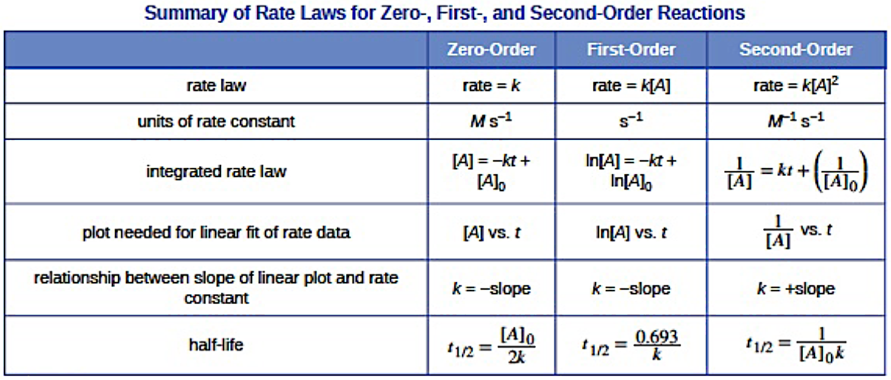
¿The reaction of butadiene gas (C4H6) with itself produces C8H12 gas, per below eq. The reaction is second order with a rate constant equal to 5.76 × 10–2 L/mol/min under certain conditions. If the initial concentration of butadiene is 0.200 M, what is the concentration remaining after 10.0 min?

$$2\,C_{\underset{4}{2}}H_6(g) \rightarrow C_{\underset{8}{2}}H_{\underset{12}{8}}(g)$$

$$\overset{\boxed{?}}{\frac{1}{[A]}} = \overset{\checkmark}{k}\overset{\checkmark}{t} + \overset{\checkmark}{\frac{1}{[A]_0}} = \begin{array}{c|c} 5.76\times10^{-2} & 10\,m \\ \hline M\ m & \end{array} + \frac{1}{0.200\,M} =$$

$$= \frac{0.576}{M} + \frac{1}{0.200\,M} = \frac{0.576}{M} + \frac{5.00}{M} = \frac{5.576}{M}$$

$$\frac{1}{[A]} = \frac{5.576}{M} \rightarrow \frac{[A]}{1} = \frac{M}{5.576} \rightarrow [A] = \boxed{0.179\,M}$$



Summary of Rate Laws for Zero-, First-, and Second-Order Reactions

	Zero-Order	First-Order	Second-Order
rate law	rate = k	rate = $k[A]$	rate = $k[A]^2$
units of rate constant	$M\ s^{-1}$	s^{-1}	$M^{-1}\ s^{-1}$
integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \left(\frac{1}{[A]_0}\right)$
plot needed for linear fit of rate data	$[A]$ vs. t	$\ln[A]$ vs. t	$\frac{1}{[A]}$ vs. t
relationship between slope of linear plot and rate constant	k = −slope	k = −slope	k = +slope
half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{[A]_0 k}$

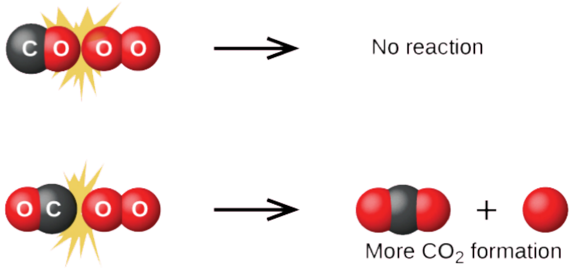
Collision Theory [12.5]

Collision Theory Postulates

① ROR $\propto$ rate of collisions $\text{ROR} \propto \frac{\#\text{ collisions}}{\text{time}}$

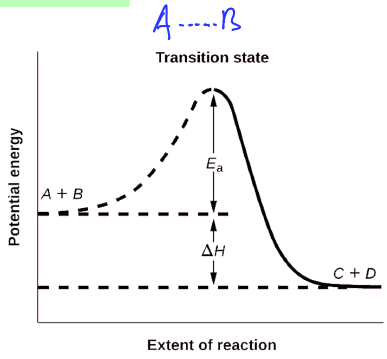
② Orientation – of colliding species must allow them to become bonded together

③ Energy – sufficient to cause mutual penetrations of valence shells



Ea and Transition State (TS)

- A TRANSITON STATE (TS) is very unstable and cannot be isolated…
- Not to be confused with an INTERMEDIATE
- A TS is, in a loose way, a morph somewhere between a reactant and a product
- A TS will define the height of the Energy of Activation (Ea)



Ea is mathematically described by the Arrhenius Equation

- The Arrhenius Equation is an important equation which arises a number of times in general chemistry… you should know it's basic forms, and be able to solve them
- the Arrhenius equation relates RATE (k) to TEMP

Exponential form

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

A = frequency factor
= f(collision freq, orientation)

$$\downarrow \ln$$

Linear form

$$\boxed{\ln k = \frac{-Ea}{R} \cdot \frac{1}{T} + \ln A}$$

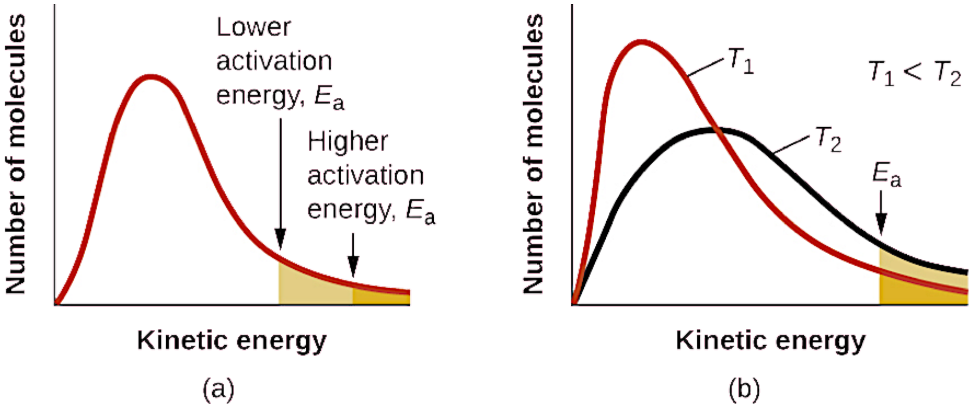
$$y = m \cdot x + b$$

Ratio

$$\ln \frac{k}{k'} = \frac{Ea}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)$$

Why Increasing Temp increases the Rate of Reaction

↳ Higher temp, more can jump the wall.



(EX) Calcuate ‘k’ at for a temperature change
¿If ‘k’ for a 1st order reaction is 0.00916 /s at 0.0 °C and Ea = 88.0 kJ/mol, what is the value at 2.0 °C?

$$\ln \frac{k}{k'} = \frac{E_a}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)$$

$$\ln \frac{k}{0.00916} = \begin{array}{c|c} 88{,}000\ \text{J} & \text{mol} \cdot \text{K} \\ \hline \text{mol} & 8.314\ \text{J} \end{array} \times \left(\frac{1}{273} - \frac{1}{275}\right) = 0.282$$

Easier math if higher temp is second

$$\frac{k}{0.00916} = e^{0.282} = 1.32$$

$$k = (1.32)(0.00916) = \boxed{0.0121\ /\text{s}}$$

logic check: $\uparrow T$, $\downarrow E_a/RT$, $\uparrow -E_a/RT$, $\uparrow e^{-E_a/RT}$, $\uparrow k$

Reaction Mechanisms [12.6]

Some Basic Terms

Reaction mechanism – one or more step pathway to a product.
Elementary reaction – each individual step
Intermediate – stable species encountered along the rxn pathway.

$$\begin{array}{rcll} O_3(g) & \longrightarrow & O_2(g) + O & \quad (\text{eq } 1) \\ O + O_3(g) & \longrightarrow & 2O_2(g) & \quad (\text{eq } 2) \\ \hline 2O_3(g) & \longrightarrow & 3O_2(g) & \quad (\text{eq } 3) \end{array}$$

molecularity – # reactant species
unimolecular reaction – single reactant species
bi molecular reaction – two " specie
termolecular reaction – three " specie

1 specie
coeff = 1

Unimolecular Elementary Reactions

1-step reactions

- unimolecular rxn/mechanism = single step <u>or</u> multi step.

$A \rightarrow$ products   rate $= k[A]$

elementary
("1-step")
$x = 1$

- b/c 1 specie + coeff = 1, necessarily $x = 1$
  ↳ rate $\propto$ concentration
- For all <u>uni</u> molecular, presented IRLE's apply

Bimolecular Elementary Reactions

Two types: (i) $A + B \rightarrow C$ (ii) $2A \rightarrow C$

rate $= k[A][B]$ rate $= k[A]^2$

NOTE: for 1-step ("elementary") reactions, x, y = coefficients !!!
but... limited to 1-step, for which one can NOT
tell just by looking at the equation.

EX: $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

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

Termolecular Elementary Reactions

- rare – unusual that 3 species collide at the same, exact time
- Ex – $2NO + O_2 \rightarrow 2NO_2$ rate = $k[NO]^2[O_2]$
  – $2NO + Cl_2 \rightarrow 2NOCl$ rate = $k[NO]^2[Cl_2]$

Relating Reaction Mechanisms to Rate Laws

- epicenter = rate-limiting step (or rate-determining step) ... determines the kinetics
- Det'n mechanism/RDS by matching proposed elementary steps, one of ~~those~~ being the RDS, to measured kinetics.

ex ⤵

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

observed

> 225°C

< 225°C

Mon Sept 23

A

$\text{rate} = \underbrace{k[NO_2][CO]}_{\text{RDS components}}$

$NO_2 + CO \xrightarrow{RDS}$ prodts

$\text{rate} = k[NO_2]^2$

$= k[NO_2][NO_2]$

RDS involves 2x NO_2's

$NO_2 + NO_2 \xrightarrow{RDS}$ prodts

propose Mech. to include this step

correct kinetics → $NO_2 + \cancel{NO_2} \xrightarrow{slow} \cancel{NO_3} + NO$

$\cancel{NO_3} + CO \xrightarrow{fast} CO_2 + \cancel{NO_2}$

B

correct eq. → $NO_2 + CO \rightarrow CO_2 + NO$ ← TARGET

C

Key Question: Is the RDS the first step?

In general, when the rate-determining (slower) step is the first step in a mechanism, the rate law for the overall reaction is the same as the rate law for this step. However, when the rate-determining step is preceded by a step involving an equilibrium reaction, the rate law for the overall reaction may be more difficult to derive.

T – 5 days

1412 | EXAM 1 HW BONUS	1412 | CHAPTER 20 HOMEWORK	1412 | CHAPTER 10 HOMEWORK	1412 | CHAPTER 11 HOMEWORK	1412 | CHAPTER 12 HOMEWORK
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(EX) Determine the reaction mechanism
¿Given that the rate for the reaction: $2\ O_3 \rightarrow 3\ O_2$
derive a mechanism which is described by rate = $k[O_3]^2/[O_2]$?

revisit earlier reaction

$2\ O_3 \rightarrow 3\ O_2$ $\quad \text{rate} = \dfrac{k[O_3]^2}{[O_2]}$

$\downarrow$

Proposl #1
1- step

$2O_3 \longrightarrow 3O_2$

↝ rate = $k[O_3]^2$
× wrong

Proposal #2
2-step, 1st = RDS

$O_3 \xrightarrow{RDS} O_2 + O$
$O_3 + O \longrightarrow 2O_2$

↝ rate = $k[O_3]$
× wrong

Proposl #3
2-step, 2ND = RDS

$O_3 \underset{}{\overset{fast}{\rightleftharpoons}} O_2 + O$
$O_3 + O \xrightarrow{RDS} 2O_2$

✓ correct
↝ rate = $[O_3]^2/[O_2]$

[see next page for derivation]

Derivation with the second step being the RDS (or slow) step . . .

① FAST REACTION

rate 1f = rate 1r

$$k_{1f}[O_3] = k_{1r}[O_2][O]$$

$$\downarrow$$

$$[O] = \frac{k_{1f}[O_3]}{k_{1r}[O_2]}$$

② SLOW RDS REACTION

rate 2

$$= k_2[O][O_3]$$

$$\downarrow$$

$$= \frac{k_2 k_{1f}[O_3][O_3]}{k_{1r}[O_2]}$$

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

$$O_3 \overset{\text{fast}}{\rightleftharpoons} O_2 + O$$

$$O_3 + O \xrightarrow{\text{RDS}} 2O_2$$

(EX) Identify the Correct Mechanism
¿Which mechanism(s) is consistent with the following reaction:

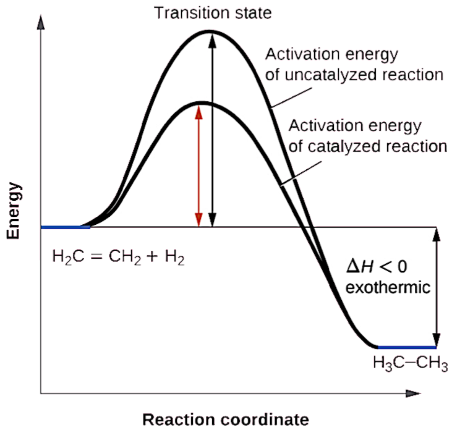
$NO + O_3 \rightarrow NO_2 + O_2$ rate = $k[O_3][NO]$

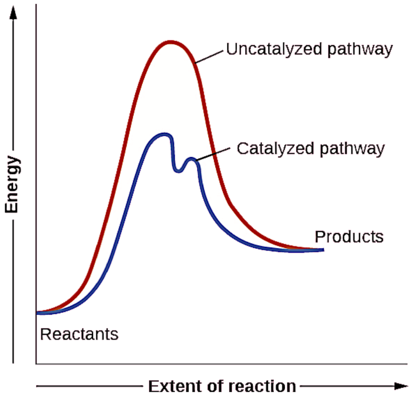
ⓐ $NO + O_3 \xrightarrow{RDS} NO_3 + O$ ✓
$NO_3 + O \longrightarrow NO_2 + O_2$

ⓑ $NO + O_3 \xrightarrow{1\text{-step}} NO_2 + O_2$ ✓

ⓒ $NO \xrightarrow{RDS} N + O$
$O_3 \longrightarrow O_2 + O$ ✗
$O_2 + N \longrightarrow NO_2$

Catalysis [12.7]





- Calatysis is NOT consumed
- Speeds up both forward & reverse reactions.
- Catalyst is zero order:
  - ↳ rate = k
  - ↳ not dependent on amt of substrate (amt of material acted upon by catalyst)

Catalytic Convertor (Pt/NiO)

heterogeneous catalyst — catalysis and rxn mixture are in different phases.

$$2NO_2 \longrightarrow N_2 + 2O_2$$

$$O_2 + 2CO \xrightarrow[NiO]{Pt} 2CO_2$$

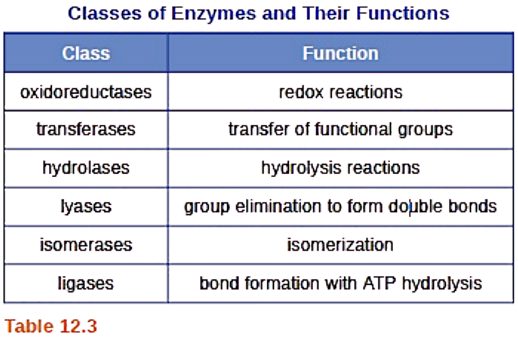
$$25O_2 + 2C_8H_{18} \longrightarrow 16CO_2 + 18H_2O$$

SO_x
NO_x ⇒ acid rain

Enzymes — Nature's Catalysts

- Control most body reactions
- homogeneous – same phase as reactants

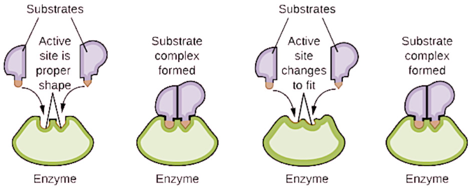
$CO_2 + H_2O \rightarrow \boxed{H_2CO_3}$



Classes of Enzymes and Their Functions

Class	Function
oxidoreductases	redox reactions
transferases	transfer of functional groups
hydrolases	hydrolysis reactions
lyases	group elimination to form double bonds
isomerases	isomerization
ligases	bond formation with ATP hydrolysis

Table 12.3



(a) Lock-and-key model (b) Induced fit model

- The conv. of CO_2 + water to carbonic acid is slow, but in presence of CARBONIC ANHYDRASE, rate ↑ to conversion of more than 1 million CO_2/second !!!

- zzz
  - ↳ zzz
  - ↳ zzz
- zzz

Relative Reaction Rate Questions

- These are typically “Before–After” type questions:
  - ↳“If this happens, then that occurs?”
  - ↳”If I change this, then the new value is _____?”
  - ↳”If this is the old value, then the new value will be _____?”
- Often, they can be easily solved using simple ratios.

(EX) Relative Reaction Rate
¿For the reaction described by: rate = $k[A][B]^2$
what happens to the reaction rate it…

Before-After type question

(a) “A” is tripled?

$$\frac{rate_b}{rate_a} = \frac{k \cdot 3 \cdot 1^2}{k \cdot 1 \cdot 1^2} = \boxed{\frac{3}{1}}$$

(b) “B” is tripled?

$$\frac{rate_b}{rate_a} = \frac{k \cdot 1 \cdot 3^2}{k \cdot 1 \cdot 1^2} = \boxed{\frac{9}{1}}$$

(c) both “A” and “B” are tripled?

$$\frac{rate_b}{rate_a} = \frac{k \cdot 3 \cdot 3^2}{k \cdot 1 \cdot 1^2} = \boxed{\frac{27}{1}}$$

(EX) Calc Rate of Disappearance at different concentration
¿The rate of decompostion of NO_2 = 5.4E–5 M/s when $[NO_2]$ = 0.0100 M.

(a) If the rate is given by: rate = $k[NO_2]$, what is the rate of disappearance at $[NO_2]$ = 0.00500 M?

Approach #1

$$\text{rate}_{(new)} = k[NO_2] = k\,(0.00500\,M) = \frac{0.0054}{s}\left|\frac{0.00500\,M}{}\right. = \boxed{2.7E\text{-}5\ M/s}$$

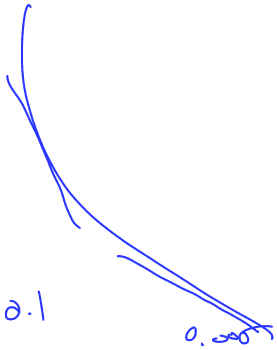
$$k = \frac{\text{rate}_{(ORIG)}}{[NO_2]} = \frac{5.4E\text{-}5\ M}{s}\left|\frac{}{0.00100\,M}\right. = \frac{0.0054}{s}$$

Approach #2 (ratio: rate = $k[NO_2]$)

$$\frac{\text{rate (new)}}{\text{rate (orig)}} = \frac{k\,(0.00500)}{k\,(0.0100)} = \frac{1}{2} = \frac{[A]}{[A]_0}$$

$$\text{rate (new)} = \frac{1}{2}\,\text{rate (orig)} = \frac{1}{2}\left|\frac{5.4E\text{-}5\ M}{s}\right. = \boxed{2.7E\text{-}5\ M/s}$$

(cont'd next page)



(b) What would the new rate be if: rate = $[NO_2]^2$?

$$\frac{\text{rate (new)}}{\text{rate (orig)}} = \frac{k\,(0.00500)^2}{k\,(0.0100)^2} = \left(\frac{1}{2}\right)^2 = \frac{1}{4}$$

$$\text{rate (new)} = \begin{array}{c|c} 1 & \text{rate (orig)} \\ \hline 4 & \end{array} = \begin{array}{c|c} 1 & 5.4\text{E-}5\ M \\ \hline 4 & s \end{array} = \boxed{1.4\text{E-}5\ M/s}$$

(EX) Calc relative reaction rates for concentration change
¿Given the rate expression: rate = $k[NO]^2[0_2]$
Two experiments were carried out at the same temperature. In EXP#2, the original EXP#1 concentration of NO is halved, and the concentration of oxygen doubled. This initial rate of EXP#2 is how many times that of EXP#1?

Since its a proportion, ASSUME the original (exp#1) concentrations of each reagent is 1.0M.

$$\frac{\text{rate } 2}{\text{rate } 1} = \frac{k \cdot (0.5)^2 \cdot 2}{k \cdot 1 \cdot 1} = \frac{k \cdot 0.5}{k \cdot 1} = \boxed{0.5} \text{ or } \boxed{1/2}$$