MONDAY, FEBRUARY 9, 2026 AP CHEMISTRY

CH. 14 CHEMICAL KINETICS

RATES OF REACTIONS AND REACTION MECHANISMS

PRACTICAL RELEVANCE

- ☆ CATALYSTS SPEED UP CHEMICAL RXNS AND A PROPELLANT GAS FOR AEROSOLS (ALSO A REFRIGERANT) BROKE DOWN IN THE STRATOSPHERE TO CATALYTICALLY DESTROY O_3 (OZONE). (CFCs)
- ☆ CLIMATE CHANGE: CO_2 HAS A LIFETIME IN THE ATMOSPHERE OF HUNDREDS OF YEARS.
- ☆ DRUG AND MATERIALS DEVELOPMENT: THE DESIGN OF SPECIFIC CATALYSTS DRIVES A LOT OF INNOVATION
- ☆ BIOLOGY: ENZYMES ARE CATALYSTS
- ☆ RATES OF RXNS ARE USED TO EXPERIMENTALLY TEST PROPOSED RXN MECHANISMS.

SCHEDULE

NOTES M 2/9
W 2/11
F 2/13 ETC.
LAB GROUP X Tu 2/24
GROUP Y Th 2/26
PROB. SET DUE Th 2/26
QUIZ M 3/2
MCQ #1 DUE Tu 2/24

TOPICS

RATES OF RXN AND FACTORS AFFECTING RATES
DIFFERENTIAL RATE LAW (RATE VS. CONC)
INTEGRATED RATE LAW (CONC. VS TIME)
HALF-LIFE
COLLISION MODEL
ACTIVATION ENERGY
REACTION MECHANISMS
CATALYSIS

14.1 FACTORS THAT AFFECT RXN RATE

THE RATE OF A REACTION IS MEASURED BY THE CHANGE IN CONC. OVER TIME: $\frac{\Delta[A]}{\Delta t}$. THIS RATE DEPENDS ON HOW MANY MOLECULES COLLIDE WITH THE RIGHT ORIENTATION AND SUFFICIENT KINETIC ENERGY. THIS IS THE COLLISION MODEL OF CHEMICAL REACTIONS: MOLECULES MUST COLLIDE FAST ENOUGH THAT BONDS CAN BREAK, WHICH ALLOWS NEW BONDS TO FORM.

☆ A REACTION IS FASTER WHEN COLLISIONS ARE MORE FREQUENT.

REACTION RATES ARE AFFECTED BY:

① STATE OF MATTER

SLOWER ⟶ FASTER

SOLID — LIQUID OR SOLUTION — GAS

THE INTERIOR OF SOLIDS CANNOT REACT, ONLY THE SURFACE. GRINDING SOLIDS INTO FINE PARTICLES INCR. RXN RATE.

(GRINDING INCR. THE $\frac{SA}{VOL}$ RATIO B/C AS RADIUS GETS SMALLER, $\frac{r^2}{r^3}$ GETS BIGGER)

SA INCR. WHEN PARTICLES GET SMALLER

SEE THE $KMnO_4$ + GLYCERIN ($C_3H_5(OH)_3$) DEMO (SH. BK. I pg 83)

SPONTANEOUS COMBUSTION IS FASTER WITH FINELY GROUND $KMnO_4$

② MOLAR CONCENTRATION

A HIGHER CONC. MEANS A FASTER RATE B/C MORE PARTICLES PER UNIT VOLUME MEANS MORE COLLISIONS PER UNIT TIME.

③ TEMPERATURE

HIGHER TEMP MEANS A FASTER RATE.

TWO THINGS:

I. COLLISIONS ARE MORE FREQUENT WHEN PARTICLES ARE MOVING FASTER ($u_{rms} = \sqrt{\frac{3RT}{M}}$)

II. IN ORDER TO REACT THE MOLECULES MUST COLLIDE WITH A MINIMUM KE AND AT HIGHER TEMP. A LARGER FRACTION OF THE POPULATION HAS ENOUGH KE TO REACT ($KE = \frac{3}{2}RT$)

④ CATALYSTS

A SUBSTANCE WHICH INCREASES A RXN RATE BUT IS NOT ITSELF CHANGED IN THE RXN IS A CATALYST. THEY WORK BY PROVIDING AN ALTERNATE RXN MECHANISM, ONE WHICH HAS A LOWER ACTIVATION ENERGY. THE ACTIVATION ENERGY IS THE MIN. KE REQUIRED FOR A MOLECULE TO REACT.

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14.2 REACTION RATES

A RATE IS A QTY WHICH SHOWS CHANGE IN SOME MEAS. AS A FUNCTION OF TIME: $\frac{mi}{hr}$ $\frac{m}{s}$ $\frac{\$}{hr}$ ETC

RXN RATE UNIT: $\boxed{\frac{M}{s}}$ OR $\frac{mol/L}{s}$ $\left(\frac{mol}{L \cdot s}\right)$ OR $\boxed{M \cdot s^{-1}}$ LESS OFTEN $\frac{M}{min}$

FOR THE RXN, $\underset{\text{COEFF.}}{a}A \rightarrow b\underset{\text{CHEM. FORMULA}}{B}$ WHERE $[A]$ = CONC OF A IN mol/L

$[B]$ = CONC OF B IN mol/L

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

($\Delta[A]$ IS NEGATIVE SO WE MAKE RATE POS. BY MULT. BY −1)

CALCULUS VERSION: $-\frac{d[A]}{dt}$

TAKING STOICH. INTO ACCOUNT, WE CAN RELATE DIFF. MEASURES OF THE RATE LIKE THIS

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

(DIVIDING BY THE STOICH. COEFF. MAKES IT SO THERE IS ONE AND ONLY ONE RATE)

CALCULATING RATES $A \rightarrow B$

DATA

t (s)	[A]	[B]
0	1.0	0
20	0.54	0.46
40	0.30	0.70

← THIS ROW IS $[A]_0$ AND $[B]_0$ OR INITIAL CONC.

↑ ↑ NOTICE STOICH. RELATIONSHIP

AVERAGE RATES

FOR 0s TO 20s

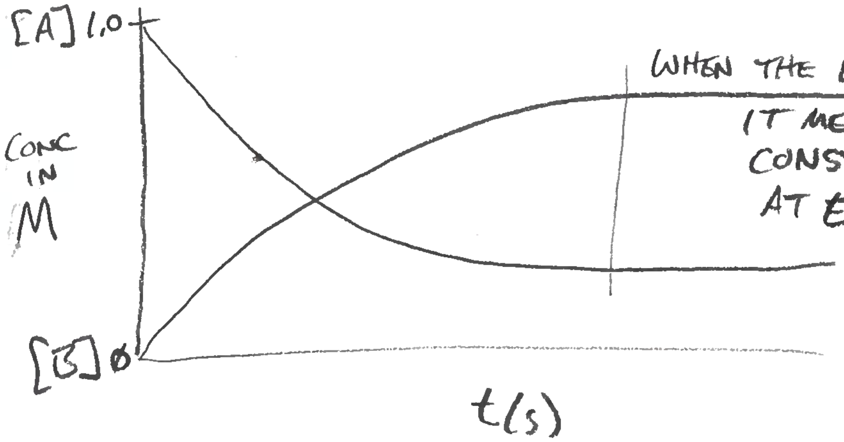
$$-\frac{\Delta[A]}{\Delta t} = \frac{-(0.54 - 1.0)}{20s} = \boxed{2.3 \times 10^{-2}\, M/s}$$

$$\left(+\frac{\Delta[B]}{\Delta t} = \frac{(0.46 - 0)}{20s} = \boxed{2.3 \times 10^{-2}\, M/s} \text{ (SAME)} \right)$$

NOTE: RATE MAY NOT BE CONSTANT! RATE DEPENDS ON CONC. AND SO AS CONC. DECREASES, SO DOES RATE:

FOR 20s TO 40s $-\frac{\Delta[A]}{\Delta t} = \frac{-(0.30 - 0.54)}{20s} = \boxed{1.2 \times 10^{-2}\, M/s}$

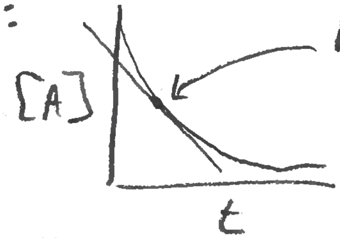
HERE IS A PLOT OF [A] AND [B] VS t FOR $A \rightarrow B$



WHEN THE [A] VS. t CURVE GOES HORIZONTAL IT MEANS THE CONC. REMAINS CONSTANT. THE RXN CONTINUES BUT AT EQUILIBRIUM NO NET CHANGE OCCURS.

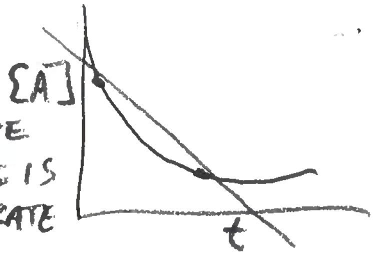
ON A GRAPH LIKE THIS THE RATE IS EQUAL TO THE SLOPE OF A LINE: $\frac{\Delta[A]}{\Delta t} = \frac{\Delta Y}{\Delta X}$

THE <u>INSTANTANEOUS RATE</u> IS THE SLOPE AT JUST ONE POINT, AS A TANGENT TO THE CURVE. IT'S LIKE WHAT A CAR'S SPEEDOMETER SHOWS:



RATE AT THIS POINT IS EQUAL TO THE SLOPE OF THE TANGENT LINE.

THE <u>AVERAGE RATE</u> IS THE SLOPE BTWN. TWO POINTS ON THE GRAPH AS ON A SECANT LINE. IT'S LIKE WHEN YOU CALC. AVG. SPEED AS $\left(\frac{\text{TOTAL DISTANCE}}{\text{TOTAL TIME}}\right)$.



THE SLOPE OF THIS LINE IS THE AVG. RATE BTWN. THESE TWO POINTS IN TIME

NOT ALL REACTANTS AND PRODUCTS HAVE CONCENTRATIONS WHICH ARE EASY TO MEASURE AS A FUNCTION OF TIME. SINCE WE WANT JUST ONE RATE, NO MATTER WHICH ONE WE ARE ABLE TO MEASURE, WE DEFINE RATE AS FOLLOWS:

$$\text{FOR } \overset{\text{COEFF.}}{a}A + bB \rightarrow cC + d\underset{\text{CHEM. FORMULA}}{D}$$

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

DO POGIL: RATES OF REACTION

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14.3 THE RATE LAW   A.K.A. THE DIFFERENTIAL RATE LAW

THE PROPORTION BETWEEN:

THE RATE OF REACTION AND THE CONC. OF REACTANTS

$$\text{RATE} \propto [A]$$

FOR A RXN: $A + 2B \rightarrow C$

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

GENERAL FORM OF THE RATE LAW (DIFFERENTIAL)

$$\boxed{\text{RATE} = k[A]^m[B]^n}$$

k IS THE RATE CONSTANT. IT IS MEASURED BY EXPERIMENT.

k INCR. WITH INCR. TEMP. $\left(k = Ae^{-E_a/RT}\right)$

k INCR. IF A CATALYST IS USED

m AND n ARE ORDERS OF REACTION WITH REPECT TO A AND B. TYPICALLY, m AND n MAY BE 0, 1, OR 2. OVERALL ORDER OF RXN IS THE SUM OF ALL EXPONENTS.

STOPPED HERE, GROUP Y M 2026-02-09

FOR A GIVEN OVERALL CHEMICAL EQUATION, m AND n MAY OR MAY NOT BE EQUAL TO THE STOICH. COEFFICIENTS. SO DON'T ASSUME THEY ARE! WE HAVE TO FIGURE OUT THE VALUES OF THE ORDERS OF RXN FOR EACH REACTANT EXPERIMENTALLY.

EX. EQNS. & RATE LAWS:

$2NO + Br_2 \rightarrow 2NOBr$ RATE $= k[NO]^2[Br_2]^1$

$NO_2 + CO \rightarrow NO + CO_2$ RATE $= k[NO_2]^2[CO]^0$

RATE $= k[NO_2]^2$

UNITS

RATES $\left(\frac{\Delta[A]}{\Delta t}\right)$

$\frac{M}{s}$ OR $M s^{-1}$ GASES $\frac{atm}{s}$ $\frac{torr}{s}$ (FOR PARTIAL PRESSURES)

(TIME UNITS CAN BE s, min, hr, d, or yr)

RATE CONSTANTS (k)

		UNITS FOR k
ZERO ORDER	$RATE = k[A]^0 = k$	$M s^{-1}$
FIRST ORDER	$RATE = k[A]^1$	s^{-1}
SECOND ORDER	$RATE = k[A]^2$ $RATE = k[A]^1[B]^1$	$M^{-1} s^{-1}$
THIRD ORDER	$RATE = k[A]^3$ $RATE = k[A]^2[B]^1$ ETC.	$M^{-2} s^{-1}$

IN GENERAL, UNITS FOR $k = M^{-(n-1)} \cdot s^{-1}$

WHERE n IS THE OVERALL ORDER OF RXN WHICH IS THE SUM OF ALL EXPONENTS.

TO DETERMINE A RATE LAW IS TO FIND OUT THE VALUES OF m, n, AND k. WE DO THIS BY MEASURING RATE WITH DIFFERENT INITIAL CONC.

IF RATE IS UNCHANGED FOR A CHANGED CONC. THEN THE RATE LAW IS ZERO ORDER FOR THAT REACTANT.

IF RATE IS DOUBLE WHEN CONC. IS DOUBLED THEN THE REACTANT IS FIRST ORDER.

IF RATE IS BIGGER BY A FACTOR OF 4 WHEN CONC. IS ×2 THEN THE REACTANT IS SECOND ORDER.

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SAMP. EX. pg 586

GIVEN $A + B \rightarrow C$

$RATE = k[A]^m[B]^n$
(GENERIC RATE LAW)

DATA

TRIAL	$[A]_0$	$[B]_0$	RATE (Ms^{-1})
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

CALC m FOR A

WE CAN SEE THAT WHEN $[A]_0$ GOES TO $2[A]_0$ THE RATE INCR. BY 4x. SO $m=2$.

ALGEBRAICALLY: RATIO OF RATES

$$\left(\frac{16 \times 10^{-5}}{4 \times 10^{-5}}\right) = \frac{k[0.2]^m[0.1]^n}{k[0.1]^m[0.1]^n}$$

$$\frac{16}{4} = \frac{\cancel{k}[0.2]^m\cancel{[0.1]^n}}{\cancel{k}[0.1]^m\cancel{[0.1]^n}} \quad \frac{\text{TRIAL 3}}{\text{TRIAL 1}} \longrightarrow \frac{16}{4} = \frac{0.2^m}{0.1^m} \text{ or } \left(\frac{0.2}{0.1}\right)^m = 2^m$$

$$2^m = 4$$

SO $m = 2$

CALC n

RATE DOESN'T CHANGE WHEN [B] CHANGES SO $n = 0$

RATE LAW: $RATE = k[A]^2[B]^0 = k[A]^2$

CALC k

PICK ANY TRIAL: $RATE = k[A]^2$

$4 \times 10^{-5} = k(0.1)^2$

$$k = \frac{4 \times 10^{-5}\ Ms^{-1}}{0.1^2\ M^2}$$

$$\boxed{k = 4.0 \times 10^{-3}\ M^{-1}s^{-1}}$$

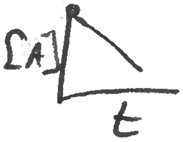
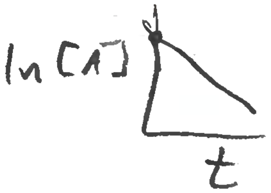
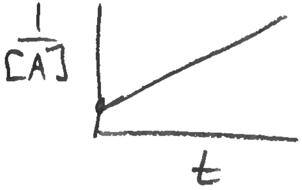
AT THIS POINT YOU ARE READY TO DO "METHOD OF INITIAL RATES" POGIL

14.4 THE CHANGE OF CONC. WITH TIME

A.K.A. THE INTEGRATED RATE LAW

THE PROPORTION BTWN. CONC. AND TIME

$$[A] \propto t$$

DIFFERENTIAL RATE LAW	ORDER	INTEGRATED RATE LAW
RATE = k	ZERO	$[A] = -kt + [A]_0$ $y = mx + b$ SLOPE ON  IS $-k$
RATE = $k[A]^1$	FIRST	$\ln[A] = -kt + \ln[A]_0$ SLOPE  IS $-k$
RATE = $k[A]^2$	SECOND	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ SLOPE  IS k

USE THE INTEGRATED RATE LAW EQUATIONS TO

① CALC $[A]$ AT TIME t, GIVEN $[A]_0$ AND k.

② DECIDE WHETHER A RATE LAW IS 0TH, 1ST OR 2ND ORDER BY PLOTTING THE CHARACTERISTIC KINETIC PLOTS.
0TH $[A]$ VS t. 1ST $\ln[A]$ VS. t 2ND $\frac{1}{[A]}$ VS. t

③ CALC. THE VALUE OF k USING A GRAPH OF $[A]$ OR $\ln[A]$ OR $\frac{1}{[A]}$ VS. t

SAMP. EX. 14.8 pg 590 INCL. HOW TO USE YOUR GRAPHING CALCULATOR

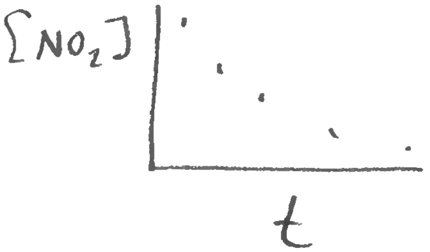
DETERMINE ORDER OF RXN AND THE VALUE OF THE RATE CONSTANT (k) USING THESE DATA:

TIME (s)	$[NO_2]$ (M)
0	0.0100
50	0.00787
100	0.00649
200	0.00481
300	0.00380

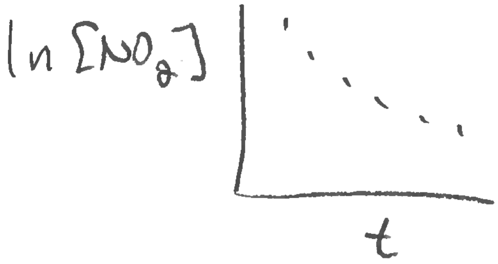
FOR $NO_2 \rightarrow NO + \frac{1}{2}O_2$

RATE = $k[NO_2]^m$

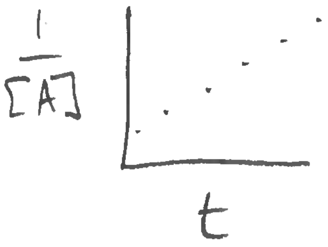
USE YOUR CALCULATOR TO PLOT THESE DATA:



NOT ZERO ORDER



NOT FIRST ORDER



IT'S SECOND ORDER!

RATE = $k[NO_2]^2$

k?

$\boxed{RATE = 0.543\,M^{-1}s^{-1}[NO_2]^2}$

FOR 2ND ORDER $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$y = mx + b$

$m = k$ Lin

$a = m = \boxed{0.543\,M^{-1}s^{-1}}$

CALC. BUTTONS

STAT → CALC → LINREG FOR L1 AND L4

x y

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LOGARITHMS

LOGARITHMS = EXPONENTS

$10^0 = 1$
$10^1 = 10$
$10^2 = 100$
$10^3 = 1000$

THE BASE 10 LOG OF EACH OF THESE IS

$10^0 = 0$
$10^1 = 1$
$10^2 = 2$
$10^3 = 3$

$\log_{10} 10000 = 4$
$\log_{10} 0.01 = -2$

EST. A LOG: WHAT IS $\log_{10} 42$?

$\log 10^1 = 1$ $\qquad \log 10^2 = 2$

SO $\log_{10} 42$ IS >1 AND <2

SO ONE POINT SOMETHING

LOGARITHMS FOLLOW EXPONENT RULES

$$x^a \cdot x^b = x^{a+b} \qquad \log A \cdot B = \log A + \log B$$

$$\frac{x^a}{x^b} = x^{a-b} \qquad \log \frac{A}{B} = \log A - \log B$$

$$(x^a)^b = x^{a \cdot b} \qquad \log A^x = x \cdot \log A$$

YOU CAN USE THESE PROPERTIES TO MANIPULATE ALGEBRAIC EQNS.

$y = x^a \qquad a = ?$

$\log y = \log x^a$

$\log y = a \cdot \log x$

$a = \dfrac{\log y}{\log x}$

$\log 0.5$?

$\log \frac{1}{2} = \log 2^{-1}$

$-\log 2 = \log \frac{1}{2}$

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BASE TEN LOGS ARE CALLED COMMON LOG.

BASE e (EULER'S NUMBER $e \cong 2.718$) LOG IS CALLED THE NATURAL LOG: $\log_e = \ln$

UNDOING LOGS: $\log 10^3 = 3$ $\quad \ln e^x = x$

$(10^{\log 10^3})$ $\quad \underline{\text{anti}\log}\, 3 = 10^3$ $\quad e^{\ln x} = x$

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USING LOGS IN EQUATIONS

INTEGRATED FIRST ORDER RATE LAW

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

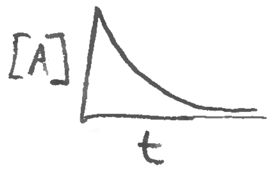
(USE TO CALC t GIVEN $[A]$ AND $[A]_0$ AND k)

$$\underbrace{\ln[A]}_{y} \underset{=}{=} \underset{m}{-k}\underset{x}{t} \underset{+}{+} \underbrace{\ln[A]_0}_{b}$$

(LINEAR FORM — USED FOR GRAPHICALLY VERIFYING A FIRST ORDER RATE LAW)

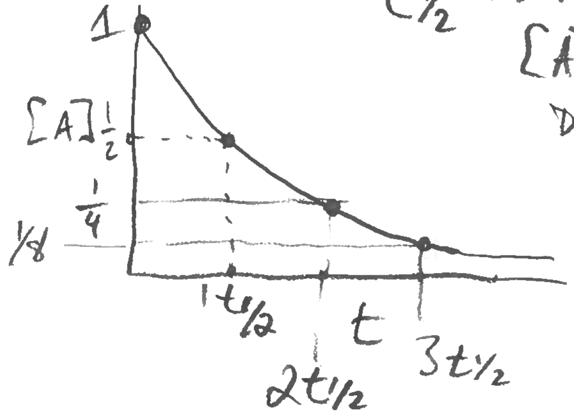
$$e^\wedge\left(\ln\frac{[A]}{[A]_0} = -kt\right)$$

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



(EXPONENTIAL FORM — GOOD FOR CALC $[A]$ GIVEN $[A]_0$ AND t AND k)

HALF-LIFE



$t_{1/2}$ IS THE LENGTH OF TIME NEEDED FOR $[A]_0$ TO CHANGE TO $\frac{1}{2}[A]_0$

DERIVING HALF-LIFE

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

$$\frac{\frac{1}{2}[A]_0}{[A]_0} = e^{-kt}$$

$\ln \frac{1}{2} = -kt$

$\ln 2^{-1} = -kt$ $\quad$ so $-\ln 2 = -kt$

$\ln 2 = k\boxed{t}$ $\quad t = t_{1/2}$

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

$^{238}U \quad t_{1/2} = 4.5\times10^{9}\text{ yrs}$

$$\text{so } k = \frac{\ln 2}{4.5\times10^{9}\text{ yrs}} = 1.54\times10^{-10}\text{ yr}^{-1}$$

YOU CAN USE $t_{1/2}$ TO CALC k, THE RATE CONSTANT, OR YOU CAN USE k TO CALC $t_{1/2}$. $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$

WE GENERALLY ONLY USE $t_{1/2}$ FOR A FIRST ORDER RATE LAW. FOR 0TH AND 2ND ORDER $t_{1/2}$ CHANGES AS THE RXN GOES ON B/C IT DEPENDS ON $[A]_0$.

HALF-LIFE EXPRESSIONS

0TH $\quad t_{1/2} = \frac{[A]_0}{2k}$ (AS TIME PASSES, $t_{1/2}$ GETS SMALLER WITH EACH NEW $[A]_0$)

* $\boxed{1^{ST} \quad t_{1/2} = \frac{\ln 2}{k}}$ A CONSTANT VALUE :)

2ND $\quad t_{1/2} = \frac{1}{k[A]_0}$ (AS TIME PASSES, $t_{1/2}$ GETS BIGGER)

14.5 TEMPERATURE AND RATE

LOW T - SLOWER RATE | HIGH T - FASTER RATE

CLASSIC RULE OF THUMB IS THAT NEAR 20°C, IF YOU INCR. OR DECR. T BY 10°C IT WILL CHANGE RATE BY A FACTOR OF TEN.

COLLISION MODEL

IN ORDER TO REACT, MOLECULES MUST:

1. COLLIDE
2. " " WITH THE CORRECT ORIENTATION
3. " " WITH SUFFICIENT KE

RATE CONSTANTS INCR. IN VALUE AS T RISES. THIS IS B/C:

- COLLISIONS HAPPEN MORE OFTEN AND
- A GREATER FRACTION OF THE POP. OF MOLECULES HAS SUFF. KE

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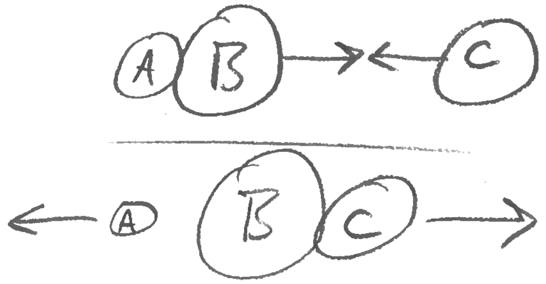
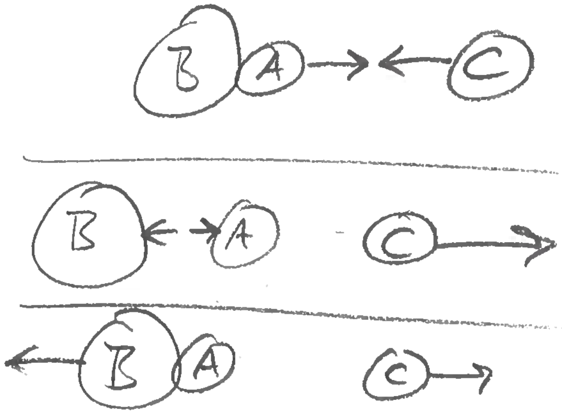
ORIENTATION FACTOR

FOR THE REACTION $AB + C \rightarrow A + BC$

EFFECTIVE COLLISION



INEFFECTIVE COLLISON

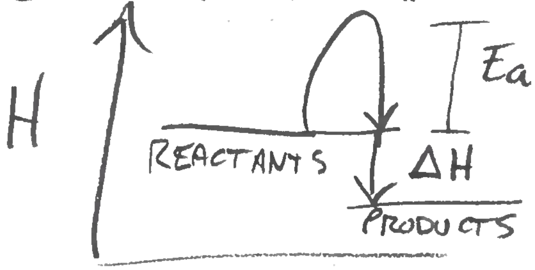


JUST A FRACTION OF ALL MOLECULAR COLLISIONS CAN RESULT IN A RXN AT THE INDIVIDUAL MOLECULES LEVEL.

ACTIVATION ENERGY (E_a)

FOR AN INDIVIDUAL MOLECULE, E_a IS THE MIN. KE IT MUST HAVE IN ORDER TO REACT. "YOU MUST BE THIS TALL TO RIDE."

ENTHALPY DIAGRAM

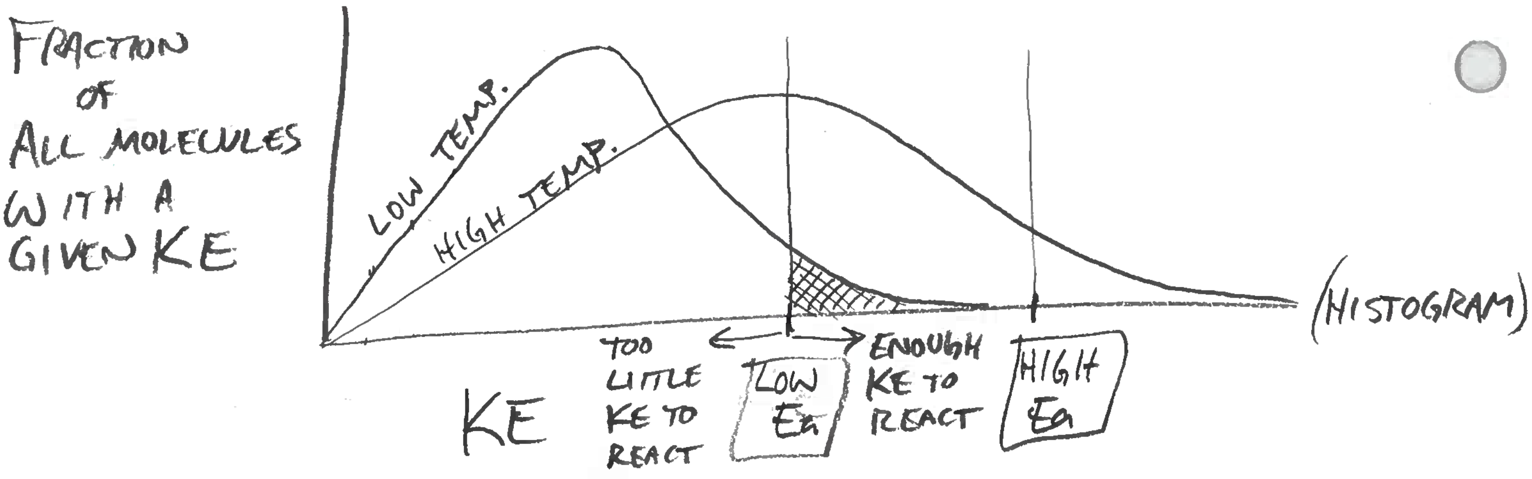


(ΔH IS NEG.)

THE BIGGER THE VALUE OF E_a IS, THE SLOWER A RXN WILL BE. THIS IS B/C WHEN E_a IS LARGER, A SMALLER FRACTION OF MOLECULES WILL HAVE A $KE \geq E_a$.

IN THIS WAY, E_a DETERMINES THE RATE.

LOOKING AT KE IN MOLECULE POPULATIONS



SHADED AREA = TOTAL NO. OF MOLECULES ABLE TO REACT

AT LOW TEMP, NO MOLECULES HAVE ENOUGH KE TO REACT FOR THE HIGH Ea. THIS IS A MATCH IN A BOX.

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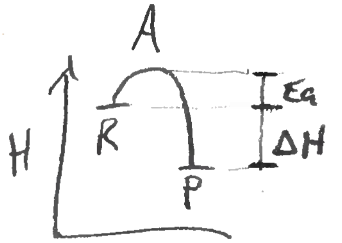
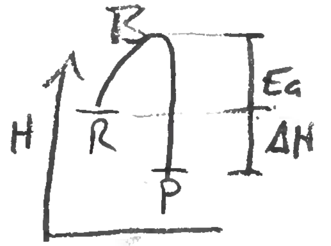
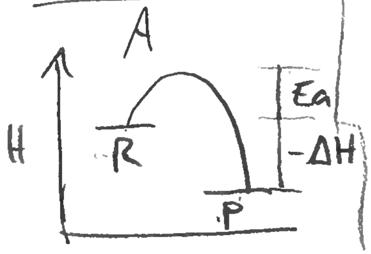
SOME ACTIVATION ENERGY COMPARISONS



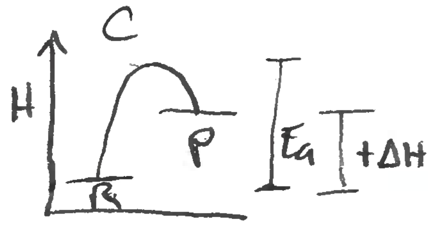


RXN A HAS A SMALLER Ea THAN RXN B. SO EVEN THOUGH ΔH IS THE SAME, RXN A IS FASTER (AT THE SAME TEMP) THAN RXN B.

RATE CONSTANTS $K_A > K_B$



FORWARD



REVERSE

RXN C IS THE REVERSE OF RXN A. NOTE THAT RXN C'S Ea IS MUCH LARGER (AND $|\Delta H_c| = |\Delta H_A|$). $K_c \ll K_a$

SO, BEING SLOWER, THE PRODUCTS OF RXN A (REACTANTS FOR RXN C) WILL BUILD UP FASTER SO THAT AT EQUILIBRIUM, MORE RXN A PRODUCTS WILL BE IN SOLN, THAN RXN A REACTANTS.

ARRHENIUS EQUATION

DETAILED CALC. WITH THIS EQN. IS NOT ASSESSED. HOWEVER, AN UNDERSTANDING OF THE QUANTITIES IN THE EQUATION AND HOW THEY ARE RELATED IS USEFUL FOR UNDERSTANDING HOW RXN RATES WORK.

$$k = Ae^{-(E_a/RT)}$$

k = RATE CONSTANT

A = COLLISION, ORIENTATION FACTOR (TAKES CARE OF UNITS FOR k)

E_a = ACTIVATION ENERGY (USE J/mol, NOT kJ/mol)

R = 8.314 J/K·mol (UNIVERSAL GAS CONSTANT)

T = TEMP IN KELVIN

THINGS TO UNDERSTAND:

① HOW DOES k CHANGE FOR HIGHER AND LOWER T?

② HOW DOES k CHANGE FOR HIGHER AND LOWER E_a?

③ HOW ABOUT CHANGES TO A

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

① CHANGES IN TEMP.

LET $A = 1\times10^{11}\ s^{-1}$ (1ST ORDER)

273K $k = Ae^{-(60{,}000\ J/mol)/(8.314\frac{J}{K\,mol})/(273K)} = 0.331\ s^{-1}$

546K (2×T) $k = Ae^{-(E_a/R/546K)} = 1.82\times10^{5}\ s^{-1}$ SO k INCR. WHEN T INCR.

② CHANGES IN E_a (SUCH AS WITH A CATALYST, WHICH MAY LOWER E_a)

LET $A = 1\times10^{11}\ s^{-1}$ $T = 273K$

E_{a1} 60 kJ/mol $k = 0.331\ s^{-1}$

E_{a2} (WITH CATALYST) 20 kJ/mol $k = Ae^{-(20{,}000\ J/mol)/(8.314\frac{J}{K\,mol})/(273K)} = 1.49\times10^{7}\ s^{-1}$

SO k INCR. WITH DECR. E_a

③ CHANGES TO A (WHICH PERHAPS A CATALYST MIGHT DO)

IF A CATALYST AFFECTS THE VALUE OF A, IT WILL INCREASE IT. SO IF A INCR., SO DOES k IN A SIMPLE, DIRECT PROPORTION.

14.6 REACTION MECHANISMS

A MECHANISM IS A DESCRIPTION OF THE ORDER IN WHICH BONDS ARE BROKEN AND FORMED IN A REACTION. THIS DESCRIPTION IS A SET OF TWO OR MORE CHEMICAL EQUATIONS KNOWN AS <u>ELEMENTARY STEPS.</u> IN A VALID MECHANISM, THE SUM OF THE ELEM. STEPS IS THE OVERALL REACTION UNDER STUDY.

UNLIKE THE OVERALL CHEMICAL RXN UNDER STUDY, THE RATE LAW FOR AN ELEMENTARY STEP TAKES ITS ORDERS OF RXN FROM THE STOICH. COEFFICIENTS IN THE EQN. OF THAT STEP.

FOR EX. UNIMOLECULAR STEP $A \rightarrow$ PRODUCTS RATE $= k[A]^1$

BIMOLECULAR STEP $A + A \rightarrow$ PRODUCTS RATE $= k[A]^2$

$A + B \rightarrow$ PRODUCTS RATE $= k[A]^1[B]^1$

VERY RARELY TERMOLECULAR STEP $A + B + C \rightarrow$ PROD. RATE $= k[A]^1[B]^1[C]$

$2A + B \rightarrow$ PROD. RATE $= k[A]^2[B]^1$

THE OVERALL RATE LAW IS DERIVED FROM THE RATE LAWS OF THE ELEMENTARY STEPS. THE ACTUAL OVERALL RATE IS THE RATE OF THE SLOWEST STEP. BUT OVERALL RATE LAWS MUST HAVE ONLY REACTANTS, NEVER INTERMEDIATES.

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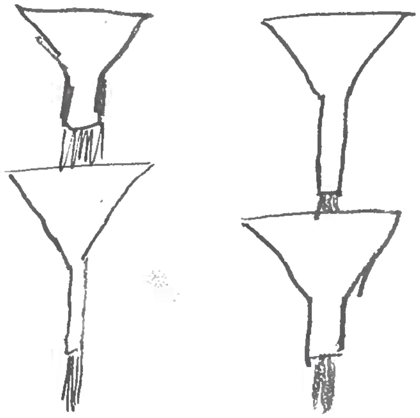
FOR MECHANISMS WITH A SLOW INITIAL STEP, THE RATE LAW OF THAT STEP, IS THE OVERALL RATE LAW.

FOR MECHANISMS WITH FAST INITIAL STEP, THE OVERALL RATE LAW WILL HAVE TO BE DERIVED ALGEBRAICALLY.

THE RATE-DETERMINING-STEP IS THE SLOWEST ONE AND IT DOES NOT MATTER WHAT ORDER IT COMES IN.

CONSIDER THE SLOWEST HIKER.
CONSIDER THESE FUNNELS ——



MECHANISMS WITH A SLOW INITIAL STEP

OVERALL EQN FOR THE RXN $\boxed{NO_2 + CO \rightarrow NO + CO_2}$

STEP 1 (SLOW) $NO_2 + \cancel{NO_2} \rightarrow \cancel{NO_3} + NO$ RATE $= k_1[NO_2]^2$

STEP 2 (FAST) $\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$ RATE $= k_2[NO_3]^1[CO]^1$

SUM OF ELEMENTARY STEPS (VERIFY) $NO_2 + CO \rightarrow NO + CO_2$ (SO IT CHECKS OUT)

(NOTE: NO_3 IS A RXN INTERMEDIATE, RECOG. B/C IT FORMS IN ONE STEP AND IS CONSUMED IN A LATER STEP)

FOR THIS MECHANISM, THE OVERALL RATE LAW IS $\boxed{\text{RATE} = k[NO_2]^2}$ B/C THE FIRST STEP WAS SLOW.

$K = k_1$

MECHANISMS WITH A SLOW 1ST STEP ARE EASY TO ANALYZE B/C THE FIRST STEP CAN NEVER INCL ANY RXN INTERMEDIATES, WHICH (BECAUSE THEIR CONC. CANNOT BE EXP. CONTROLLED) CANNOT APPEAR IN THE OVERALL RATE LAW.

MECHANISMS WITH A FAST INITIAL STEP

EXAMPLE 1 RXN: $2NO + Br_2 \rightarrow 2NOBr$

EXPERIMENTALLY DETERMINED RATE LAW IS $RATE = k[NO]^2[Br_2]$

(THIS RATE LAW COULD BE DUE TO A TERMOLECULAR STEP, WHICH IS HIGHLY UNLIKELY)

STEP 1
(FAST)
(EQUILIBRIUM)

$$NO + Br_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOBr_2$$

FORWARD RATE
$RATE = k_1[NO]^1[Br_2]^1$
REVERSE RATE
$RATE = k_{-1}[NOBr_2]$

B/C THIS RXN QUICKLY REACHES EQUILIBRIUM, THE FORWARD AND REVERSE RATES ARE EQUAL

$$k_1[NO][Br_2] = k_{-1}[NOBr_2]$$

STEP 2
(SLOW STEP)

$$NOBr_2 + NO \xrightarrow{k_2} 2NOBr \quad RATE = k_2[NOBr_2][NO]$$

MENTALLY CHECK: THE ELEM. STEPS HAVE TO ADD UP TO THE OVERALL RXN

OVERALL RATE LAW IS <u>NOT</u> $RATE = k_2[NOBr_2][NO]$

BECAUSE $NOBr_2$ IS AN INTERMEDIATE.

WE HAVE TO USE ALGEBRA TO WRITE A RATE LAW BASED ONLY ON REACTANTS.

① $k_1[NO][Br_2] = k_{-1}[NOBr_2]$ SO $[NOBr_2] = \boxed{\frac{k_1}{k_{-1}}[NO][Br_2]}$

(SOLVE FOR THE CONC. OF THE INTERMEDIATE)

② SUBST. THE CONC. OF THE INTERMED. INTO THE RATE LAW OF THE SLOW STEP:

$$RATE = k_2[NOBr_2][NO] \longrightarrow RATE = k_2\frac{k_1}{k_{-1}}[NO][Br_2][NO]$$

③ SIMPLIFY

$$\boxed{RATE = k[NO]^2[Br_2]} \quad \left(B/C\ k = k_2 \cdot \frac{k_1}{k_{-1}}\right)$$

EXAMPLE 2 $2O_3 \rightarrow 3O_2$

USE THE PROPOSED MECH. TO WRITE AN OVERALL RATE LAW.

PROPOSED MECHANISM

STEP 1 (FAST) EQUIL. $O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ $\quad$ RATE $= k_1[O_3] = k_{-1}[O_2][O]$

STEP 2 (SLOW) $O_3 + O \xrightarrow{k_2} 2O_2$ $\quad$ RATE $= k_2[O_3][O]$

SUM $2O_3 \rightarrow 3O_2$ ✓

$$[O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

SLOW STEP RATE $= k_2[O_3][O]$

INTERMEDIATE

$$\text{RATE} = k_2[O_3]\frac{[O_3]}{[O_2]}\frac{k_1}{k_{-1}} = k[O_3]^2[O_2]^{-1}$$

14.7 CATALYSIS

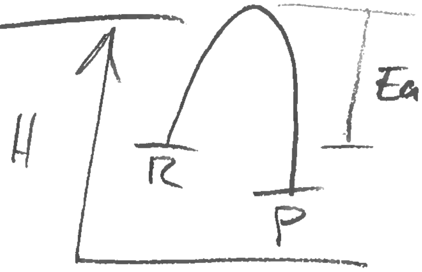
A CATALYST IS A SUBSTANCE WHICH INCREASES A REACTION RATE WITHOUT BEING TRANSFORMED INTO SOMETHING ELSE.

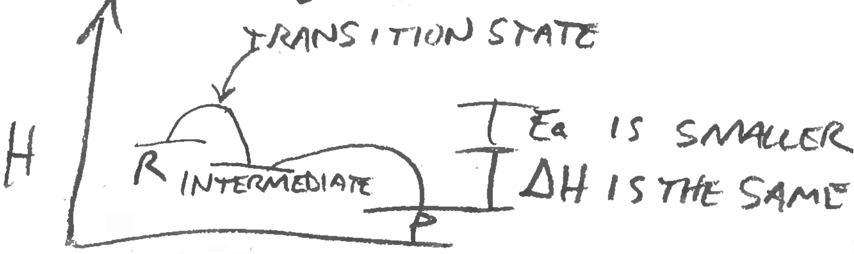
CATALYSTS DO THIS BY CREATING AN ALTERNATE RXN MECHANISM WITH A LOWER E_a (OR A HIGHER A)

ACTIVATION ENERGY

COLLISION FACTOR

LOWER E_a





CATALYTIC MECHANISM

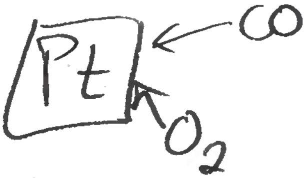
REMEMBER, AS E_a DECR., THE RATE CONSTANT INCR. AND THE LARGER k IS, THE FASTER THE RATE.

HETEROGENEOUS VS. HOMOGENEOUS CATALYSIS

IN HETERO. CATALYSIS THE CATALYTIC SUBSTANCE DOES NOT APPEAR IN THE RXN MECHANISM ELEM. STEPS. GENERALLY, SUCH A CATALYST IS A SOLID TO WHOSE SURFACE MOLECULES TEMPORARILY BIND AND WHERE THE E_a IS LOWER WHILE THEY ARE BOUND.

THE TERM HETEROGENEOUS REFERS TO PHASE OF MATTER — SUCH CATALYSTS ARE USUALLY SOLIDS.

CATALYTIC CONVERTER IN CAR EXHAUST SYSTEM

① 

$$2CO + O_2 \rightarrow 2CO_2$$

② PRODUCING NH_3 (AMMONIA) DEPENDS ON A SOLID IRON-BASED CATALYST

③ HYDROGENATION OF VEG. OILS TO ADD H AND REMOVE DOUBLE BONDS TO RAISE MP.

IN HOMOG. CATALYSIS EVERYTHING IS IN THE SAME PHASE, USUALLY AQUEOUS. IN THE MECHANISM THE CATALYST MOLECULE IS CONSUMED AND REGENERATED:

$2H_2O_2 \rightarrow 2H_2O + O_2$ — ADD HBr (H^+ AND Br^- IONS)

STEP 1 $H_2O_2 + 2Br^- + 2H^+ \rightarrow Br_2 + 2H_2O$

STEP 2 $H_2O_2 + Br_2 \rightarrow 2Br^- + 2H^+ + O_2$

H^+ AND Br^- ARE CONSUMED AND REGENERATED.