CHM 1311 LE.

Kinetics.

- Higher Concentration = Higher Reaction Rate.
- Physical State influences reaction rate.
- Higher Temperature = Higher Reaction Rate.
- Reaction Rate is measured in terms of changes in concentration of reactants/products per unit of time.
- For the general reaction '$A \rightarrow B$':

$$\text{rate} = -\frac{\Delta \text{conc. } A}{\Delta \text{time}}$$

- Use the -ve sign b/c [A] is decreasing ⇒ rate is +ve.
- For the general reaction '$aA + bB \rightarrow cC + dD$':

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

Ex. $2H_2 + O_2 \rightarrow 2H_2O$

a) Express the rate in terms of changes in $[H_2]$, $[O_2]$ & $[H_2O]$ with time.

b) When $[O_2]$ is decreasing @ 0.23 mol/L·s, @ what rate is $[H_2O]$ increasing?

- Use 'O_2' as a reference point b/c its coefficient is 1.

a) $$\boxed{\text{Rate} = -\frac{1}{1}\frac{\Delta[O_2]}{\Delta t} = -\frac{1}{2}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}}$$

b) $$\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = -(-0.23 \text{ mol/L·s})$$

$$\frac{\Delta[H_2O]}{\Delta t} = 2(0.23 \text{ mol/L·s})$$

$$\boxed{\frac{\Delta[H_2O]}{\Delta t} = 0.46 \frac{\text{mol}}{\text{L·s}}}$$

Mechanisms with a Slow Initial Step:

- Overall Rxn: $2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$
- Experimental Rate Law: Rate $= k[NO_2][F_2]$
- Mechanism:

1) $NO_{2(g)} + F_{2(g)} \rightarrow NO_2F_{(g)} + F_{(g)}$ [slow: rate determining]
2) $NO_{2(g)} + F_{(g)} \rightarrow NO_2F_{(g)}$ [fast]

$2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$

- Elementary Steps sum to overall balanced equation.
- Rate Laws:

1) $rate_1 = k_1[NO_2][F_2]$
2) $rate_2 = k_2[NO_2][F]$

* Slow step rate law correlates with observed rate law.

- Therefore, the Mechanism is reasonable.

Mechanisms with a fast Initial Step:

- Overall Rxn: $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$
- Experimental Rate Law: $rate = k[NO]^2[O_2]$
- Mechanism:

1) $NO_{(g)} + O_{2(g)} \rightleftarrows NO_{3(g)}$ [fast]
2) $NO_{3(g)} + NO_{(g)} \rightarrow 2NO_{2(g)}$ [slow: rate determining]

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

- Elementary Steps sum up to overall balanced equation.
- Both steps are bimolecular, therefore reasonable.
- Rate Laws:

1) $rate_{1(fwd)} = k_1[NO][O_2]$
2) $rate_{1(rev)} = k_{-1}[NO_3]$
3) $rate_2 = k_2[NO_3][NO]$

* When equilibrium for step 1 has been established, $rate_{1(fwd)} = rate_{1(rev)}$

$$\Rightarrow k_1[NO][O_2] = k_{-1}[NO_3]$$

$$[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$$

$$rate_2 = k_2[NO_3][NO]$$
$$= k_2\left(\frac{k_1}{k_{-1}}[NO][O_2]\right)[NO]$$

- The ratio of rate constants is itself a constant, equal to overall rate constant for rxn.

$\Rightarrow rate_2 = k[NO]^2[O_2]$, consistent with observed rate law.

- For any Mechanism, only reactants involved up to and including the slow step, appear in the overall rate law.

CHM 1311

Kinetics

Rate Laws for General Elementary Steps:

Elementary Steps	Molecularity	Rate Law
$A \rightarrow$ Product	Unimolecular	Rate = $[A]$
$2A \rightarrow$ Product	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow$ Product	Bimolecolar	Rate = $k[A][B]$
$2A + B \rightarrow$ Product	Termolecolar	Rate = $k[A]^2[B]$

Ex: Determing Molecularity & Rate Laws for Elementary Steps

- Elementary Steps: 1) $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{(g)}$
  2) $NO_2Cl_{(g)} + Cl_{(g)} \rightarrow NO_{2(g)} + Cl_{2(g)}$

a) Write the overall balanced Equation.
b) Determine the molecularity of each Step.
c) Write the rate law for each Step.

a) $NO_2Cl_{(g)} \rightarrow NO_{2(g)} + \cancel{Cl_{(g)}}$
$NO_2Cl_{(g)} + \cancel{Cl_{(g)}} \rightarrow NO_{2(g)} + Cl_{2(g)}$
$= \boxed{2NO_2Cl_{(g)} \rightarrow 2NO_{2(g)} + Cl_{2(g)}}$

b) 1) unimolecular
2) bimolecular

c) 1) Rate = $k[NO_2Cl]$
2) Rate = $k[NO_2Cl][Cl]$

The Rate-Determining Step of a Reaction:

- The Rate-Determining/Limiting Step is the slowest step in a reaction.
- The Rate Law for the Rate Determining Step becomes the rate law for the overall reaction.

Correlating Mechanism with the Rate Law:

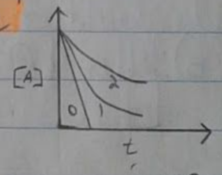
- A valid Mechanism must meet 3 criteria:
  - ↳ Elementary Steps must add up to the overall balanced equation.
  - ↳ Elementary Steps must be reasonable.
  - ↳ Mechanism must correlate with observed rate law.
- A Mechanism is a hypothesis, cannot be proven correct, but if data is consistent, the mechanism can be used to predict results accurately
  - ↳ useful model for the reaction.

The Rate Law:

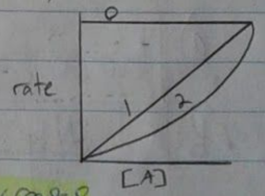
- For any general reaction occuring @ a fixed temperature:
  - ↳ $aA + bB + \dots \rightarrow cC + dD + \dots$
    - ■ $\text{Rate} = k[A]^m[B]^n \dots$
  - ↳ 'k' is a rate constant, specific to a given temperature.
  - ↳ 'm' & 'n' are reaction orders, determined by experiment (not coefficient)

Reaction Orders:

- A reaction has an individual order in each reactant.
- For the general reaction: '$A \rightarrow \text{Products}$'
  - ↳ if rate doubles when [A] doubles, then [A] is a first order reaction ($[A]^1$).
  - ↳ if rate quadruples when [A] doubles, then [A] is a second order reaction ($[A]^2$).
  - ↳ if rate does not change when [A] doubles, then [A] is a zero order reaction (rate doesn't depend on [A]).
- On the graph of 'concentration vs. time'
  - ↳ Zero order reactions are linear
  - ↳ First order is the most steep
  - ↳ Less steep as order number increases.



- On the graph of 'rate vs. concentration'
  - ↳ Zero order is horizontal
  - ↳ First order is linear.
  - ↳ More steep of a curve as order number increases.



Individual & Overall Reaction Orders:

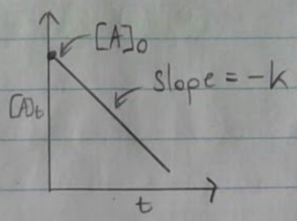
- For the general reaction, '$aA + bB \rightarrow cC + dD$':
  - ↳ $\text{rate} = k[A]^m[B]^n$
  - ↳ the overall reaction order is 'm' + 'n'.
- Overall Reaction Order is the sum of the individual reaction orders.

CHM 1311

Kinetics

- Graphical methods for finding the reaction order from the integrated rate law:
  - ↳ Zero Order Reaction:
    - $[A]_t - [A]_0 = -kt$

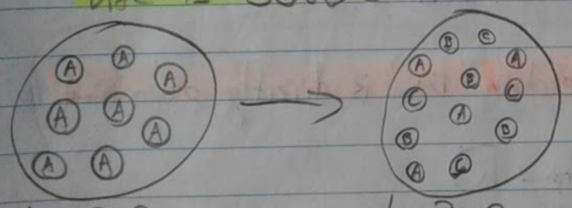
      $[A]_t = -kt + [A]_0$



Reaction Half-Life:

- Half-Life ($t_{\frac{1}{2}}$) for a reaction is the time taken for the concentration of a reactant to drop to half its initial value.
- First Order Reaction, $t_{1/2}$ does not depend on an initial value:
  - ↳ $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$ * $t_{1/2}$ for a 1st Order Rxn is a constant.

Ex: 'A' decomposes into 'B' & 'C', in a first-order rxn. 'A''s half-life is 30.0 s.



t = 0.0s

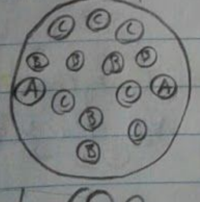
t = 30.0s.

a) Draw a similar molecular scene of the rxn mixture @ t = 60.0s.

b) Find the rate constant of the rxn.

c) If 'P_{Total}' @ 90.0s is 5.00 atm, what is the partial pressure of 'B', 'P_B'.

a)



t = 60.0s.

b) $t_{\frac{1}{2}} = \frac{0.693}{k}$

$k = \frac{0.693}{30.0s}$

$k = 2.31 \times 10^{-2} s^{-1}$

c) $P_B = \%_B \times P_{Total}$

$= 0.467 \times 5.00 atm$

$= 2.33 atm$

$\%_B = \frac{7 B's}{15_{particles}} = 0.467$

Ex: Determining the Half-Life of a 1st Order Reaction

- Given: ↳ $k = 9.2\ s^{-1}$
  ↳ 1st Order Reaction

a) What is the Half-Life of the reaction?

b) How long does it take for the concentration to reach one quarter of the initial value.

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

$t_{1/2} = \boxed{0.0753 s}$

b) $\frac{1}{4} = 2t_{1/2}$

$\frac{1}{4} = \boxed{0.151 s}$

Half-Life Equations:

- For a second-order reaction, '$t_{1/2}$' is inversely proportional to the initial concentration:

$$t_{1/2} = \frac{1}{k[A]_0} \quad (rate = k[A]^2)$$

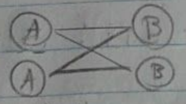
- For a zero-order reaction, '$t_{1/2}$' is directly proportional to the initial concentration:

$$t_{1/2} = \frac{[A]_0}{2k} \quad (rate = k)$$

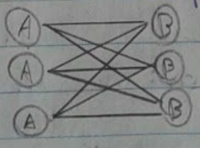
Collision Theory & Concentration:

- Collision Theory states that particles must collide to react.
- Rate depends on product of ~~concentration~~ number of reactant particles, not the sum.

Ex:



4 collisions



9 collisions

Temperature & the Rate Constant:

- 'k' increases exponentially as 'T' increases. (T = Temperature)
  ↳ Expressed in the Arrhenius Equation:

$$k = Ae^{-E_a/RT} \quad \begin{cases} A = \text{frequency factor} \\ E_a = \text{Activation Energy} \end{cases}$$

CHM1311

Kinetics

Activation Energy:

- For collisions between particles to be effective, they must exceed a certain energy threshold.
  - ↳ if a particle collides effectively, it has reached an activated state.
- Activation Energy (E_a) is the energy difference between the reactants and the activated state.
- Lower 'E_a' = faster reaction.

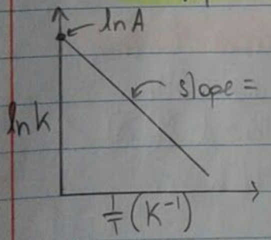
Temperature & Collision Energy:

- At a higher temperature, the fractions of collisions with energy $\geq E_a$ increases. Therefore 'Rate' increases.
- The Fraction of Collisions is inversely proportional to 'E_a'
- The Fraction of Collisions (f) is directly proportional to 'T'.

Calculating Activation Energy:

$k = Ae^{-E_a/RT}$ (take the ln of both sides) $\ln k = \ln A - \frac{E_a}{RT}$ * Straight line graphically

- if you are given 2 different temperatures:
  - ↳ $\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$



Ex: The Rxn has rate constants of $9.51\times10^{-9}\ \frac{L}{mol\cdot s}$ @ 500 K & $1.10\times10^{-5}\ \frac{L}{mol\cdot s}$ @ 600K. Find 'E_a'.

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$E_a = -R\left(\ln\frac{k_2}{k_1}\right)\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1}$$

$$E_a = -8.314\left(\ln\left(\frac{1.10\times10^{-5}}{9.51\times10^{-9}}\right)\right)\left(\frac{1}{600}-\frac{1}{500}\right)^{-1}$$

$$E_a = \boxed{1.76\times10^{5}\ J/mol}$$

Molecular Structure & Reaction Rate:

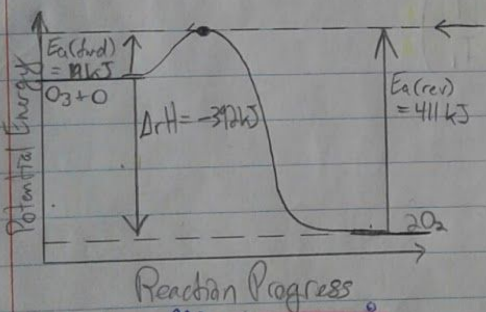
- Another criterion that must be met for the collision between particles to be effective is: the appropriate relative orientation between the reacting particles.
- $k = Ae^{-E_a/RT}$ $(A = \rho z)$ } ρ = orientation probability factor
  Z = collision frequency

Transition State Theory:

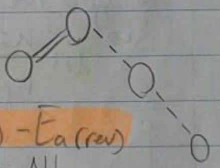
- An effective collision leads to the formation of a transition state or activated complex.
- Transition State: an unstable species that contains partial bonds.
  - Species partway between reactants & products.
  - exists @ the point of max potential energy.

Ex: Drawing Reaction Energy Diagrams & Transition States

- $O_{3(g)} + O_{(g)} = 2O_{2(g)}$: ↳ $E_{a(fwd)} = 19\,kJ$ * very close to transition state.
  ↳ $\Delta H_{rxn} = -392\,kJ$ * very large exothermic gap
- Draw a Reaction Energy Diagram, Predict a Structure for the Transition State & Calculate $E_{a(rev)}$.



← Transition State.



$\Delta H_{rxn} = E_{a(fwd)} - E_{a(rev)}$

$E_{a(rev)} = E_{a(fwd)} - \Delta H_{rxn}$

$= 19kJ - (-392kJ)$

$= 411\,kJ.$

Reaction Mechanisms:

- Mechanism, the single reaction steps which make up the overall equation.
  - the individual steps are called elementary steps
  - each one describes a single molecular event.
- Each elementary step is characterized by its molecularity
  - the number of particles involved in the reaction.
- The rate law for an elementary step can be deduced from the rxn stoichiometry.
  - reaction order = molecularity for an elementary step only.

CHM1311

Kinetics

Determing Reaction Orders:

- For the eq'n, '$rate = k[A]^m[B]^n$':
  - ↳ to determine 'm' & 'n', run experiments where one concentration changes whilst the other remains constant
  - ↳ measure the effect on initial rate in each experiment.

Ex: ^^^

Experiment	Initial Rate (mol/L·s)	Initial [A] (mol/L)	Initial [B] (mol/L)
1	1.75×10^{-3}	2.50×10^{-2}	3.00×10^{-2}
2	3.50×10^{-3}	5.00×10^{-2}	3.00×10^{-2}
3	3.50×10^{-3}	2.50×10^{-2}	6.00×10^{-2}
4	7.00×10^{-3}	5.00×10^{-2}	6.00×10^{-2}

- Finding 'm', order with respect to A:

↳ $$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{\cancel{k}[A]_2^m \cancel{[B]_2^n}}{\cancel{k}[A]_1^m \cancel{[B]_1^n}} = \left(\frac{[A]_2}{[A]_1}\right)^m$$

$$\frac{3.50 \times 10^{-3} \text{ mol/L·s}}{1.75 \times 10^{-3} \text{ mol/L·s}} = \left(\frac{5.00 \times 10^{-2} \text{ mol/L}}{2.50 \times 10^{-2} \text{ mol/L}}\right)^m$$

$$2.00 = (2.00)^m$$

$$m = 1$$

- Finding 'n', order with respect to B:

↳ $$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{\cancel{k}\cancel{[A]_3^m}[B]_3^n}{\cancel{k}\cancel{[A]_1^m}[B]_1^n} = \left(\frac{[B]_3}{[B]_1}\right)^n$$

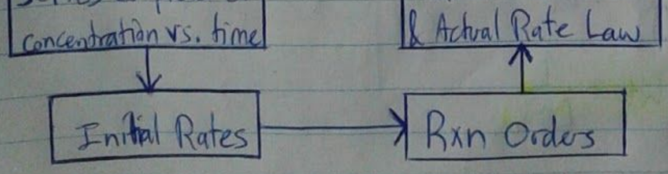
$$\frac{3.50 \times 10^{-3} \text{ mol/L·s}}{1.75 \times 10^{-3} \text{ mol/L·s}} = \left(\frac{6.00 \times 10^{-2} \text{ mol/L}}{3.00 \times 10^{-2} \text{ mol/L}}\right)^n$$

$$2.00 = (2.00)^n$$

$$n = 1$$

- Therefore, '$rate = k[A]^1[B]^1$'.

Determing Kinetic Parameters of a Reaction:



Integrated Rate Laws:

- includes time as a variables
- First Order Rate Equation:
  - ↳ $\ln\frac{[A]_0}{[A]_t} = kt$
- Second Order Rate Equation:
  - ↳ $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$
- Zero Order Rate Equation:
  - ↳ $[A]_t - [A]_0 = -kt$

Ex: At 1000°C, C_4H_8 decomposes in a first-order reaction, with a rate constant of $87s^{-1}$, to 2 molecules of (C_2H_4).

a) if $[C_4H_8]_0 = 2.00M$, what is the concentration after 0.010s?

b) What fraction of C_4H_8 has decomposed @ this time?

a) $\ln\frac{[2.00\,mol/L]}{[C_4H_8]_t} = (87s^{-1})(0.010s)$

$\frac{2.00\,mol/L}{[C_4H_8]_t} = e^{0.87}$ * raise to the 'e' to get rid of 'ln'.

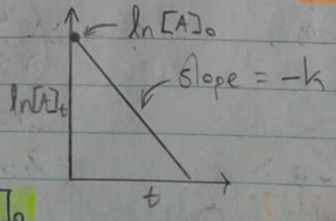
$[C_4H_8]_t = \boxed{0.84\,mol/L}$

b) $\frac{[C_4H_8]_0 - [C_4H_8]_t}{[C_4H_8]_0} = \frac{2.00\,mol/L - 0.84\,mol/L}{2.00\,mol/L} = \boxed{0.58}$

- Graphical methods for finding the reaction order from the integrated rate law:
  - ↳ First Order Reaction:
    - $\ln\frac{[A]_0}{[A]_t} = kt$

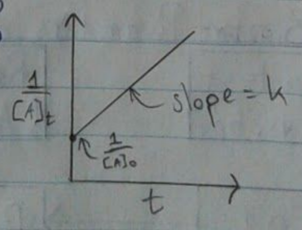
$\ln[A]_0 - \ln[A]_t = kt$

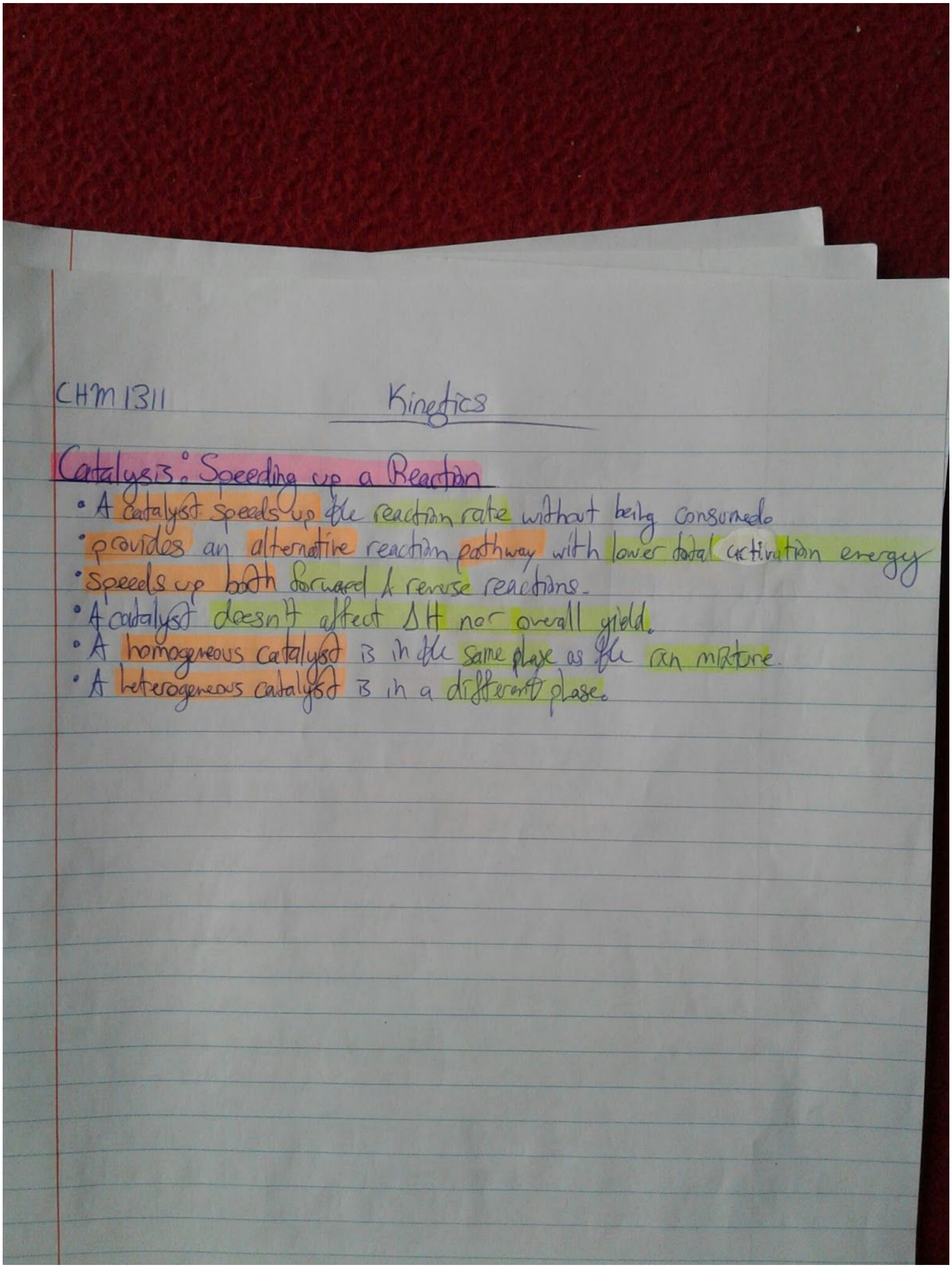
$\ln[A]_t = -kt + \ln[A]_0$



  - ↳ Second Order Reaction:
    - $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$

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





CHM 1311

Kinetics

Catalysis: Speeding up a Reaction

- A catalyst speeds up the reaction rate without being consumed.
- provides an alternative reaction pathway with lower total activation energy
- speeds up both forward & reverse reactions.
- A catalyst doesn't affect ΔH nor overall yield.
- A homogeneous catalyst is in the same phase as the rxn mixture.
- A heterogeneous catalyst is in a different phase.