Chemistry 104, Dr. Batterton
Help Sheet #8 – Chapter 15 (Part II) - Kinetics
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INTEGRATED RATE LAW (again)

Order	Differential Rate Law	Integrated Rate Law	y-axis vs x-axis (y = mx + b)	Slope	y-intercept	$t_{1/2}$ (half life)	Units of k
0	$\Delta[A]/\Delta t = k[A]^0 = k$	$[A]_t = -kt + [A]_o$	[A] vs t	m = -k	$[A]_o$	$t_{1/2} = [A]_o/2k$	$M/time$
1	$\Delta[A]/\Delta t = k[A]^1$	$\ln[A]_t = -kt + \ln[A]_o$	ln[A] vs t	m = -k	$\ln[A]_o$	$t_{1/2} = 0.693/k$	$1/time$
2	$\Delta[A]/\Delta t = k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$1/[A]$ vs t	m = k	$1/[A]_o$	$t_{1/2} = 1/k[A]_0$	$1/[(M)(time)]$

HALF-LIFE $t_{1/2}$ – The time it takes for half the substance to react or decay; $[A]_t = [A]_o/2$; all *radioactive decays* are 1st order with $t_{1/2} = 0.693/k$

1st order rate law: $\ln[A]_t = -kt + \ln[A]_0$ can also be written: $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$

REACTION COORDINATE DIAGRAMS (Fig 15.13)

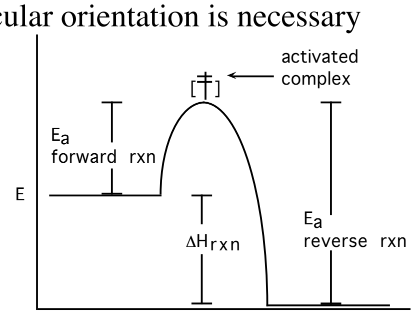
Reactants, Products, Reaction Progress (sometimes called Reaction Coordinate), Energy, Activated Complex/Transition State, ΔH_{rxn}, endothermic versus exothermic, $E_{a\ forward}$, $E_{a\ reverse}$.

Activation Energy, E_a - energy required to get over the "barrier"

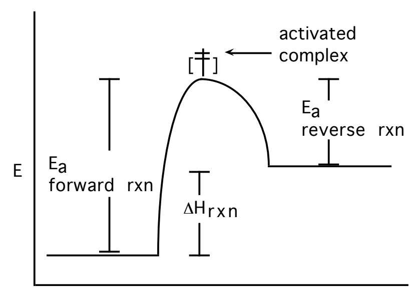
Activated complex or transition state - complex that exists at the top of the curve

For a reaction to proceed:

1. A collision must occur
2. Sufficient energy is needed
3. Correct molecular orientation is necessary



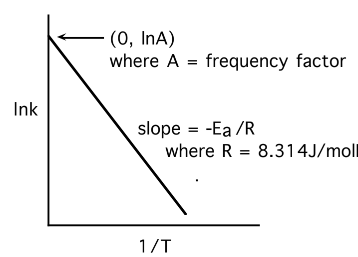
Exothermic Reaction



Endothermic Reaction

ARRHENIUS EQUATION: $k = Ae^{-E_a/RT}$ which can be changed algebraically to:

$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$ this is an equation of a line, y = mx + b with y axis = lnk and x-axis = $1/T$ and yields:



Plot of Arrhenius Equation

To find activation energy, E_a, use: $\ln k_2 - \ln k_1 = \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

R = 8.314 J/molK; E_a in J though often given in kJ; rate constants, k, can have any appropriate units as long as they are the same; T in K

MECHANISMS
Rxn mechanisms: series of chemical steps called *elementary steps*, *elementary reactions*, or *elementary processes*
Molecularity: number of species that collide
Unimolecular step: A → products
Bimolecular step: A + B → products or A + A → products
Termolecular step: A + B + C → products or A + A + B → products

The **rate law for an elementary reaction,** nA + mB → products, is written: **Rate = k[A]^n[B]^m where n and m are the <u>stoichiometric coefficients</u>, that is, numbers!** For example, A + A → products, Rate = k[A]^2; this method of writing rate laws applies **only to elementary reactions not overall reactions.**

Intermediate: initially appears as a *product* in the reaction mechanism and then appears as a *reactant*; does not appear in the final reaction
Catalysis: initially appears as a *reactant* in the reaction mechanism and then appears as a *product*; does not appear in the final reaction
Rate-determining step: the **slow step** in a reaction mechanism is the step with the ***largest activation energy***; **use the rate-determining step in the mechanism to determine rate law**
All chemicals in the rate law must be reactants or products in the overall reaction, or be a catalyst; **no intermediates are allowed in the rate law**; substitutions are sometimes necessary

Temperature: changes *both* the <u>rate of the reaction</u> and <u>k</u>

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1. Given the reaction below between hydrogen and iodine:
$H_2 + I_2 \rightarrow 2HI$
which of the following will increase the <u>rate of the reaction</u>?
a. increasing the temperature
b. adding a catalyst
c. increasing the reactant concentrations
d. a and c will
e. a, b, and c will

2. Given the reaction and data below, answer the questions shown.
$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

time (s)	**$[NO_2]$**
0	0.0100
50	0.0079
100	0.0065
150	0.0055
200	0.0048
250	0.0043
300	0.0038
350	0.0034
400	0.0031

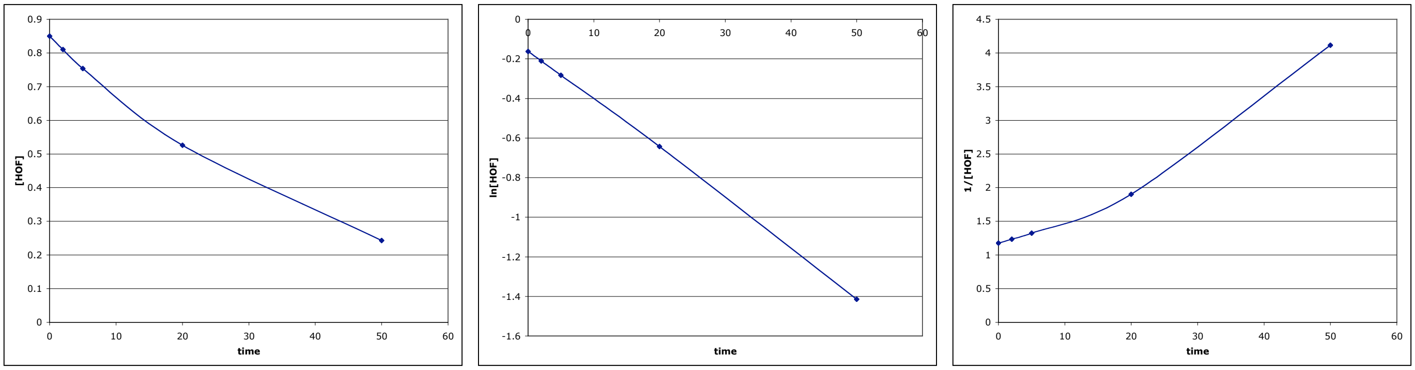
a. What is the best value of the initial rate of consumption for nitrogen dioxide, rate = $-\Delta[NO_2]/\Delta t$?
b. What is the concentration of nitrogen dioxide at 100 seconds?
c. What is the average rate of consumption of nitrogen dioxide, rate = $-\Delta[NO_2]/\Delta t$, at 100 seconds?
d. What is the concentration of nitrogen dioxide at 350 seconds?
e. What is the average rate of consumption of nitrogen dioxide, rate = $-\Delta[NO_2]/\Delta t$, at 350 seconds?
f. Write the general rate law for the loss of nitrogen dioxide?
g. What is the order of the reaction?
h. What is the value of k at 350 seconds?

3. The decomposition of SO_2Cl_2 is a first-order reaction

$SO_2Cl_2 \rightarrow SO_2 + Cl_2$

The rate constant for the reaction is 2.8×10^{-3} min^{-1} at 600K. If the initial concentration of SO_2Cl_2 is 1.24×10^{-3} M, how many minutes will it take for the concentration to drop to 0.31×10^{-3}M?

4. The reaction, $2HOF \rightarrow 2HF + O_2$ was analyzed and kinetic data was plotted below.



a. What is the rate law for this reaction? b. What is the value of the rate constant?
c. What was the initial concentration of HOF? d. What is the concentration of HOF after 120s?

5. One of the reactions in a breeder reactor involves the first order conversion of ^{239}U to ^{239}Np

$^{239}U \rightarrow {}^{239}Np + e^-$

The half-life of ^{239}U is 23.5 minutes. How long does it take for 35% of the ^{239}U to be consumed?

6. The reaction, A → B, is first order with a half-life of 2.75days. What fraction of A remains after 13.75days?

a. $^1/_4$ b. $^1/_5$ c. $^1/_{16}$ d. $^1/_8$ e. $^1/_{32}$

7. Below are two possible mechanisms for the reaction of NO_2 to produce CO_2.

Mechanism I:

Slow	a. $NO_2 + NO_2 \rightarrow NO_3 + NO$
Fast	b. $NO_3 + CO \rightarrow NO_2 + CO_2$

Mechanism II:

Slow	a. $NO_2 \rightarrow NO + O$
Fast	b. $CO + O \rightarrow CO_2$

a. What is the overall reaction for NO_2 reacting with CO_2?
b. What is the molecularity of each step of each mechanism?
c. It is found that the rate of the reactions quadruples when the concentration of NO_2 is doubled and a change in the concentration of CO doesn't change the reaction rate. Which mechanism is more valid and why?

8. a. Describe briefly how increasing the temperature increases the rate of reaction.
b. Describe briefly how adding a catalyst increases the rate of reaction.

9. Assume that the mechanism for the reaction, $NO + NO + Br_2 \rightarrow 2NOBr$, is

Slow	I. $NO + Br_2 \rightarrow Br_2NO$	($\Delta H_I = 50$ kJ/mol)
Fast	II. $Br_2NO + NO \rightarrow 2NOBr$	($\Delta H_{II} = -100$ kJ/mol)

Draw the reaction coordinate diagram for the above mechanism. Include the axes' labels, identify the reactants and products for each step, the activation energies for each step (just label these E_a - no numbers needed), note the ΔH values for each step and for the overall reaction, and identify where the activated complexes are.

10. For a chemical reaction that has a ΔH_{rxn} = -100kJ exothermic, the activation energy is 25kJ. What is the activation energy for the reverse reaction? (Hint: Draw a reaction coordinate diagram.)

11. During a certain reaction, it was found that the rate constant at 18˚C was 1.5 x $10^{-3}$$min^{-1}$ and that at 25˚C it increased to 9.0 x $10^{-3}$$min^{-1}$. What is the activation energy for this reaction?

12. For a first order gas-phase reaction, the activation energy was determined to be 72.5kJ/mol, and the rate constant at 25.5˚C was 7.85 x $10^{-2}$$hr^{-1}$. What would be the rate constant at 58.5˚C?

13. In a reaction it was determined that the rate would triple when the temperature was increased 10˚C from 35˚C. What is the activation energy for the reaction.

14. For each of the mechanisms below
a. Write the overall reaction. b. Identify any catalysts that are present. If there are none, write "none."
c. Identify any intermediates that are present. If there are none, write "none."
d. Identify the reactants. e. Identify the products. f. Determine a rate law from the mechanism.

I. $NO_2 + NO_2 \rightarrow NO_3 + NO$ fast
$NO_3 + CO \rightarrow NO_2 + CO_2$ slow

II. $E + A_2 \rightarrow EA_2$ fast
$EA_2 + C_2 \rightarrow EA + AC_2$ slow
$AC_2 \rightarrow AC + C$ fast
$C + EA \rightarrow AC + E$ fast

III. $H_2O_2 \rightarrow 2OH$ fast
$H_2O_2 + OH \rightarrow H_2O + HO_2$ slow
$HO_2 + OH \rightarrow H_2O + O_2$ fast

ANSWERS

1. e
2. a. rate = $-\Delta[NO_2]/\Delta t = 4.2 \times 10^{-5}$ M/s b. 0.0065M c. rate = $-\Delta[NO_2]/\Delta t = 2.4 \times 10^{-5}$ M/s
   d. 0.0034M e. rate = $-\Delta[NO_2]/\Delta t = 7.0 \times 10^{-6}$M/s
   f. rate = $k[NO_2]^2$ {when you do the calculations you get the order of NO_2 being 1.90; round this to 2}
   g. 2nd order h. $k = 0.606\ M^{-1}s^{-1}$
3. 495 min
4. a. rate = k[HOF] b. $2.5 \times 10^{-2}\ s^{-1}$ c. 0.85M d. 0.042M
5. 14.6 minutes {$t_{1/2} = 0.693/k$ with $t_{1/2} = 23.5$ min → k = 0.0295; $\ln([A]/[A]_o) = -kt$; [A] is the amount that is left over; $[A]/[A]_o$ = 65% = 0.65; ln(0.65) = -(0.0295)t; solve for t}
6. e
7. a. $NO_2 + CO \rightarrow NO + CO_2$

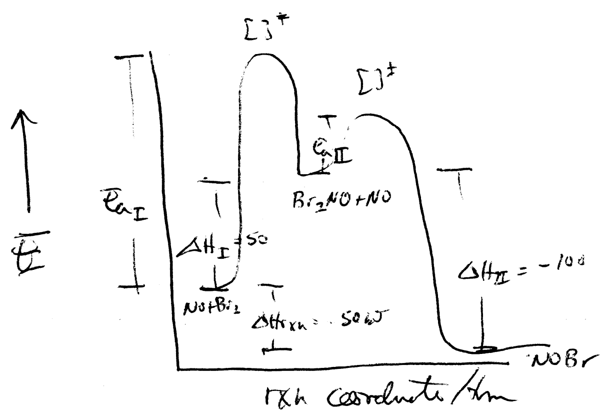
b. Mechanism I, step a: bimolecular, step b: bimolecular; Mechanism II, step a: unimolecular, step b: bimolecular

c. The general rate law from the rate information yields: rate = $k[NO_2]^2$. The rate laws written from the 2 mechanisms are, Mechanism I: rate = $k[NO_2]^2$ and Mechanism II: rate = $k[NO_2]$. Therefore, Mechanism I makes sense with the data available while Mechanism II doesn't.

8. a. As the temperature is increased, the molecules move faster. As they move faster, the number of collisions increases (*i.e.*, frequency of collisions increases) and the energy at which the molecules collide increase (*i.e.*, more molecules will have energy greater than E_a). If there are more collisions and they occur with greater energy, the number of molecules that react (as opposed to simply bouncing off) will increase.

b. A catalyst provides another mechanism at lower energy for the reaction to occur; that is, the E_a is lowered. If the E_a is lowered, then the number of molecules that can react increases since more will have sufficient energy to complete the reaction.

9. See below.



10. 125kJ 11. 184.5 kJ 12. $1.44 hr^{-1}$ 13. 89.5kJ
14. I a. $NO_2 + CO \rightarrow NO + CO_2$ b. none c. NO_3 d. NO_2, CO e. NO, CO_2
   f. rate = $k_2(k_1/k_{-1})[NO_2]^2/[NO])[CO]$

II. a. $C_2 + A_2 \rightarrow 2AC$ b. E c. EA_2, EA, AC_2, C d. C_2, A_2 e. AC
   f. rate = $k_2(k_1/k_{-1})[E][A_2][C_2]$

III. a. $2H_2O_2 \rightarrow 2H_2O + O_2$ b. none c. OH, HO_2 d. H_2O_2 e. H_2O, O_2
   f. rate = $k_2(k_1/k_{-1})^{1/2}[H_2O_2]^{3/2}$