CHEMISTRY 112 LECTURE

EXAM IV MATERIAL

PART I Chemical Kinetics

Chapter 13

Chemical Kinetics is the study of the rates of reactions
Reaction Rate is the decrease of the concentration of reactants and the increase of the concentration of products per unit time

I. Variables that Effect Reaction Rates

1. Concentrations of reactants

2. Concentration of a Catalyst

3. Temperature.

4. Surface area of a solid reactant or catalyst

II. Reaction Rates

Calculations:
1. What is the relationship of the rate of formation of NO_2F to the rate of disappearance of NO_2 and F_2?

$$2NO_2 + F_2 \rightarrow 2NO_2F$$

Rates of reaction continued:
2. Calculate the average rate of N_2O_5 decomposition by the following reaction:

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

Time	$[N_2O_5]$
600 s	1.24 x $^{-2}$ M
1200 s	0.93 x 10^{-2} M

III. Rate Law and Reaction Order

Rate Law

The Rate Law is an equation that equate the rate of a reaction to the concentration of the reactants:

Chemical Eqn.: $aA + bB + cC \rightarrow dD + eE$

$$\text{Rate of Rxn} = k\,[A]^x\,[B]^y\,[C]^z$$

Reaction Order

The Order of a particular species in a rate law is the exponent that the concentration of the species is raised to. The Reaction Order is the sum of all the exponents a rate law.

1. $2\ N_2O_5 \text{ ---> } 4\ NO_2 + O_2$

   Rate = $k[N_2O_5]$

2. $2\ NO + Cl_2 \text{ ---> } 2\ NOCl$

   Rate = $k[NO]^2\ [Cl_2]$

3. $2\ NH_3 \text{ ---> } N_2 + 3\ H_2$

   Rate = $k[NH_3]^0$

4. $BrO_3^- + 5\ Br^- + 6\ H^+ \text{ ---> } 3\ Br_2 + 3\ H_2O$

   Rate = $k[BrO_3^-]\ [Br^-]\ [H^+]^2$

<u>Determination of Reaction Order and Rate Constant from Experimental Data:</u>
The Relationship between the rate and concentration of reactant must be determined experimentally:
Determine the Reaction Order and Rate Constants for the following:

1. $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Experiment	Initial Conc. $[N_2O_5]$	Initial Rate [mol/L sec]
1	0.010	4.8×10^{-6}
2	0.020	9.6×10^{-6}

2. H_2O_2 + 3 I^- + 2 H^+ ---> I_3^- + 2 H_2O

Experiment	Initial Conc. $[H_2O_2]$	$[I^-]$	$[H^+]$	Initial Rate [mol/L sec]
1	0.010	0.010	0.00050	1.15×10^{-6}
2	0.020	0.010	0.00050	2.30×10^{-6}
3	0.010	0.020	0.00050	2.30×10^{-6}
4	0.010	0.010	0.0010	1.15×10^{-6}

3. 2 NO + O_2 ---> 2 NO_2

Experiment	Initial Conc. [NO]	[O_2]	Initial Rate [mol/L sec]
1	0.020	0.010	0.028
2	0.020	0.020	0.057
3	0.020	0.040	0.114
4	0.040	0.020	0.227
5	0.010	0.020	0.014

IV. Concentration-Time Equations - The Integrated Rate Law:

First Order Rate Law

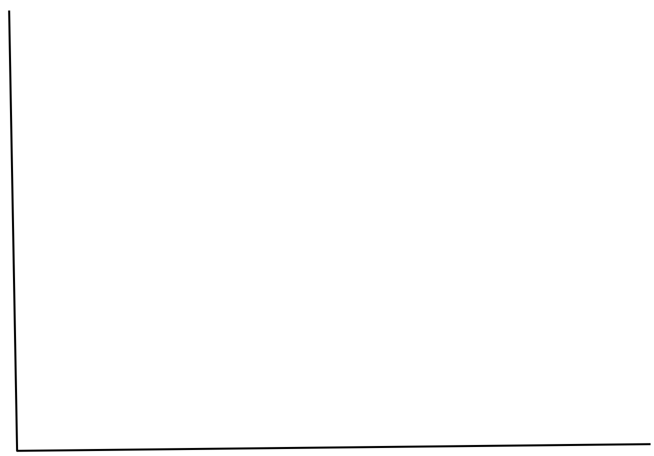
$$2\ N_2O_5 \ \text{--->}\ 4\ NO_2 + O_2$$

The Rate Law is:

The graph:

Using calculus the following equation is derived:

Graphing ln $[A]_t$ vs time:



Problem: The decomposition of $N_2O_5$is first order with a rate constant of 4.80×10^{-4} /sec at 45°C.

a. If the initial Molarity of N_2O_5 is 1.65×10^{-2} mol/L, what is the concentration at 825 s?

b. At what time would the N_2O_5 concentration be 1.00×10^{-2} mol/L ?

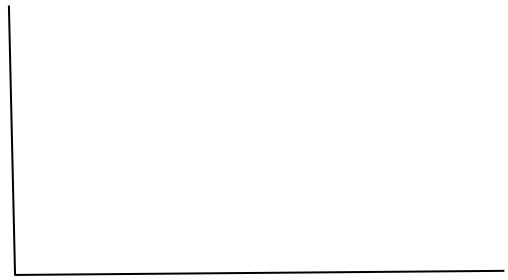
c. At what time would 25% of N_2O_5 remain?

Second Order Rate Law

$$2\ NO_2 \longrightarrow 2\ NO + O_2$$

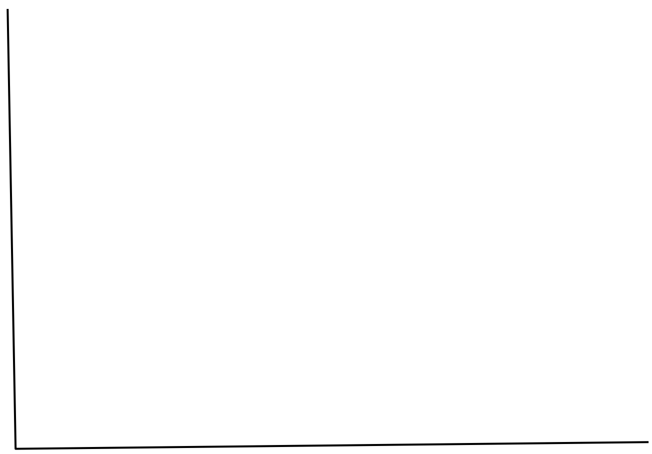
The Rate Law is:

The graph:



Using calculus the following equation is derived:

Graphing $\frac{1}{[A]_t}$ vs time:



Problem: The decomposition of NO_2 is second order with a rate constant of 0.775 L/mol·s at 330°C.
If the initial Molarity of N_2O_5 is 0.0030 mol/L, what is the concentration at 645 s?

Half - Life of a Reaction

The half-life of a reaction is when the reactant concentration has decreased by 1/2 of its original concentration:

Example: 1.0 M “A”

$$t_{1/2} = \frac{0.693}{k} \quad \text{for a first order rxn}$$

Problem: What is the half-life for N_2O_5 if $k = 4.80 \times 10^{-4}$/s, a first order reaction.

V. The Effect of Temperature on the Rate Constant

Svante Arrhenius in 1889 found that for most reactions, the rate of reaction increased with increasing temperature and that it is nonlinear. He found that most reactions obeyed the following equation:

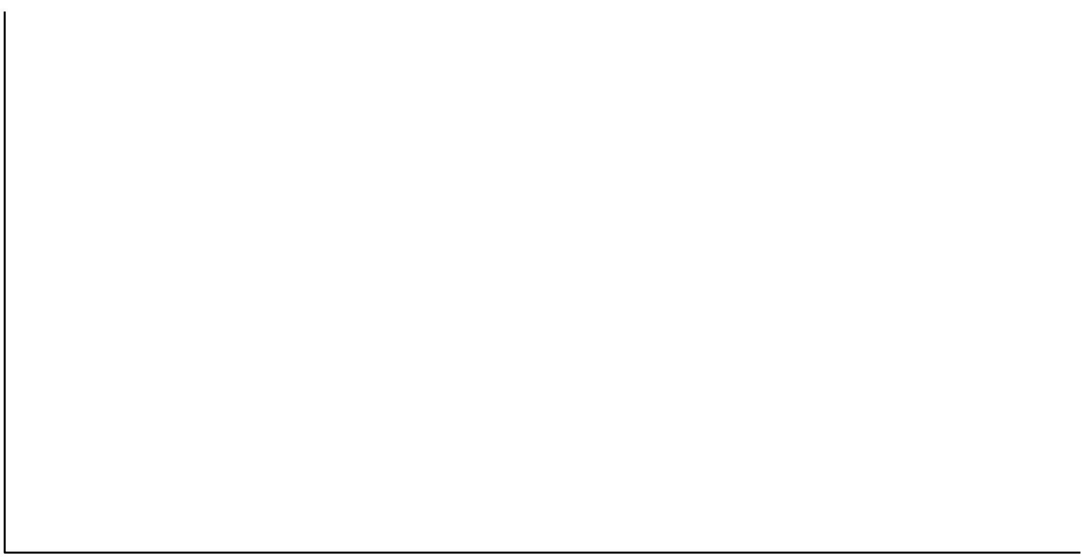
$$k = Ae^{-Ea/RT}$$

Where:
k = Rate Constant
A = The Frequency Factor related to the orientation and probability of collisions.
Ea = Energy of Activation
R = 8.31 J/mol-K

Problem:
Using the information from the following table, for the reaction of methyl isonitrile at various temperatures:
a. Calculate the Ea for the reaction
b. Calculate the rate constant at 430.0 K

Temperature, °C	k,(s^{-1}) .
189.7	2.52×10^{-5}
230.3	6.30×10^{-4}

VI. Transition-State Theory



VI. Reaction Mechanisms

A Reaction Mechanism is the sequence of sequence of the bond-making and bond-breaking process which results in a reaction taking place:

Rate Determining Step

The rate of the overall reaction is limited by the slowest elementary step. The slowest elementary step is called the rate determining step (RDS) or the rate limiting step.

Example 1

Slow Step: $NO_2 + F_2 \text{ ---> } NO_2F + F$

Fast Step: $F + NO_2 \text{ ---> } NO_2F$

Example 2

Rate = k[NO_2] [O_3]

$NO_2 + O_3 \text{ ---> } NO_3 + O_2$

$NO_2 + NO_3 \text{ ---> } N_2O_5$

Rate Determining Step, cont'd

Example 3

Rate=k[NO_2Cl]

Elementary step 1 $NO_2Cl \rightarrow NO_2 + Cl$

Elementary step 2 $NO_2Cl + Cl \rightarrow NO_2 + Cl_2$

1. What is the overall rxn
2. Which is the slow step? Fast step?
3. Which is the Rate Determining Step?
4. What is the reaction order
5. What are the rxn intermediates?
6. Draw the Energy diagram

Example 4

Fast Step: $NH_3 + OCl^- \longrightarrow NH_2Cl + OH^-$

Slow Step: $NH_2Cl + NH_3 \longrightarrow N_2H_5^+ + Cl^-$

Fast Step: $N_2H_5^+ + OH^- \longrightarrow N_2H_4 + H_2O$

1. What is the overall rxn
2. Which is the Rate Determining Step?
3. Write the rate equation

4. What are the rxn intermediates?
5. What is the reaction order?
6. Draw the energy diagram.

PART II Organic Chemistry

Chapter 20

Organic Chemistry is the study of compounds that contain carbon
Carbon is Unique! It has the ability to form 4 bonds including double and triple bond. It can catenate-Carbon forms chans!

A. Types of Organic Compounds

1. Hydrocarbons
2. Alcohols
3. Ethers
4. Aldehydes
5. Ketones
6. Carboxylic Acids
7. Esters
8. Amines

B. Hydrocarbons

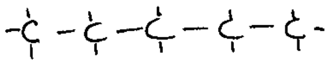
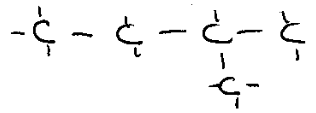
Hydrocarbons are the simplest of organic compounds, they contain only hydrogen and carbon.

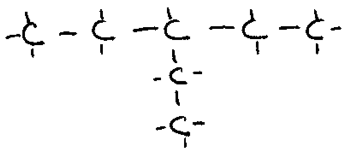
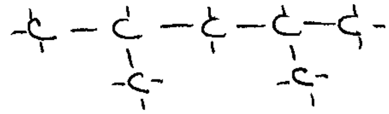
1. Aliphatic

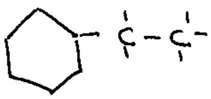
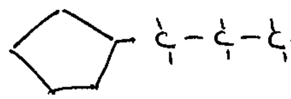
	General	Molecular Formula	Full structure	condensed structure
a. Alkanes	C_nH_{2n+2}	ex. C_3H_8		$CH_3CH_2CH_3$
b. Alkenes	C_nH_{2n}	ex. C_3H_6		$CH_3CH=CH_2$
c. Alkynes	C_nH_{2n-2}	ex. C_3H_4		$CH_3C\equiv CH$
d. Cycloalkanes	C_nH_{2n}	ex. C_4H_6		

2. Aromatic

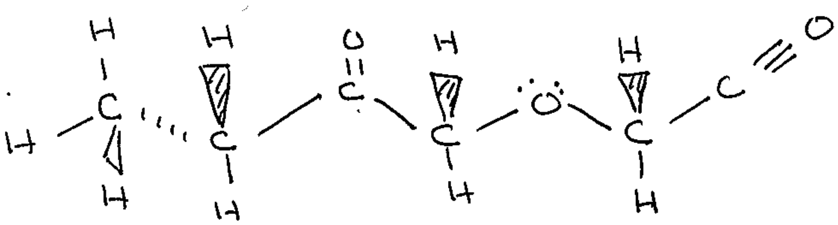
C. Alkanes and Their Isomers

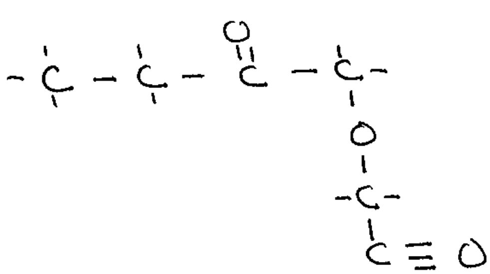
(1)  and 

(2)  and 

(3)  and 

D. Bonding





E. Nomenclature

Organic Chemistry IUPAC System of Nomenclature Rules for Alkanes

1. Determine the parent/main structure, which is the longest continuous chain

2. The carbon atoms of the longest continuous chain are numbered consecutively from one end to the other, beginning at the end which gives the lowest number to the site of first difference. The position of each substituent group on the chain is then denoted by the corresponding number.

3. The position of each branching alkyl group is specified by the number of the carbon atom to which it is attached in the basic chain.

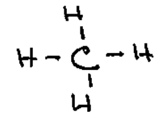
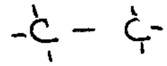
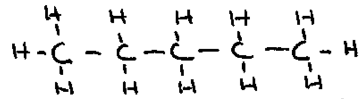
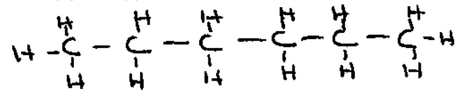
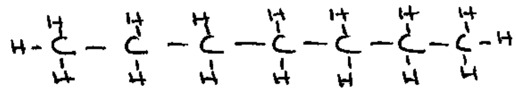
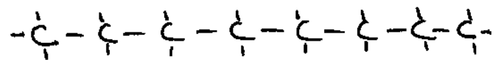
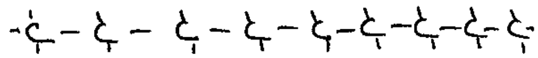
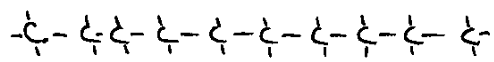
4. The number designating the position of each of the various substituent groups on the main chain is placed before the name of the substituent group and separated from the name by a hyphen.

5. If the same alkyl group occurs more than once as a side chain, indicate by the prefix: di, tri, tetra, penta, etc., to show how many of these alkyl groups there are. (The numbers of these groups are listed together, separated by commas.)

6. If there are several different alkyl groups attached to the parent chain, name them in alphabetical order.

7. Cycloalkanes are named by placing the prefix, “cyclo” before the appropriate alkane names for the number of the carbon atoms in the cyclic chain. If more than one side group is present, the number “1” carbon is assigned alphabetically.

8. The IUPAC name of the alkane is written as one word.

Name	# Carbons	Condensed Structural Formula	Full Structure	Molecular Structure
Methane	1	CH_4		CH_4
Ethane	2	CH_3CH_3		C_2H_6
Propane	3			
Butane	4			
Pentane	5	$CH_3CH_2CH_2CH_2CH_3$		C_5H_{12}
Hexane	6	$CH_3CH_2CH_2CH_2CH_2CH_3$		C_6H_{14}
Heptane	7	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$		C_7H_{16}
Octane	8	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$		C_8H_{18}
Nonane	9	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$		C_9H_{20}
Decane	10	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$		$C_{10}H_{22}$

Side Chains

<table>
<tr><th>Name</th><th># Carbons</th><th>Condensed Structure</th><th>Full Structure</th></tr>
<tr><td>methyl</td><td>1</td><td>$-CH_3$</td><td></td></tr>
<tr><td>ethyl</td><td>2</td><td>$-CH_2CH_3$</td><td></td></tr>
<tr><td>propyl</td><td>3</td><td>$-CH_2CH_2CH_3$</td><td></td></tr>
<tr><td>iso-propyl</td><td>3</td><td>$-CH_2CH_3$
|
CH_3</td><td></td></tr>
<tr><td>butyl</td><td>4</td><td>$-CH_2CH_2CH_2CH_3$</td><td></td></tr>
<tr><td>iso-butyl</td><td>4</td><td></td><td></td></tr>
<tr><td>sec-butyl</td><td>4</td><td></td><td></td></tr>
<tr><td>tert-butyl</td><td>4</td><td></td><td></td></tr>
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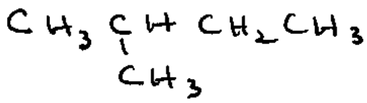
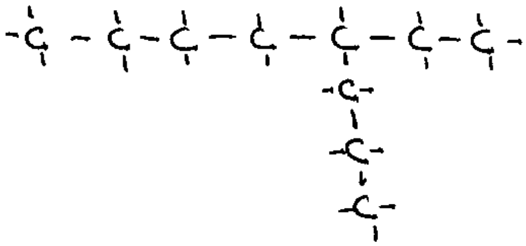
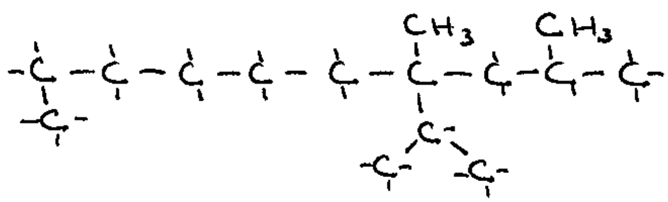
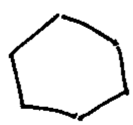
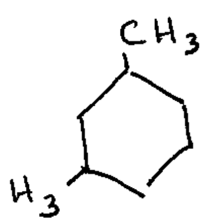
EXAMPLES

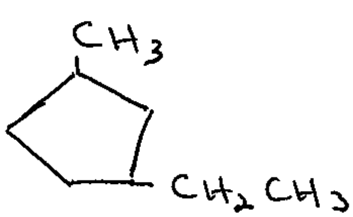












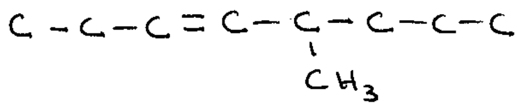
CLASSES OF ORGANIC COMPOUNDS

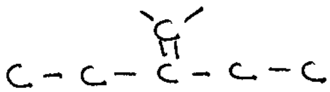
CLASS	GENERAL FORMULA	CONDENSED GENERAL FORMULA	FUNCTIONAL GROUP	FUNCTIONAL GROUP NAME	NAMING
ALKANE	C_nH_{2n+2}				alkane
ALKENE	C_nH_{2n}		C=C		#–alk***ENE***
ALKYNE	C_nH_{2n-2}		C≡C		#–alk***YNE***
ALCOHOL	R–O–H	ROH	C–O–H	hydroxyl	#–alkan***OL***
ETHER	R –O–R'	ROR'	C–O–C		#–alk***OXY***alkane
ALDEHYDE	R–C(=O)–H	RCHO	–C(=O)–H	carbonyl	alkan***AL***
KETONE	R–C(=O)–R'	RCOR'	C–C(=O)–C	carbonyl	#–alkan***ONE***
CARBOXYLIC ACID	R–C(=O)–O–H	RCOOH	–C(=O)–O–H	carboxyl	alkan***OIC ACID***
ESTER	R–C(=O)–O–R'	RCOOR'	–C(=O)–O–C		alkyl alkan***OATE***
PRIMARY AMINE	R–N(–H)–H	RNH_2	C–N(–H)–H	amino	#–***AMINO***alkane

G. NOMENCLATURE OF FUNCTIONAL GROUPS

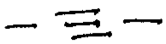
ALKENES

$CH_2=CHCH_2CH_3$

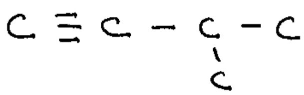


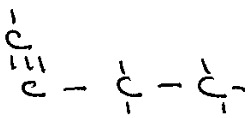


ALKYNES



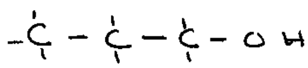
$C-C-C\equiv C-C$

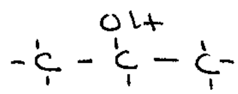


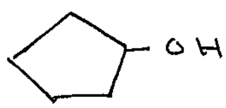


ALCOHOLS, ROH

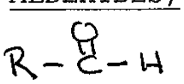
ROH

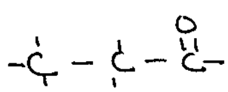


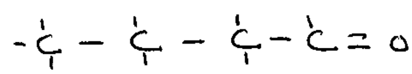


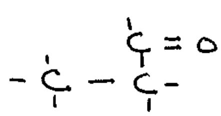


ALDEHYDES,



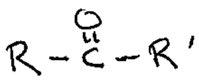


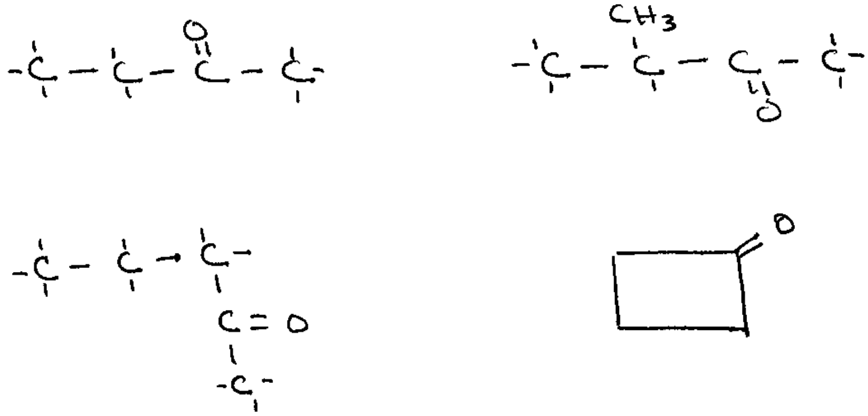




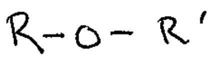
Nomenclature cont'd

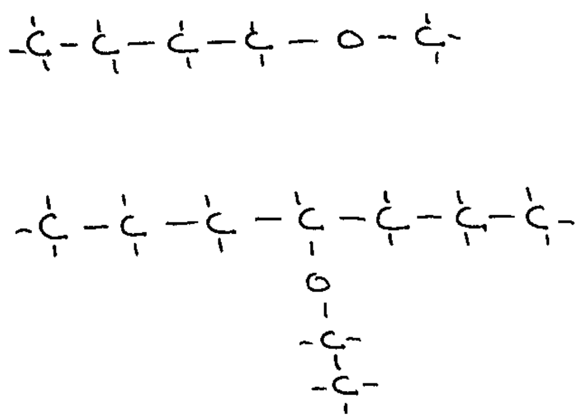
KETONES



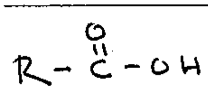


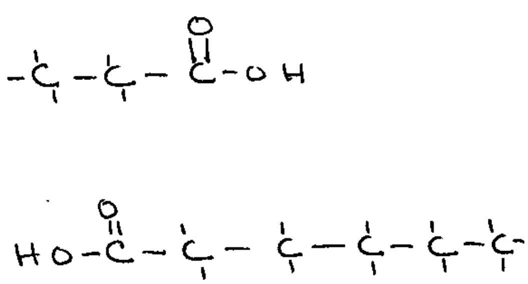
ETHERS





CARBOXYLIC ACIDS





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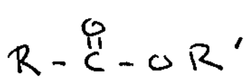
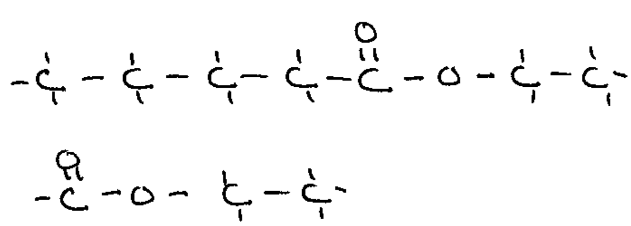
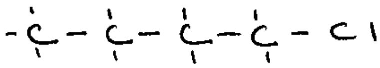
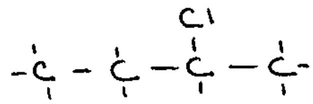


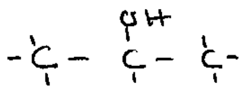
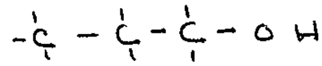


H. DRAWING ISOMERS.

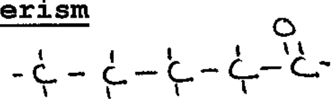
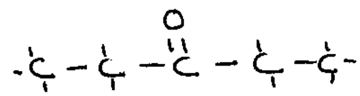
1. Structural Isomerism

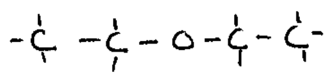
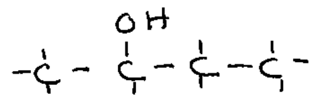
a. Positional Isomerism

(1)  & 

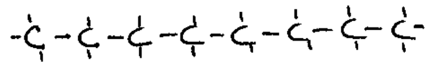
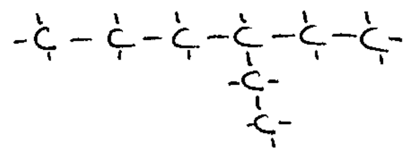
(2)  & 

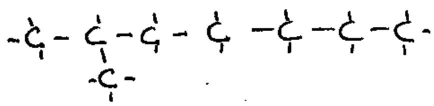
b. Functional Isomerism

(1) $C_5H_{10}O$  & 

(2) $C_4H_{10}O$  

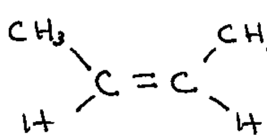
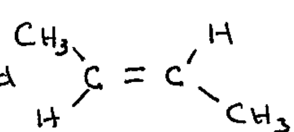
c. Skeletal Isomerism

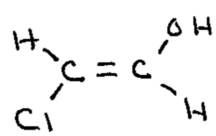
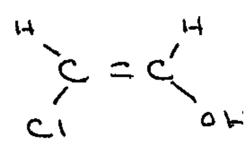
C_8H_{12}  



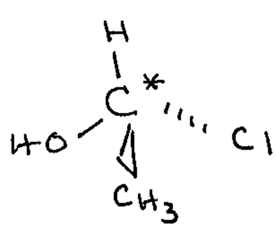
2. Stereo Isomerism

a. Geometric Isomerism

(1)  and 

(2)  and 

b. Optical Isomerism



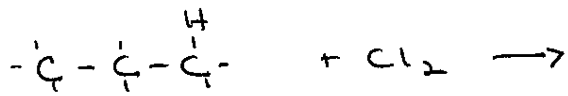
I. ORGANIC REACTIONS

COMBUSTION OF ORGANIC COMPOUNDS

$$C_xH_z + O_2 \rightarrow CO_2 + H_2O$$

REACTIONS OF ALKANES

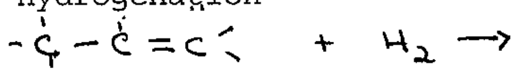
Substitution/Halogenation of Alkanes



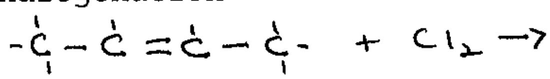
REACTIONS OF ALKENES AND ALKYNES

Addition Reactions

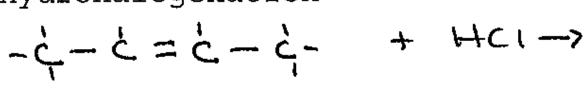
Hydrogenation



Halogenation



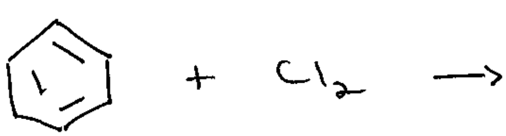
Hydrohalogenation



H_2O Addition

REACTIONS OF Benzene

Substitution Reactions

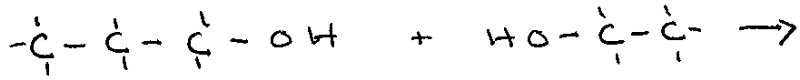


Reactions of Alcohols

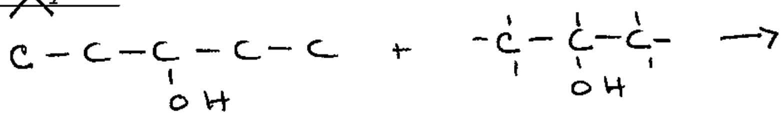
Condensation

Alcohol + Alcohol

Ether



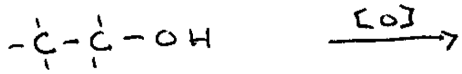
Hydrolysis



Oxidation

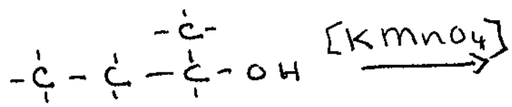
aldehyde

Primary alcohol, 1°

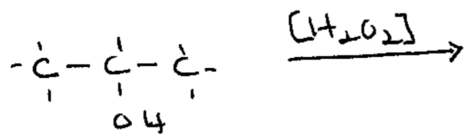


Ketone

Secondary alcohol, 2°



Tertiary alcohol, 3°



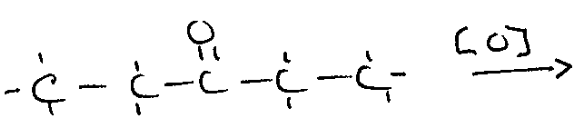
Reactions of Aldehydes

Oxidation

carboxylic Acid

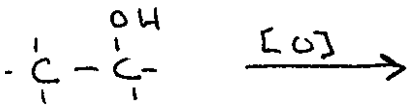
Reactions of Ketones

Oxidation

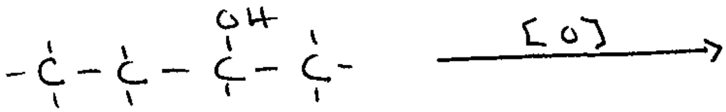


SUMMARY

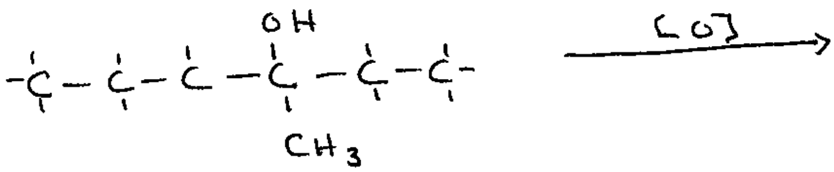
1° Alcohol



2° Alcohol

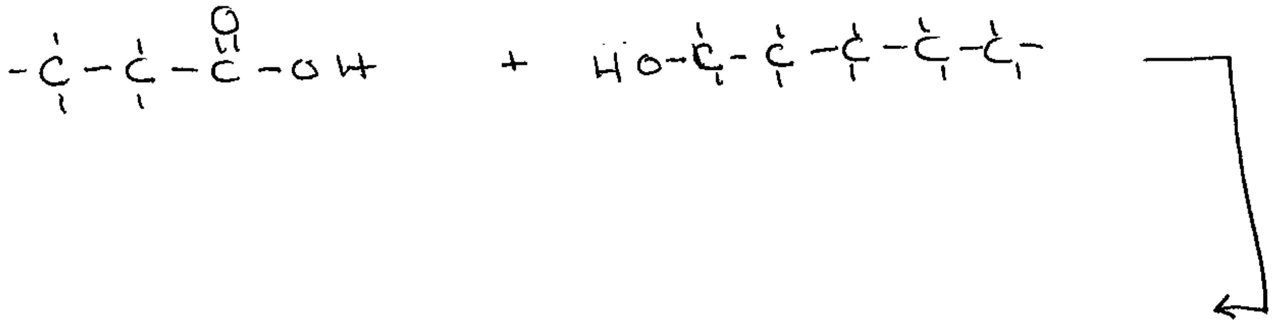


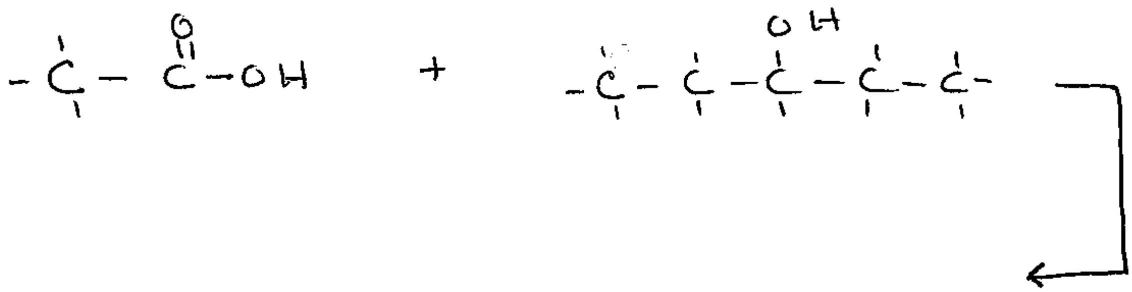
3° Alcohol



Reactions of Esters

Formation of Esters





PART III Nuclear Chemistry

Chapter 19

Nuclear Chemistry is the study of the properties and the reactions that occur in the nucleus of an atom.
Nucleons are the particles (protons and neutrons) found in the nucleus of an atom.
Isotopes are atoms with the same number of protons but a different number of neutrons.
Nuclides are isotopes with a particular nuclear composition.

An unstable nucleus exhibits radioactivity. Radioactivity is the spontaneous emission of radiation from the nucleus.

1. 67 out of 350 isotopes in nature are radioactive
2. All atoms with an atomic number > 83 are radioactive (With a few exceptions)
3. Isotopes decay to new elements due to an unstable nuclei with the emission of ionizing radiation
4. Radioactive Emissions- α, β and γ

A. Radioactive Emissions- α, β and γ

a. Alpha Particles , α,
- $^{4}He^{2+}$
- $^{4}\alpha$
- Mass = 6.65×10^{-24}g

b. Beta Particles , β,
- ^{o}e
- $^{o}\beta$
- Mass = 9.11×10^{-28}g

c. Gamma Radiation ,γ,
- γ
- photon
- No charge
- No mass

B. Relative Penetrating Power of α, β and γ Radiation

C. Nuclear Reactions vs Chemical Reactions

D. Types of Nuclear Reactions- α, β and γ

1. Alpha decay involves the emission of an α particle:

2. Beta decay involves the emission of a β particle from the nucleus-a neutron is converted to a proton and a β particle.

3. Positron decay involves the emission of a positron, $^{0}\beta$ from the nucleus- a proton is converted to a neutron and a positron

4. Electron Capture-An inner shell electron is captured by the nucleus.

A nuclear proton is then converted into a neutron:

5. Gamma Emission-γ rays are essentially a stream of high energy photons and almost always accompanies β and α emission (even though it is not shown in the equation)

D. Nuclear Stability- α, β and γ

The stability of a particular isotope can be predicted by the $\frac{\text{Neutron}}{\text{Proton}}$ ratio, N/Z.

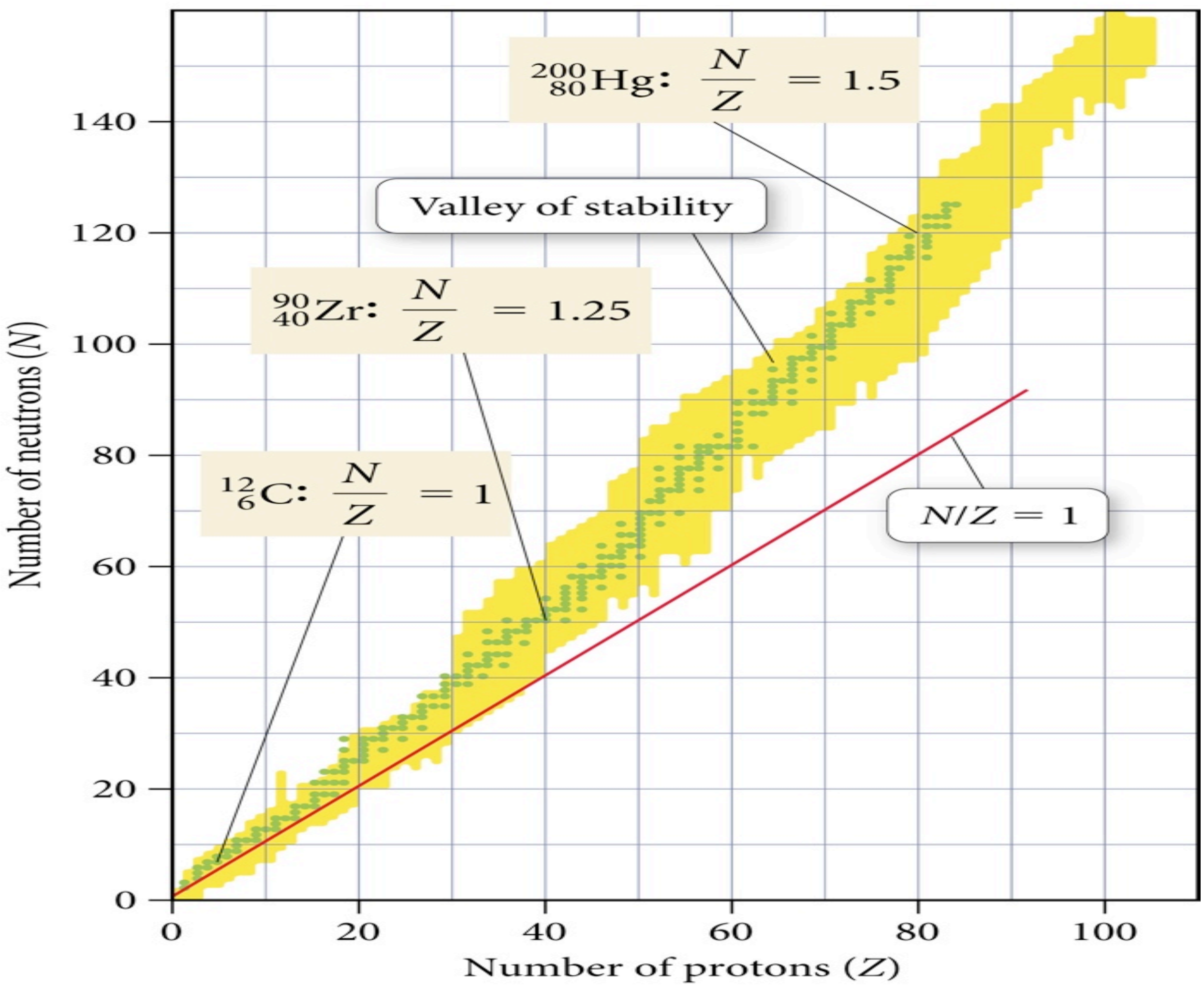
1. All nuclides with Z > 83 are unstable and are radioisotopes.

2. Elements with an even Z (number of protons) usually have a larger number of stable nuclides than elements with an odd Z.

3. The N/Z ratio of stable nuclides increases as Z increases.

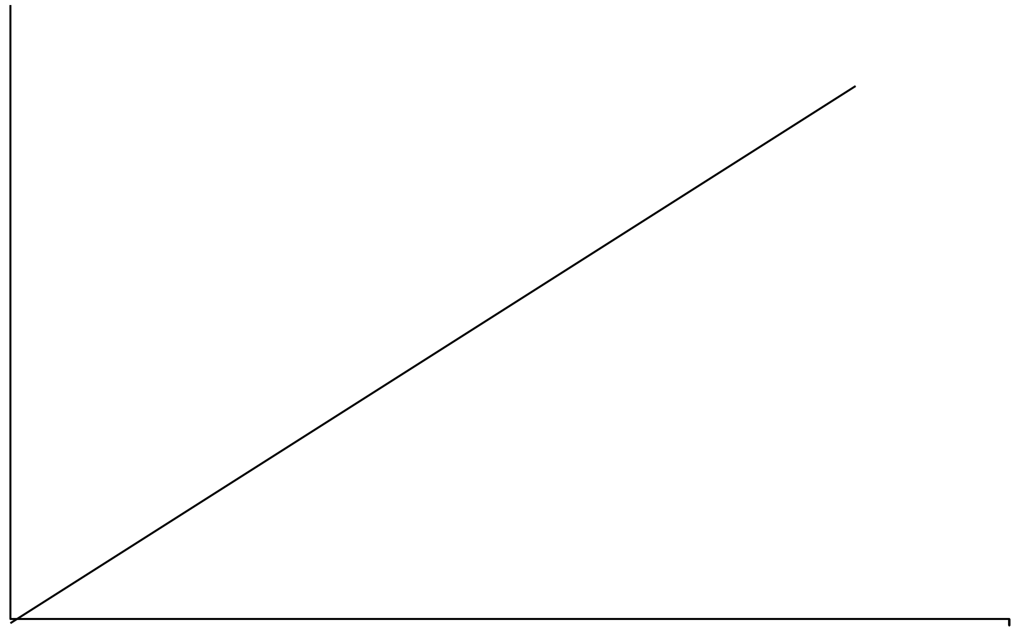
4. Elements with N or Z values of 2,8,20,28,50, or 82 are exceptionally stable These are called “magic numbers” and perhaps correspond to numbers of protons or neutrons in “filled” nucleon shells. (There are exceptions) If the N and Z value are both a magic number then the isotope “double magic” and is very exceptionally stable

Valley of Stability



Valley of Stability: Number of neutrons vs protons

 # neutrons



 # protons

A. Below the Valley of Stability (Band or belt of stability), radioisotopes undergo:

1.   Positron emission

2.   Electron capture

B. Above the Band of Stability/Valley of stability, radioisotopes undergo Beta emission

E. Radioactive Decay

a. Half-life, $T_{1/2}$

Prob. 3 g of C-14 is left after 17190 years. What was the orginal amount if $t_{1/2}$ = 5730 years for C-14?

b. $\ln \frac{N}{N_o} = -kt$ and $t_{1/2} = \frac{0.693}{k}$

Problems:

1. A sample of radon-222 is initially undergoes 7.0×10^4 disintegrations per second (dps). After 6.6 days, the disintegrations decrease to 2.1×10^4 dps. What is the half-life of radon-222?

2. A wooden artifact is found to give 9.0 C-14 dpm. What is the approximate age of the wooden artifact? The half-life of C-14 is 5730 years and the initial dpm for C-14 is 15 dpm.

3. A sample of a wooden object was found to give 8.00 C-14 dpm. Calculate the approximate age of the object if the activity of C-14 in living plants is found to be 15 dpm. The half-life of C-14 is 5730 years

4. Initially, 0.05 mg Tc-99, t ½ = 6.0 hr. How long will it take to reduce Tc-99 to 1.0×10^{-3} mg.

F. Transmutation

Transmutation is the process of artificially transforming (transmuting) one nucleus into another

(a) Neutron bombardment

(b) Alpha bombardment

G. Fission and Fusion

In nuclear fission, a heavy nucleus splits into two lighter nuclei while emitting several small particles. In nuclear fusion, two lighter nuclei will combine to form a heavier nucleus.

1. Mass Defect and Nuclear Binding Energy

$$\Delta E = \Delta mc^2$$

Mass of 1 proton = 1.0072 amu
Mass of 1 neutron = 1.00867 amu
Mass of 1 electron = 0.0005489 amu

Calculate the binding energy of the Fe-56 nucleus in MeV?

2. Nuclear Fission

3. Nuclear Fusion