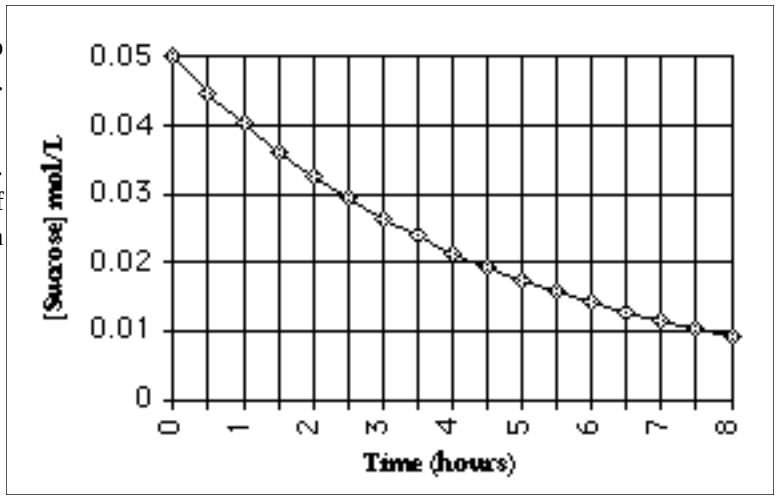
KINETICS

1. (13 points) Sucrose decomposes to fructose and glucose in acid solution.

   Sucrose → Fructose + glucose

   The reaction is *first order* in sucrose. A plot of the concentration of sucrose as a function of time is given here.



   a) Write the *rate law* for the reaction.

   b) What is the approximate rate of change of the sucrose concentration over the first two hours?

      i) -0.025 mol/L•hour

      ii) -0.010 mol/L•hour

      iii) -0.009 mol/L•hour

      iv) -0.005 mol/L•hour

   c) What is the approximate half-life for the decomposition of sucrose?

      i) 0.5 hour

      ii) 1.1 hour

      iii) 2.5 hours

      iv) 3.2 hours

      v) 4.5 hours

   d) If the beginning concentration of sucrose was 0.050 M, what is its approximate concentration after 24 hours?

      i) 0.025 M

      ii) 0.0063 M

      iii) 0.00078 M

      iv) 0.00024 M

      v) 0.00010 M

   e) Why does the rate of sucrose decomposition decline with time?

2. (3 points) (SQ 15-63) At temperatures below 500 K the reaction between carbon monoxide and nitrogen dioxide

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

has the rate equation Rate = $k[NO_2]^2$. Which of the three mechanisms suggested here best agrees with the experimentally observed rate equation?

a) **Mechanism 1** single, elementary step

$NO_2 + CO \rightarrow CO_2 + NO$

b) **Mechanism 2** two steps

slow $NO_2 + NO_2 \rightarrow NO_3 + NO$

fast $NO_3 + CO \rightarrow NO_2 + CO_2$

c) **Mechanism 3** two steps

slow $NO_2 \rightarrow NO + O$

fast $CO + O \rightarrow CO_2$

3. (4 points) (SQ 15-75) The ozone in the ozone layer decomposes according to the equation

$$2\ O_3(g) \rightarrow 3\ O_2(g)$$

The mechanism of the reaction is thought to proceed through an initial fast equilibrium and a slow step.

Step 1 fast, reversible $O_3(g)$, $O_2(g) + O(g)$

Step 2 slow $O_3(g) + O(g) \rightarrow 2\ O_2(g)$

What is the *molecularity* of the second step? _____

Which rate law below best corresponds with the postulated mechanism?

i) Rate = $k\ [O_3]$

ii) Rate = $k\ [O_3][O]$

iii) Rate = $k\ [O_3]^2$

(iv) Rate = $k\ [O_3]^2/[O_2]$

4. (6 points) (SQ 15-57) Which of the following statements is (are) false and which is (are) true?

_____A catalyst can change the course of a reaction so that different products are formed.

_____A catalyst changes the rate determining step in a reaction.

_____The energy evolved in a reaction with a catalyst is different than the energy evolved in a reaction in which a catalyst is NOT present.

_____The rate determining elementary step in a reaction is the slowest step in a mechanism.

_____As a reaction proceeds at constant temperature, the rate always remains constant.

_____It is possible to change the rate constant by changing the temperature.

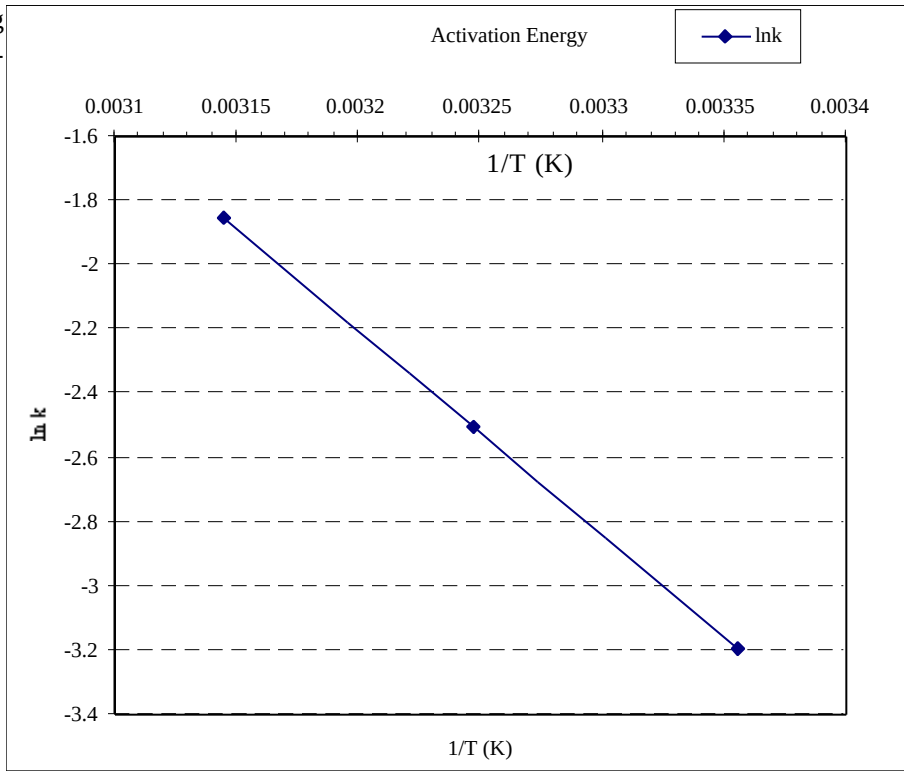
5. (6 points) (SQ 15-81) Determining an activation energy. Data for the following reaction

$[Mn(CO)_5(CH_3CN)]^+ + NC_5H_5 \rightarrow [Mn(CO)_5(NC_5H_5)]^+ + CH_3CN$

have been collected. Calculate E_a from a plot of ln *k* vs 1/T. *(The following table gives the values of k and T from which the ln k vs. 1/T plot was generated.)*

***k* (min^{-1})**	**T (K)**
0.0409	298
0.0818	308
0.157	318

Show your work carefully.



6. (4 points) (SQ 15-69) The decomposition of gaseous dimethyl ether at ordinary pressures is first order. Its half life is 25.0 min at 500 ˚C.

$$CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$$

(a) Starting with 8.00 g of dimethyl ether, what mass remains (in grams) after 75.0 min?

_____g

(b) What *fraction* of the original dimethyl ether remains after 150. min? _____

7. (4 points) Hundreds of different reactions can occur in the stratosphere, among them reactions that destroy the Earth's ozone layer. The table below lists several (2nd order) reactions of Cl atoms with ozone and organic compounds; each is given with its rate constant:

Reaction	*Rate Constant (298 K, cm^3/molecule•s)*
a) $Cl + O_3 \rightarrow ClO + O_2$	1.2×10^{-11}
b) $Cl + CH_4 \rightarrow HCl + CH_3$	1.0×10^{-13}
c) $Cl + C_3H_8 \rightarrow HCl + C_3H_7$	1.4×10^{-10}
d) $Cl + CH_2FCl$ $HCl + CHFCl$	3.0×10^{-18}

(Note that CH_2FCl is a chlorofluorocarbon. You know them as a family of compounds sold under the tradename Freon.)

For equal concentrations of Cl and other reactant, which is the slowest reaction? _____ Which is the fastest reaction? _____

8. (8 points) (SQ 15-85) Many biochemical reactions are catalyzed by acids. A typical mechanism consistent with the experimental results (in which HA is the acid and X is the reactant) is

Step 1	fast, reversible	$HA \rightleftharpoons H^+ + A^-$	(Equilibrium constant = K_1)
Step 2	fast, reversible	$X + H^+ \rightleftharpoons XH^+$	(Equilibrium constant = K_2)
Step 3	slow	$XH^+ \rightarrow$ products	(Rate constant = k)

a) What is the rate-determining, elementary step in the reaction? _____

b) The rate law for the process is

$$\text{Rate} = k \cdot K_1 K_2 \cdot \frac{[X][HA]}{[A^-]}$$

If the concentration of acid HA is doubled, the reaction rate _____ *(answer by stating the rate increases, decreases, or stays the same).* If A^-, the conjugate base of the acid is added to the reaction mixture, the reaction rate _____ *(increases, decreases, stays the same).* If the concentration of reactant X decreases, the reaction rate _____ *(increases, decreases, stays the same).*

9. (2 points) Iodine has three radioactive isotopes that are used in medical studies.

Isotope	*Half-Life*	*Use*
^{131}I	8.04 days	brain scans, pancreatic function
^{125}I	60.1 days	blood volume
^{123}I	13.2 hours	Renal blood flow

If you begin with equal numbers of atoms of each isotope, which will be present in the largest abundance after a week?

a) ^{131}I b) ^{125}I c) ^{123}I

10. (9 points) The fluorine-18 isotope is radioactive (decays by positron emission). It is used in in the form of sodium fluoride in hospitals to perform bone scans. The half-life of ^{18}F is 1.9 hours.

What is the rate constant for the decay of ^{18}F?

a) 0.365 hr^{-1}

b) 0.693 hr^{-1}

c) 0.891 hr^{-1}

d) 1.90 hr^{-1}

If a bone scan takes about a day, what *fraction* of the original ^{18}F isotope would remain after 7.6 hours?_____

What *fraction* would remain after exactly 24.0 hours?

a) 0.33

b) 0.25

c) 2.0×10^{-3}

d) 1.6×10^{-4}

e) 1.2×10^{-4}

INTERMOLECULAR FORCES AND LIQUIDS

1. (22 points Use the figure and molecular models on the next page to answer the following questions about the three volatile liquids carbon disulfide (CS_2), ethanol (CH_3CH_2OH), and heptane (C_7H_{16}):

   a) Which liquid has the highest normal boiling point? _____

   b) Which liquid has the highest vapor pressure at room temperature? _____

   c) What is the vapor pressure of ethanol at 70 ˚C? _____ mm Hg

   d) At what temperature does heptane have a vapor pressure of 400 mm Hg? _____

   e) Suppose each of these liquids is placed in a flask and the pressure is reduced to 300 mm Hg (at about 25 ˚C, room temperature). Decide whether each substance is converted completely to a vapor under these conditions or if some liquid remains.

Compound	*State (Completely vapor, completely liquid, or liquid-vapor mixture)*
CS_2	_____
CH_3CH_2OH	_____
C_7H_{16}	_____

   f) Which of the three compounds has the weakest intermolecular forces in the liquid state?

   _____

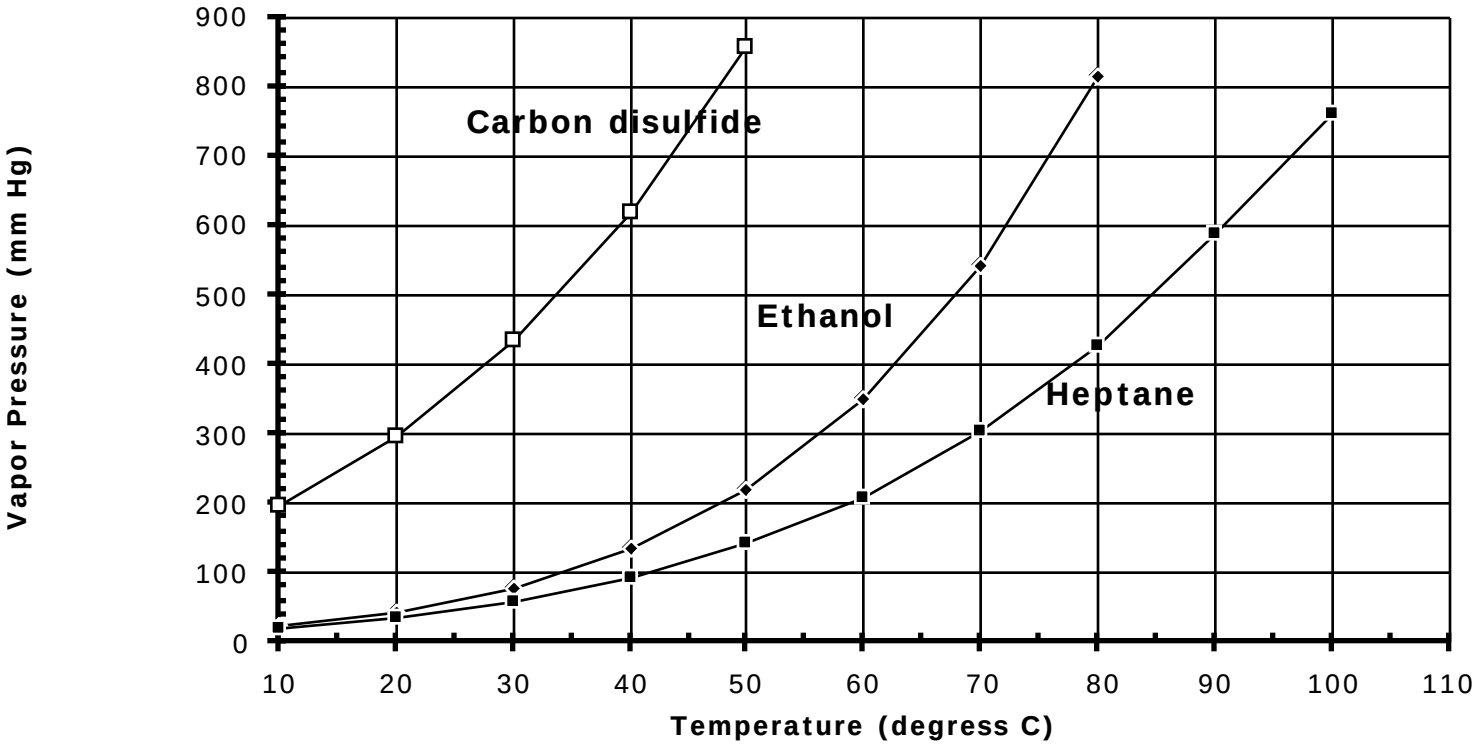
   g) For each compound, state what type of intermolecular forces exist between two molecules of that substance. *(Choices are dipole-dipole, hydrogen bonds, or induced dipole-induced dipole).*

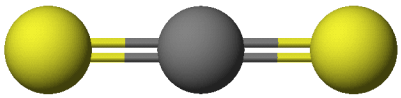
Compound	*Intermolecular Force*
CS_2	_____
CH_3CH_2OH	_____
C_7H_{16}	_____

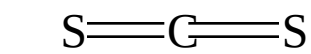
2. (4 points) Refer to Figure 13.19 (page 603) as an aid in answering these questions:

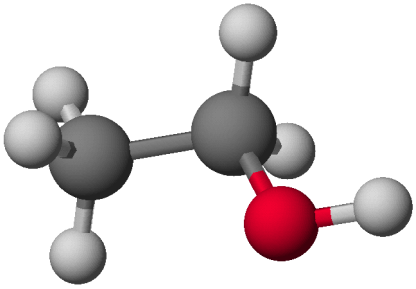
   (a) You put some water at 60 ˚C in a plastic milk carton and seal the top very tightly so gas cannot enter or leave the carton. What happens when the water cools?

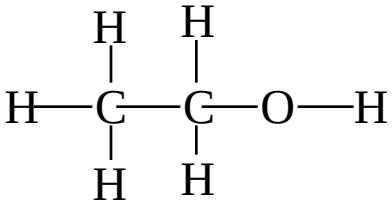
   (b) If you put a few drops of liquid diethyl ether on your hand, does it evaporate completely or remain a liquid?

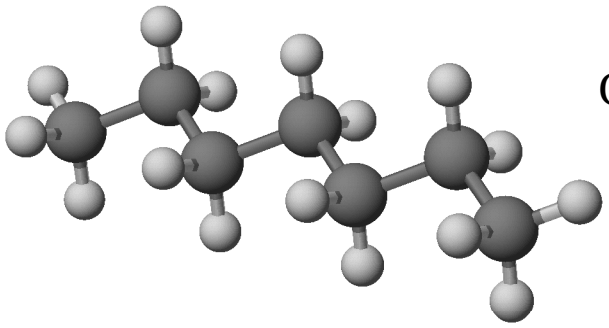

Vapor Pressure (mm Hg)
900
800
700
600
500
400
300
200
100
0
Carbon disulfide
Ethanol
Heptane
10
20
30
40
50
60
70
80
90
100
110
Temperature (degress C)

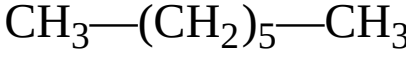



S═C═S

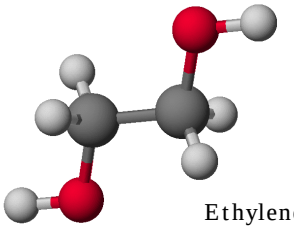


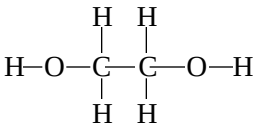

H H
H—C—C—O—H
H H




CH3—(CH2)5—CH3

3. (3 points) Explain fully why ethylene glycol (antifreeze) dissolves very well in water, whereas a hydrocarbon such as heptane (see page 7) does not.





Ethylene glycol

4. (12 points) *Intermolecular Forces*

A. When $MgSO_4$ (epsom salts) dissolves in water, what types of forces must be broken?

(a) ion-ion forces (b) H-bonds

(c) ion-dipole forces (d) ion-ion forces and H-bonds

B. Which of the following solids is held in the solid state primarily by induced dipole-induced dipole forces?

(a) ice (b) KBr

(c) solid NH_3 at low temperature (d) CO_2

C. Using the list of intermolecular forces below,

(i) induced dipole forces (iii) hydrogen bonds

(ii) ion-ion forces (iv) ion-dipole forces

tell what type of intermolecular forces must be overcome to

(a) boil liquid CH_4 (methane) _____

(b) boil liquid methanol (CH_3OH) _____

(c) dehydrate $CoCl_2 \cdot 6H_2O$ _____

D. Rank the following molecules in order of *increasing* intermolecular forces: CH_3Cl, HCO_2H (formic acid), and CO_2.

(a) $CO_2 < CH_3Cl < HCO_2H$ (b) $CH_3Cl < CO_2 < HCO_2H$

(c) $CO_2 < HCO_2H < CH_3Cl$ (d) $CH_3Cl < HCO_2H < CO_2$

(e) $HCO_2H < CH_3Cl < CO_2$ (f) $HCO_2H < CO_2 < CH_3Cl$