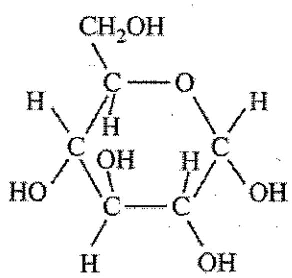
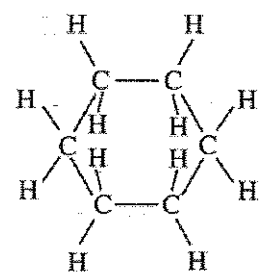
Question 6

6. Answer each of the following in terms of principles of molecular behavior and chemical concepts.

(a) The structures for glucose, $C_6H_{12}O_6$, and cyclohexane, C_6H_{12}, are shown below.





Identify the type(s) of intermolecular attractive forces in

(i) pure glucose

Hydrogen bonding OR dipole-dipole interactions OR van der Waals interactions (London dispersion forces may also be mentioned.)	One point is earned for a correct answer.

(ii) pure cyclohexane

London dispersion forces	One point is earned for London dispersion forces.

(b) Glucose is soluble in water but cyclohexane is not soluble in water. Explain.

The hydroxyl groups in glucose molecules can form strong hydrogen bonds with the solvent (water) molecules, so glucose is soluble in water. In contrast, cyclohexane is not capable of forming strong intermolecular attractions with water (no hydrogen bonding), so the water-cyclohexane interactions are not as energetically favorable as the interactions that already exist among polar water molecules. **OR** • Glucose is polar and cyclohexane is nonpolar. • Polar solutes (such as glucose) are generally soluble in polar solvents such as water. • Nonpolar solutes (such as cyclohexane) are not soluble in the polar solvent.	One point is earned for explaining the solubility of glucose in terms of hydrogen bonding or dipole-dipole interactions with water. One point is earned for explaining the difference in the polarity of cyclohexane and water. **OR** One point is earned for any one of the three concepts; two points are earned for any two of the three concepts.

Question 6 (continued)

(c) Consider the two processes represented below.

Process 1: $H_2O(l) \rightarrow H_2O(g)$ $\Delta H° = +44.0 \text{ kJ mol}^{-1}$

Process 2: $H_2O(l) \rightarrow H_2(g) + \frac{1}{2} O_2(g)$ $\Delta H° = +286 \text{ kJ mol}^{-1}$

(i) For each of the two processes, identify the type(s) of intermolecular or intramolecular attractive forces that must be overcome for the process to occur.

In process 1, hydrogen bonds (or dipole-dipole interactions) in liquid water are overcome to produce distinct water molecules in the vapor phase.	One point is earned for identifying the type of intermolecular force involved in process 1.
In process 2, covalent bonds (or sigma bonds, or electron-pair bonds) within water molecules must be broken to allow the atoms to recombine into molecular hydrogen and oxygen.	One point is earned for identifying the type of intramolecular bonding involved in process 2.

(ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

When water boils, H_2O molecules break apart to form hydrogen molecules and oxygen molecules.

I disagree with the statement. Boiling is simply Process 1, in which only intermolecular forces are broken and the water molecules stay intact. No intramolecular or covalent bonds break in this process.	One point is earned for disagreeing with the statement <u>and</u> providing a correct explanation.

Question 6 (continued)

(d) Consider the four reaction-energy profile diagrams shown below.

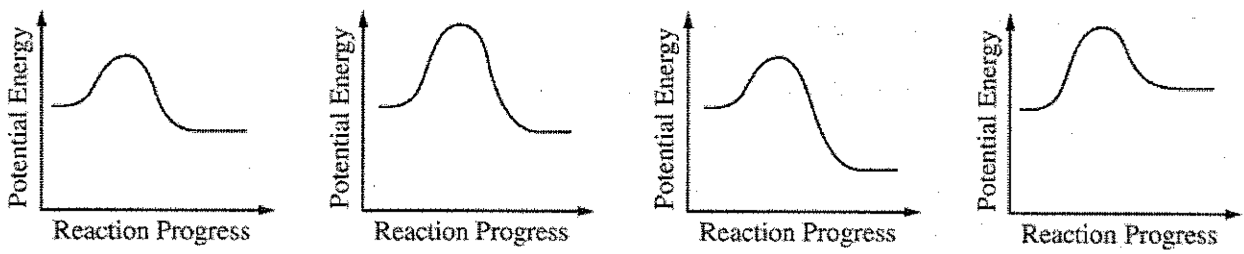


Diagram 1 Diagram 2 Diagram 3 Diagram 4

(i) Identify the two diagrams that could represent a catalyzed and an uncatalyzed reaction pathway for the same reaction. Indicate which of the two diagrams represents the catalyzed reaction pathway for the reaction.

Diagram 1 represents a catalyzed pathway and diagram 2 represents an uncatalyzed pathway for the same reaction.	One point is earned for identifying the correct graphs and indicating which represents which pathway.

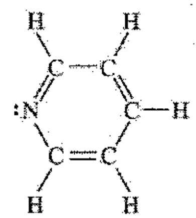
(ii) Indicate whether you agree or disagree with the statement in the box below. Support your answer with a short explanation.

Adding a catalyst to a reaction mixture adds energy that causes the reaction to proceed more quickly.

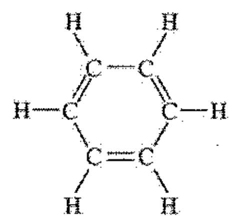
I disagree with the statement. A catalyst does not add energy, but provides an alternate reaction pathway with a lower activation energy.	One point is earned for disagreeing with the statement and providing an explanation.

Question 6

(a) Structures of the pyridine molecule and the benzene molecule are shown below. Pyridine is soluble in water, whereas benzene is not soluble in water. Account for the difference in solubility. You must discuss both of the substances in your answer.



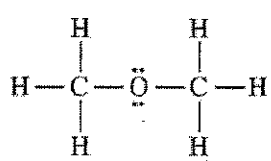
Pyridine



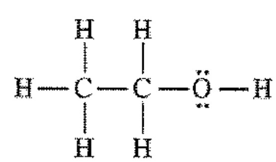
Benzene

Pyridine is polar (and capable of forming hydrogen bonds with water), while the nonpolar benzene is not capable of forming hydrogen bonds. Pyridine will dissolve in water because of the strong hydrogen bonds (or dipole-dipole intermolecular interactions) that exist between the lone pair of electrons on pyridine's nitrogen atom and the solvent water molecules. No such strong intermolecular interaction can exist between benzene and water, so benzene is insoluble in water.	One point is earned for identifying a relevant structural difference between pyridine and benzene. One point is earned for indicating that pyridine is soluble in water because pyridine can form strong dipole-dipole interactions (or hydrogen bonds) with water, while benzene cannot.

(b) Structures of the dimethyl ether molecule and the ethanol molecule are shown below. The normal boiling point of dimethyl ether is 250 K, whereas the normal boiling point of ethanol is 351 K. Account for the difference in boiling points. You must discuss both of the substances in your answer.



Dimethyl Ether



Ethanol

Question 6 (continued)

The intermolecular forces of attraction among molecules of dimethyl ether consist of London (dispersion) forces and weak dipole-dipole interactions. In addition to London forces and dipole-dipole interactions that are comparable in strength to those in dimethyl ether, ethanol can form hydrogen bonds between the H of one molecule and the O of a nearby ethanol molecule. Hydrogen bonds are particularly strong intermolecular forces, so they require more energy to overcome during the boiling process. As a result, a higher temperature is needed to boil ethanol than is needed to boil dimethyl ether.	One point is earned for recognizing that ethanol molecules can form intermolecular hydrogen bonds, whereas dimethyl ether molecules do not form intermolecular hydrogen bonds. One point is earned for recognizing that, compared to the energy required to overcome the weaker intermolecular forces in liquid dimethyl ether, more energy is required to overcome the stronger hydrogen bonds in liquid ethanol, leading to a higher boiling point.

(c) SO_2 melts at 201 K, whereas SiO_2 melts at 1,883 K. Account for the difference in melting points. You must discuss both of the substances in your answer.

In the solid phase, SO_2 consists of discrete molecules with dipole-dipole and London (dispersion) forces among the molecules. These forces are relatively weak and are easily overcome at a relatively low temperature, consistent with the low melting point of SO_2.	One point is earned for recognizing that SO_2 is a molecular solid with only weak dipole-dipole and London forces among SO_2 molecules.
In solid SiO_2, a network of Si and O atoms, linked by strong covalent bonds, exists. These covalent bonds are much stronger than typical intermolecular interactions, so very high temperatures are needed to overcome the covalent bonds in SiO_2. This is consistent with the very high melting point for SiO_2.	One point is earned for recognizing that SiO_2 is a covalent network solid, and that strong covalent bonds must be broken for SiO_2 to melt.

Question 6 (continued)

(d) The normal boiling point of $Cl_2(l)$ (238 K) is <u>higher</u> than the normal boiling point of $HCl(l)$ (188 K). Account for the difference in normal boiling points based on the types of intermolecular forces in the substances. You must discuss <u>both</u> of the substances in your answer.

The intermolecular forces in liquid Cl_2 are London (dispersion) forces, whereas the intermolecular forces in liquid HCl consist of London forces and dipole-dipole interactions. Since the boiling point of Cl_2 is higher than the boiling point of HCl, the London forces among Cl_2 molecules must be greater than the London and dipole-dipole forces among HCl molecules. The greater strength of the London forces between Cl_2 molecules occurs because Cl_2 has more electrons than HCl, and the strength of the London interaction is proportional to the total number of electrons.	One point is earned for recognizing that the London forces among Cl_2 molecules must be larger than the intermolecular forces (London and dipole-dipole) among HCl molecules. One point is earned for recognizing that the strength of the London forces among molecules is proportional to the total number of electrons in each molecule.

Question 2
(9 points)

An 8.55 mol sample of methanol, CH_3OH, is placed in a 15.0 L evacuated rigid tank and heated to 327°C. At that temperature, all of the methanol is vaporized and some of the methanol decomposes to form carbon monoxide gas and hydrogen gas, as represented in the equation below.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\,H_2(g)$$

(a) The reaction mixture contains 6.30 mol of $CO(g)$ at equilibrium at 327°C.

(i) Calculate the number of moles of $H_2(g)$ in the tank.

$6.30 \text{ mol CO} \times \dfrac{2 \text{ mol } H_2}{1 \text{ mol CO}} = 12.6 \text{ mol } H_2$	1 point is earned for the correct number of moles.

(ii) Calculate the number of grams of $CH_3OH(g)$ remaining in the tank.

$6.30 \text{ mol CO} \times \dfrac{1 \text{ mol } CH_3OH}{1 \text{ mol CO}} = 6.30 \text{ mol } CH_3OH \text{ reacted}$ $8.55 \text{ mol } CH_3OH_{\text{initial}} - 6.30 \text{ mol } CH_3OH_{\text{reacted}} = 2.25 \text{ mol } CH_3OH$ $2.25 \text{ mol} \times \dfrac{32.042 \text{ g}}{1 \text{ mol}} = 72.1 \text{ g}$	1 point is earned for the correct number of grams.

(iii) Calculate the mole fraction of $H_2(g)$ in the tank.

$\dfrac{12.6 \text{ mol } H_2}{2.25 \text{ mol } CH_3OH + 6.30 \text{ mol CO} + 12.6 \text{ mol } H_2}$ $= \dfrac{12.6}{21.15} = 0.596$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

(iv) Calculate the total pressure, in atm, in the tank at 327°C.

$PV = nRT \Rightarrow P = \dfrac{nRT}{V}$ $= \dfrac{(21.15 \text{ mol})(0.0821 \frac{\text{L atm}}{\text{mol K}})(600 \text{ K})}{15.0 \text{ L}}$ $= 69.5 \text{ atm}$	1 point is earned for the correct setup. 1 point is earned for the correct answer.

Question 2 (continued)

(b) Consider the three gases in the tank at 327°C: $CH_3OH(g)$, $CO(g)$, and $H_2(g)$.

(i) How do the average kinetic energies of the molecules of the gases compare? Explain.

The average kinetic energies are the same because all three gases are at the same temperature.	1 point is earned for the correct answer and explanation.

(ii) Which gas has the highest average molecular speed? Explain.

$KE = \frac{1}{2}mv^2$, so at a given temperature the molecules with the lowest mass have the highest average speed. Therefore the molecules in H_2 gas have the highest average molecular speed.	1 point is earned for the correct answer and explanation.

(c) The tank is cooled to 25°C, which is well below the boiling point of methanol. It is found that small amounts of $H_2(g)$ and $CO(g)$ have dissolved in the liquid CH_3OH. Which of the two gases would you expect to be more soluble in methanol at 25°C? Justify your answer.

The only attractive forces between molecules of H_2 and CH_3OH would be due to weak London dispersion forces (LDFs). In contrast, the LDFs are stronger between CO molecules and CH_3OH molecules because CO has more electrons than H_2. In addition CO is slightly polar; thus intermolecular dipole-dipole attractions can form between CO molecules and CH_3OH molecules. With stronger intermolecular interactions between molecules of CO and CH_3OH, CO would be expected to be more soluble in CH_3OH than H_2.	1 point is earned for the correct answer and justification.

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Question 2
(10 points)

A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127°C.

(a) Calculate the number of moles of the hydrocarbon in the vessel.

$n = \frac{PV}{RT} = \frac{(0.200\text{ atm})(1.00\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})}$	1 point is earned for the setup.
$n = 6.09 \times 10^{-3}$ mol	1 point is earned for the numerical answer.

(b) $O_2(g)$ is introduced into the same vessel containing the hydrocarbon. After the addition of the $O_2(g)$, the total pressure of the gas mixture in the vessel is 1.40 atm at 127°C. Calculate the partial pressure of $O_2(g)$ in the vessel.

$P_{O_2} = 1.40\text{ atm} - 0.200\text{ atm} = 1.20\text{ atm}$	1 point is earned for the correct pressure.

The mixture of the hydrocarbon and oxygen is sparked so that a complete combustion reaction occurs, producing $CO_2(g)$ and $H_2O(g)$. The partial pressures of these gases at 127°C are 0.600 atm for $CO_2(g)$ and 0.800 atm for $H_2O(g)$. There is $O_2(g)$ remaining in the container after the reaction is complete.

(c) Use the partial pressures of $CO_2(g)$ and $H_2O(g)$ to calculate the partial pressure of the $O_2(g)$ consumed in the combustion.

	. . . C_xH_y +	. . . O_2 →	. . . CO_2 +	. . . H_2O
before rxn:	0.200 atm	1.20 atm	-	-
after rxn:	0 atm	? atm	0.600 atm	0.800 atm

$0.600\text{ atm } CO_2 \left(\frac{1\text{ atm } O_2}{1\text{ atm } CO_2}\right) = 0.600\text{ atm } O_2$

$0.800\text{ atm } H_2O \left(\frac{1\text{ atm } O_2}{2\text{ atm } H_2O}\right) = 0.400\text{ atm } O_2$ Total O_2 consumed = 1.000 atm

OR, based on $PV = nRT$ and mole calculations:

$n_{H_2O} = \frac{PV}{RT} = \frac{(0.800\text{ atm})(1.00\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})} = 0.0244\text{ mol } H_2O \times \frac{1\text{ mol } O_2}{2\text{ mol } H_2O}$

$= 0.0122\text{ mol } O_2$

$n_{CO_2} = \frac{PV}{RT} = \frac{(0.600\text{ atm})(1.00\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})} = 0.0183\text{ mol } CO_2 \times \frac{1\text{ mol } O_2}{1\text{ mol } CO_2}$

$= 0.0183\text{ mol } O_2$

Total moles $O_2 = 0.0305$; $P = \frac{nRT}{V} = \frac{(0.0305\text{ mol})(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})}{1.00\text{ L}}$

$P = 1.00\text{ atm } O_2$

1 point is earned for the correct stoichiometry in O_2 consumption.

1 point is earned for the calculated result.

Question 2 (continued)

(d) On the basis of your answers above, write the balanced chemical equation for the combustion reaction and determine the formula of the hydrocarbon.

The partial pressures occur in the same proportions as the number of moles. $P_{\text{hydrocarbon}} : P_{O_2} : P_{CO_2} : P_{H_2O}$ 0.200 atm : 1.00 atm : 0.600 atm : 0.800 atm = 1 : 5 : 3 : 4 $C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$ **OR** $n_{H_2O} = \frac{PV}{RT} = \frac{(0.800\text{ atm})(1.00\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})} = 0.0244\text{ mol }H_2O \times \frac{2\text{ mol H}}{1\text{ mol }H_2O}$ $= 0.0487$ mol H $n_{CO_2} = \frac{PV}{RT} = \frac{(0.600\text{ atm})(1.00\text{ L})}{(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(400.\text{ K})} = 0.0183\text{ mol }CO_2 \times \frac{1\text{ mol C}}{1\text{ mol }CO_2}$ $= 0.0183$ mol C $\frac{0.0487\text{ mol H}}{0.0183\text{ mol C}} = \left(\frac{2.66\text{ mol H}}{1\text{ mol C}}\right)\left(\frac{3}{3}\right) = \frac{8\text{ mol H}}{3\text{ mol C}} \Rightarrow C_3H_8$ $C_3H_8 + 5\,O_2 \rightarrow 3\,CO_2 + 4\,H_2O$	1 point is earned for the formula of the hydrocarbon. 1 point is earned for a balanced equation with the correct proportions among reactants and products.

(e) Calculate the mass of the hydrocarbon that was combusted.

mass = (number of moles)(molar mass) $= (6.09 \times 10^{-3}\text{ mol})(44.1\text{ g/mol}) = 0.269\text{ g}$	1 point is earned for using the number of moles combusted from part (a). 1 point is earned for the calculated mass.

(f) As the vessel cools to room temperature, droplets of liquid water form on the inside walls of the container. Predict whether the pH of the water in the vessel is less than 7, equal to 7, or greater than 7. Explain your prediction.

The pH will be less than 7 because CO_2 is soluble in water, with which it reacts to form H^+ ions.	1 point is earned for the correct choice and explanation.