CHEMISTRY

Section II

(Total time—95 minutes)

Part A

Time—55 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

$$C(s) + CO_2(g) \rightleftarrows 2\ CO(g)$$

1. Solid carbon and carbon dioxide gas at 1,160 K were placed in a rigid 2.00 L container, and the reaction represented above occurred. As the reaction proceeded, the total pressure in the container was monitored. When equilibrium was reached, there was still some $C(s)$ remaining in the container. Results are recorded in the table below.

Time (hours)	Total Pressure of Gases in Container at 1,160 K (atm)
0.0	5.00
2.0	6.26
4.0	7.09
6.0	7.75
8.0	8.37
10.0	8.37

(a) Write the expression for the equilibrium constant, K_p, for the reaction.

(b) Calculate the number of moles of $CO_2(g)$ initially placed in the container. (Assume that the volume of the solid carbon is negligible.)

(c) For the reaction mixture at equilibrium at 1,160 K, the partial pressure of the $CO_2(g)$ is 1.63 atm. Calculate

(i) the partial pressure of $CO(g)$, and

(ii) the value of the equilibrium constant, K_p.

(d) If a suitable solid catalyst were placed in the reaction vessel, would the final total pressure of the gases at equilibrium be greater than, less than, or equal to the final total pressure of the gases at equilibrium without the catalyst? Justify your answer. (Assume that the volume of the solid catalyst is negligible.)

In another experiment involving the same reaction, a rigid 2.00 L container initially contains 10.0 g of $C(s)$, plus $CO(g)$ and $CO_2(g)$, each at a partial pressure of 2.00 atm at 1,160 K.

(e) Predict whether the partial pressure of $CO_2(g)$ will increase, decrease, or remain the same as this system approaches equilibrium. Justify your prediction with a calculation.

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2. Answer the following questions relating to gravimetric analysis.

In the first of two experiments, a student is assigned the task of determining the number of moles of water in one mole of $MgCl_2 \cdot n\,H_2O$. The student collects the data shown in the following table.

Mass of empty container	22.347 g
Initial mass of sample and container	25.825 g
Mass of sample and container after first heating	23.982 g
Mass of sample and container after second heating	23.976 g
Mass of sample and container after third heating	23.977 g

(a) Explain why the student can correctly conclude that the hydrate was heated a sufficient number of times in the experiment.

(b) Use the data above to

(i) calculate the total number of moles of water lost when the sample was heated, and

(ii) determine the formula of the hydrated compound.

(c) A different student heats the hydrate in an uncovered crucible, and some of the solid spatters out of the crucible. This spattering will have what effect on the calculated mass of the water lost by the hydrate? Justify your answer.

In the second experiment, a student is given 2.94 g of a mixture containing anhydrous $MgCl_2$ and KNO_3. To determine the percentage by mass of $MgCl_2$ in the mixture, the student uses excess $AgNO_3(aq)$ to precipitate the chloride ion as $AgCl(s)$.

(d) Starting with the 2.94 g sample of the mixture dissolved in water, briefly describe the steps necessary to quantitatively determine the mass of the AgCl precipitate.

(e) The student determines the mass of the AgCl precipitate to be 5.48 g. On the basis of this information, calculate each of the following.

(i) The number of moles of $MgCl_2$ in the original mixture

(ii) The percent by mass of $MgCl_2$ in the original mixture

3. Answer the following questions related to chemical reactions involving nitrogen monoxide, $NO(g)$.

The reaction between solid copper and nitric acid to form copper(II) ion, nitrogen monoxide gas, and water is represented by the following equation.

$$3\ Cu(s) + 2\ NO_3^-(aq) + 8\ H^+(aq) \rightarrow 3\ Cu^{2+}(aq) + 2\ NO(g) + 4\ H_2O(l) \qquad E^\circ = +0.62\ V$$

(a) Using the information above and in the table below, calculate the standard reduction potential, E°, for the reduction of NO_3^- in acidic solution.

Half-Reaction	Standard Reduction Potential, E°
$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	+0.34 V
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \rightarrow NO(g) + 2\ H_2O(l)$	?

(b) Calculate the value of the standard free energy change, ΔG°, for the overall reaction between solid copper and nitric acid.

(c) Predict whether the value of the standard entropy change, ΔS°, for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.

Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

A rate study of the reaction yielded the data recorded in the table below.

Experiment	Initial Concentration of NO (mol L^{-1})	Initial Concentration of O_2 (mol L^{-1})	Initial Rate of Formation of NO_2 (mol L^{-1} s^{-1})
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

(i) NO

(ii) O_2

(e) Write the expression for the rate law for the reaction as determined from the experimental data.

(f) Determine the value of the rate constant for the reaction, clearly indicating the units.

STOP

If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.

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CHEMISTRY

Part B

Time—40 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 10 percent.

4. For each of the following three reactions, in part (i) write a balanced equation for the reaction and in part (ii) answer the question about the reaction. In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:

$$Mg + 2Ag^{+} \longrightarrow Mg^{2+} + 2Ag$$

(ii) Which substance is oxidized in the reaction?

Mg is oxidized.

(a) Aqueous sodium hydroxide is added to a saturated solution of aluminum hydroxide, forming a complex ion.

(i) Balanced equation:

(ii) If the resulting mixture is acidified, would the concentration of the complex ion increase, decrease, or remain the same? Explain.

(b) Hydrogen chloride gas is oxidized by oxygen gas.

(i) Balanced equation:

(ii) If three moles of hydrogen chloride gas and three moles of oxygen gas react as completely as possible, which reactant, if any, is present in excess? Justify your answer.

(c) Solid potassium oxide is added to water.

(i) Balanced equation:

(ii) If a few drops of phenolphthalein are added to the resulting solution, what would be observed? Explain.

YOU MAY USE THE SPACE BELOW FOR SCRATCH WORK, BUT ONLY EQUATIONS THAT ARE WRITTEN IN THE ANSWER BOXES PROVIDED WILL BE GRADED.

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. Using principles of atomic and molecular structure and the information in the table below, answer the following questions about atomic fluorine, oxygen, and xenon, as well as some of their compounds.

Atom	First Ionization Energy ($kJ\ mol^{-1}$)
F	1,681.0
O	1,313.9
Xe	?

(a) Write the equation for the ionization of atomic fluorine that requires 1,681.0 $kJ\ mol^{-1}$.

(b) Account for the fact that the first ionization energy of atomic fluorine is greater than that of atomic oxygen. (You must discuss both atoms in your response.)

(c) Predict whether the first ionization energy of atomic xenon is greater than, less than, or equal to the first ionization energy of atomic fluorine. Justify your prediction.

(d) Xenon can react with oxygen and fluorine to form compounds such as XeO_3 and XeF_4. In the boxes provided, draw the complete Lewis electron-dot diagram for each of the molecules represented below.

XeO_3

XeF_4

(e) On the basis of the Lewis electron-dot diagrams you drew for part (d), predict the following:

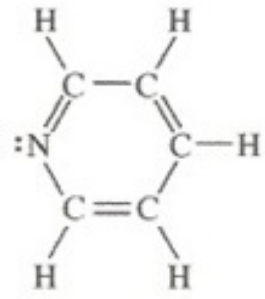
(i) The geometric shape of the XeO_3 molecule

(ii) The hybridization of the valence orbitals of xenon in XeF_4

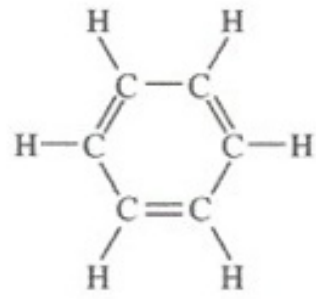
(f) Predict whether the XeO_3 molecule is polar or nonpolar. Justify your prediction.

6. Answer the following questions by using principles of molecular structure and intermolecular forces.

(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.

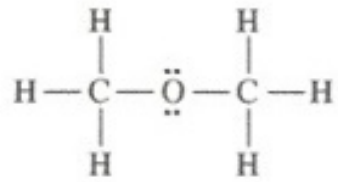


Pyridine

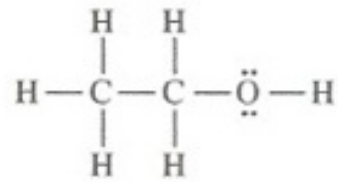


Benzene

(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

(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.

(d) The normal boiling point of $Cl_2(l)$ (238 K) is higher 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 both of the substances in your answer.

STOP

END OF EXAM

1] $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$

a. $K_p = \dfrac{[CO]^2}{[CO_2]}$

b. $n = \dfrac{PV}{RT}$

$$n = \frac{(5\,atm)(2L)}{\left(0.0821 \frac{L\,atm}{mol\,K}\right)(1160K)}$$

$$= 0.105\,mol\,CO_2$$

c. $P_T = P_{CO_2} + P_{CO}$

$$8.37\,atm = 1.63\,atm_{CO_2} + P_{CO}$$

$$P_{CO} = 6.74$$

1] c ii $$K_p = \frac{(6.74)^2}{1.63}$$

$K_p = 27.9$

d. The pressure in the containes would be unaffected. Catalyst speed up the forward and reverse rates of reaction equally and have no effect on position of equilibrium.

e. $C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$

$$Q = \frac{(2)^2}{2}$$

$= 2$ $\quad Q < K$

since Q is less than K the equilibrium will shift towards products. This will increase the pressure in the container

2 a. The mass has not changed from the 2nd to the 3rd massing.

b. $25.825\,g - 23.976\,g =$

grams H_2O lost

$$1.849\,g\ H_2O \times \frac{1\ mol}{18.016\,g} = 0.1026\ mol\ H_2O$$

ii $23.977\,g$ sample + container

$-\ 22.347\,g$ container

$1.630\,g\ MgCl_2$

$$1.630\,g\ MgCl_2 \times \frac{1\ mol\ MgCl_2}{95.20\,g} = 0.01712\ mol\ MgCl_2$$

$$\frac{0.1026\ mol\ H_2O}{0.01712\ mol\ MgCl} = \frac{6\ mol\ H_2O}{1\ mol\ MgCl_2}$$

$MgCl_2 \cdot 6H_2O$

2] c. Loosing Material would make the mass of water lost greater than it sould be.

d. Add $AgNO_3$ until all of the Cl^- ions have precipitated
- Filter out AgCl
- Dry it and mass it

e. $5.48g\ AgCl \times \frac{1mol\ AgCl}{143.32g} \times \frac{1mol\ Cl^-}{1mol\ AgCl} \times \frac{1mol\ MgCl_2}{2mol\ Cl^-} = 0.0191mol\ MgCl_2$

ii $0.0191mol\ MgCl_2 \times \frac{95.20g}{1mol\ MgCl_2} = 1.82g\ MgCl_2$

$\frac{1.82g\ MgCl_2}{2.94g\ Mixture} = 61.9\%$

3

a. $E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$

$0.62V = -0.34V + E^\circ_{red}$

$E^\circ_{red} = 0.96V$

b. $\Delta G^\circ = -nfE^\circ$

$3Cu + 3NO_3^- + 8H^+ \longrightarrow 3Cu^{2+} + 2NO + 4H_2O$

$\Delta G^\circ = -6\,mol\,e^- \times \frac{96500\,C}{1\,mol\,e^-} \times \frac{0.62\,J}{C} \times \frac{1\,kJ}{1000\,J} = -358.9\,kJ$

$= 3.6 \times 10^2\,kJ$

c. $\Delta S(+)$

Gas is produced during the reaction.

3]

d. $\frac{0.09}{0.03} = 3 \qquad \frac{0.256}{0.0852} = 3$

$[O_2]$

$\frac{0.06}{0.02} = 3 \qquad \frac{0.767}{0.0852} = 9$

$[NO]^2$

e. $\text{Rate} = k[NO]^2[O_2]$

f. $8.52 \times 10^{-2} \frac{mol}{L\,s} = k(0.20)^2(0.30)$

$k = 7.10 \times 10^3 \frac{L^2}{mol^2\,s}$

4) a. $3NaOH + Al(OH)_3 \rightarrow Al(OH)_6^{3+} + 3Na^+$

$6OH^- + Al^{3+} \rightarrow Al(OH)_6^{3-}$

ii If H^+ is added OH^- will be removed and shift the equilibrium towards the reactants. This will lower the complex concentration.

b $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$

3 mol 3 mol

$3 \text{ mol } HCl \times \frac{1 \text{ mol } O_2}{4 \text{ mol } HCl} = 0.75 \text{ mol } O_2 \text{ needed}$

O_2 is in excess

4] ci $K_2O_{(s)} \rightleftharpoons O_{2(aq)}^{-} + 2K^+_{(aq)}$

ii $O_2^- + H_2O \rightleftharpoons OH^- + OH^-$

Oxide produces hydroxide in water. phenolphthalein will turn pink due to the OH^- concentration

5] a. $F \rightleftharpoons F^+ + 1e^-$

b. There is the same amount of valence electron shielding in both O and F. However F has a larger nuclear charge.

F: 9P+ $1s^2 2s^2 2p^5$

O: 8P+ $1s^2 2s^2 2p^4$

5] c. Xe would have a lower 1st ionization energy due to larger shielding of its valence electrons

Xe [Kr] $5s^2 4d^{10} 5p^6$

6] pyridine is a polar molecule, Benzene is a non polar molecule. Polar molecules are more soluble in polar solvents (like dissolves like) water and pyridine have similar intermolecular attractions

dipole - dipole

Benzene is a nonpolar molecule Benzene and water would be characterized Induced dipole - dipole

6 b. Ethanol has an O-H group which makes ethanol capable of H-Bonding. H-Bonds are stronger attractions than regular dipole-dipole attractions. Dimethyl ether is only capable of ordinary dipole-dipole attractions.

c. SO_2 $:\ddot{O}=S=\ddot{O}:$ is an example of a molecular crystal, held together by Vander walls forces.

SiO_2 is an example of a covalent crystal held together by covalent bonds.

d. Cl_2 is an example of a non polar molecule. Induced dipole-Induced dipole forces keep Cl_2 in the liquid phase.