CHEMISTRY

Section II

(Total time—90 minutes)

Part A

Time—40 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 Question 1 below. The Section II score weighting for this question is 20 percent.

1. Answer the following questions that relate to solubility of salts of lead and barium.

   (a) A saturated solution is prepared by adding excess $PbI_2(s)$ to distilled water to form 1.0 L of solution at 25°C. The concentration of $Pb^{2+}(aq)$ in the saturated solution is found to be $1.3 \times 10^{-3}\ M$. The chemical equation for the dissolution of $PbI_2(s)$ in water is shown below.

   $$PbI_2(s) \rightleftarrows Pb^{2+}(aq) + 2\ I^-(aq)$$

   (i) Write the equilibrium-constant expression for the equation.

   (ii) Calculate the molar concentration of $I^-(aq)$ in the solution.

   (iii) Calculate the value of the equilibrium constant, K_{sp}.

   (b) A saturated solution is prepared by adding $PbI_2(s)$ to distilled water to form 2.0 L of solution at 25°C. What are the molar concentrations of $Pb^{2+}(aq)$ and $I^-(aq)$ in the solution? Justify your answer.

   (c) Solid NaI is added to a saturated solution of PbI_2 at 25°C. Assuming that the volume of the solution does not change, does the molar concentration of $Pb^{2+}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer.

   (d) The value of K_{sp} for the salt $BaCrO_4$ is 1.2×10^{-10}. When a 500. mL sample of $8.2 \times 10^{-6}\ M$ $Ba(NO_3)_2$ is added to 500. mL of $8.2 \times 10^{-6}\ M$ Na_2CrO_4, no precipitate is observed.

   (i) Assuming that volumes are additive, calculate the molar concentrations of $Ba^{2+}(aq)$ and $CrO_4^{2-}(aq)$ in the 1.00 L of solution.

   (ii) Use the molar concentrations of $Ba^{2+}(aq)$ ions and $CrO_4^{2-}(aq)$ ions as determined above to show why a precipitate does not form. You must include a calculation as part of your answer.

CHEMISTRY

Section II

(Total time—95 minutes)

Part A

Time—55 minutes

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

1. A sample of solid U_3O_8 is placed in a rigid 1.500 L flask. Chlorine gas, $Cl_2(g)$, is added, and the flask is heated to 862°C. The equation for the reaction that takes place and the equilibrium-constant expression for the reaction are given below.

$$U_3O_8(s) + 3\,Cl_2(g) \rightleftarrows 3\,UO_2Cl_2(g) + O_2(g) \qquad K_p = \frac{(p_{UO_2Cl_2})^3(p_{O_2})}{(p_{Cl_2})^3}$$

When the system is at equilibrium, the partial pressure of $Cl_2(g)$ is 1.007 atm and the partial pressure of $UO_2Cl_2(g)$ is 9.734×10^{-4} atm.

(a) Calculate the partial pressure of $O_2(g)$ at equilibrium at 862°C.

(b) Calculate the value of the equilibrium constant, K_p, for the system at 862°C.

(c) Calculate the Gibbs free-energy change, $\Delta G°$, for the reaction at 862°C.

(d) State whether the entropy change, $\Delta S°$, for the reaction at 862°C is positive, negative, or zero. Justify your answer.

(e) State whether the enthalpy change, $\Delta H°$, for the reaction at 862°C is positive, negative, or zero. Justify your answer.

(f) After a certain period of time, 1.000 mol of $O_2(g)$ is added to the mixture in the flask. Does the mass of $U_3O_8(s)$ in the flask increase, decrease, or remain the same? Justify your answer.

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

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

1. Answer the following questions regarding the decomposition of arsenic pentafluoride, $AsF_5(g)$.

   (a) A 55.8 g sample of $AsF_5(g)$ is introduced into an evacuated 10.5 L container at 105°C.

      (i) What is the initial molar concentration of $AsF_5(g)$ in the container?

      (ii) What is the initial pressure, in atmospheres, of the $AsF_5(g)$ in the container?

   At 105°C, $AsF_5(g)$ decomposes into $AsF_3(g)$ and $F_2(g)$ according to the following chemical equation.

   $$AsF_5(g) \rightleftarrows AsF_3(g) + F_2(g)$$

   (b) In terms of molar concentrations, write the equilibrium-constant expression for the decomposition of $AsF_5(g)$.

   (c) When equilibrium is established, 27.7 percent of the original number of moles of $AsF_5(g)$ has decomposed.

      (i) Calculate the molar concentration of $AsF_5(g)$ at equilibrium.

      (ii) Using molar concentrations, calculate the value of the equilibrium constant, K_{eq}, at 105°C.

   (d) Calculate the mole fraction of $F_2(g)$ in the container at equilibrium.

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

1. Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product constant, K_{sp}, is 5.0×10^{-13} at 298 K.

   (a) Write the expression for the solubility-product constant, K_{sp}, of AgBr.

   (b) Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

   (c) A 50.0 mL sample of distilled water is added to the solution described in part (b), which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part (b) ? Justify your answer.

   (d) Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(s) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}.)

   (e) A student mixes 10.0 mL of 1.5×10^{-4} M $AgNO_3$ with 2.0 mL of 5.0×10^{-4} M NaBr and stirs the resulting mixture. What will the student observe? Justify your answer with calculations.

   (f) The color of another salt of silver, AgI(s), is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

      (i) Write the chemical equation for the reaction that occurred in the test tube.

      (ii) Which salt has the greater value of K_{sp}: AgBr or AgI ? Justify your answer.

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

1. The compound butane, C_4H_{10}, occurs in two isomeric forms, *n*-butane and isobutane (2-methyl propane). Both compounds exist as gases at 25°C and 1.0 atm.

   (a) Draw the structural formula of each of the isomers (include all atoms). Clearly label each structure.

   (b) On the basis of molecular structure, identify the isomer that has the higher boiling point. Justify your answer.

   The two isomers exist in equilibrium as represented by the equation below.

   $$n\text{-butane}(g) \rightleftarrows \text{isobutane}(g) \qquad K_c = 2.5 \text{ at } 25°C$$

   Suppose that a 0.010 mol sample of pure *n*-butane is placed in an evacuated 1.0 L rigid container at 25°C.

   (c) Write the expression for the equilibrium constant, K_c, for the reaction.

   (d) Calculate the initial pressure in the container when the *n*-butane is first introduced (before the reaction starts).

   (e) The *n*-butane reacts until equilibrium has been established at 25°C.

      (i) Calculate the total pressure in the container at equilibrium. Justify your answer.

      (ii) Calculate the molar concentration of each species at equilibrium.

      (iii) If the volume of the system is reduced to half of its original volume, what will be the new concentration of *n*-butane after equilibrium has been reestablished at 25°C ? Justify your answer.

   Suppose that in another experiment a 0.010 mol sample of pure isobutane is placed in an evacuated 1.0 L rigid container and allowed to come to equilibrium at 25°C.

   (f) Calculate the molar concentration of each species after equilibrium has been established.

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

1. Answer the following questions about the solubility and reactions of the ionic compounds $M(OH)_2$ and MCO_3, where M represents an unidentified metal.

   (a) Identify the charge of the M ion in the ionic compounds above.

   (b) At 25°C, a saturated solution of $M(OH)_2$ has a pH of 9.15.

      (i) Calculate the molar concentration of $OH^-(aq)$ in the saturated solution.

      (ii) Write the solubility-product constant expression for $M(OH)_2$.

      (iii) Calculate the value of the solubility-product constant, K_{sp}, for $M(OH)_2$ at 25°C.

   (c) For the metal carbonate, MCO_3, the value of the solubility-product constant, K_{sp}, is 7.4×10^{-14} at 25°C. On the basis of this information and your results in part (b), which compound, $M(OH)_2$ or MCO_3, has the greater molar solubility in water at 25°C ? Justify your answer with a calculation.

   (d) MCO_3 decomposes at high temperatures, as shown by the reaction represented below.

$$MCO_3(s) \rightleftarrows MO(s) + CO_2(g)$$

   A sample of MCO_3 is placed in a previously evacuated container, heated to 423 K, and allowed to come to equilibrium. Some solid MCO_3 remains in the container. The value of K_p for the reaction at 423 K is 0.0012.

      (i) Write the equilibrium-constant expression for K_p of the reaction.

      (ii) Determine the pressure, in atm, of $CO_2(g)$ in the container at equilibrium at 423 K.

      (iii) Indicate whether the value of $\Delta G°$ for the reaction at 423 K is positive, negative, or zero. Justify your answer.