2000 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

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 STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, because you may earn 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 this booklet.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

\[
2 \, \text{H}_2\text{S}(g) \rightleftharpoons 2 \, \text{H}_2(g) + \text{S}_2(g)
\]

1. When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of \( \text{H}_2\text{S}(g) \) is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and \( 3.72 \times 10^{-2} \) mol of \( \text{S}_2(g) \) is present at equilibrium.

(a) Write the expression for the equilibrium constant, \( K_c \), for the decomposition reaction represented above.

(b) Calculate the equilibrium concentration, in mol L\(^{-1}\), of the following gases in the container at 483 K.

(i) \( \text{H}_2(g) \)

(ii) \( \text{H}_2\text{S}(g) \)

(c) Calculate the value of the equilibrium constant, \( K_c \), for the decomposition reaction at 483 K.

(d) Calculate the partial pressure of \( \text{S}_2(g) \) in the container at equilibrium at 483 K.

(e) For the reaction \( \text{H}_2(g) + \frac{1}{2} \text{S}_2(g) \rightleftharpoons \text{H}_2\text{S}(g) \) at 483 K, calculate the value of the equilibrium constant, \( K_c \).
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 goldenrod booklet. Do NOT write your answers on the lavender insert.

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

1. A sample of solid \( \text{U}_3\text{O}_8 \) is placed in a rigid 1.500 L flask. Chlorine gas, \( \text{Cl}_2(g) \), 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.

\[
\text{U}_3\text{O}_8(s) + 3 \text{Cl}_2(g) \rightleftharpoons 3 \text{UO}_2\text{Cl}_2(g) + \text{O}_2(g) \quad K_p = \frac{(P_{\text{UO}_2\text{Cl}_2})^3(P_{\text{O}_2})}{(P_{\text{Cl}_2})^3}
\]

When the system is at equilibrium, the partial pressure of \( \text{Cl}_2(g) \) is 1.007 atm and the partial pressure of \( \text{UO}_2\text{Cl}_2(g) \) is \( 9.734 \times 10^{-4} \) atm.

(a) Calculate the partial pressure of \( \text{O}_2(g) \) 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, \( \Delta G^\circ \), for the reaction at 862°C.

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

(e) State whether the enthalpy change, \( \Delta H^\circ \), 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 \( \text{O}_2(g) \) is added to the mixture in the flask. Does the mass of \( \text{U}_3\text{O}_8(s) \) in the flask increase, decrease, or remain the same? Justify your answer.
1. Answer the following questions relating to the solubilities of two silver compounds, $\text{Ag}_2\text{CrO}_4$ and $\text{Ag}_3\text{PO}_4$.

Silver chromate dissociates in water according to the equation shown below.

$$\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \quad K_{sp} = 2.6 \times 10^{-12} \text{ at } 25^\circ\text{C}$$

(a) Write the equilibrium-constant expression for the dissolving of $\text{Ag}_2\text{CrO}_4(s)$.

(b) Calculate the concentration, in mol L$^{-1}$, of $\text{Ag}^+(aq)$ in a saturated solution of $\text{Ag}_2\text{CrO}_4$ at 25°C.

(c) Calculate the maximum mass, in grams, of $\text{Ag}_2\text{CrO}_4$ that can dissolve in 100 mL of water at 25°C.

(d) A 0.100 mol sample of solid $\text{AgNO}_3$ is added to a 1.00 L saturated solution of $\text{Ag}_2\text{CrO}_4$. Assuming no volume change, does $[\text{CrO}_4^{2-}]$ increase, decrease, or remain the same? Justify your answer.

In a saturated solution of $\text{Ag}_3\text{PO}_4$ at 25°C, the concentration of $\text{Ag}^+(aq)$ is $5.3 \times 10^{-5} \text{ M}$. The equilibrium-constant expression for the dissolving of $\text{Ag}_3\text{PO}_4(s)$ in water is shown below.

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

(e) Write the balanced equation for the dissolving of $\text{Ag}_3\text{PO}_4$ in water.

(f) Calculate the value of $K_{sp}$ for $\text{Ag}_3\text{PO}_4$ at 25°C.

(g) A 1.00 L sample of saturated $\text{Ag}_3\text{PO}_4$ solution is allowed to evaporate at 25°C to a final volume of 500 mL. What is $[\text{Ag}^+]$ in the solution? Justify your answer.
CHEMISTRY
Section II
(Total time—90 minutes)

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

1. Answer the following questions relating to the solubility of the chlorides of silver and lead.

   (a) At 10°C, 8.9 × 10⁻⁵ g of AgCl(s) will dissolve in 100. mL of water.

      (i) Write the equation for the dissociation of AgCl(s) in water.

      (ii) Calculate the solubility, in mol L⁻¹, of AgCl(s) in water at 10°C.

      (iii) Calculate the value of the solubility-product constant, \(K_{sp}\), for AgCl(s) at 10°C.

   (b) At 25°C, the value of \(K_{sp}\) for PbCl₂(s) is 1.6 × 10⁻⁵ and the value of \(K_{sp}\) for AgCl(s) is 1.8 × 10⁻¹⁰.

      (i) If 60.0 mL of 0.0400 M NaCl(aq) is added to 60.0 mL of 0.0300 M Pb(NO₃)₂(aq), will a precipitate form? Assume that volumes are additive. Show calculations to support your answer.

      (ii) Calculate the equilibrium value of \([\text{Pb}^{2+}(aq)]\) in 1.00 L of saturated PbCl₂ solution to which 0.250 mole of NaCl(s) has been added. Assume that no volume change occurs.

      (iii) If 0.100 M NaCl(aq) is added slowly to a beaker containing both 0.120 M AgNO₃(aq) and 0.150 M Pb(NO₃)₂(aq) at 25°C, which will precipitate first, AgCl(s) or PbCl₂(s)? Show calculations to support your answer.
1. Lactic acid, HC$_3$H$_5$O$_3$, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M HC$_3$H$_5$O$_3(aq)$ at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.

(a) Write the expression for the acid-dissociation constant, $K_a$, for lactic acid and calculate its value.

(b) Calculate the pH of 0.50 M HC$_3$H$_5$O$_3$.

(c) Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, NaC$_3$H$_5$O$_3$, in 250. mL of 0.50 M HC$_3$H$_5$O$_3$. Assume that volume change is negligible.

(d) A 100. mL sample of 0.10 M HCl is added to 100. mL of 0.50 M HC$_3$H$_5$O$_3$. Calculate the molar concentration of lactate ion, C$_3$H$_5$O$_3^-$, in the resulting solution.
2007 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

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.

\[ \text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \quad K_a = 7.2 \times 10^{-4} \]

1. Hydrofluoric acid, \text{HF}(aq), dissociates in water as represented by the equation above.

   (a) Write the equilibrium-constant expression for the dissociation of \text{HF}(aq) in water.
   
   (b) Calculate the molar concentration of \text{H}_3\text{O}^+ in a 0.40 \text{ M} \text{ HF}(aq) solution.

   \text{HF}(aq) \text{ reacts with NaOH}(aq) \text{ according to the reaction represented below.}

   \[ \text{HF}(aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O}(l) + \text{F}^-(aq) \]

   A volume of 15 mL of 0.40 \text{ M} \text{ NaOH}(aq) is added to 25 mL of 0.40 \text{ M} \text{ HF}(aq) solution. Assume that volumes are additive.

   (c) Calculate the number of moles of \text{HF}(aq) remaining in the solution.
   
   (d) Calculate the molar concentration of \text{F}^-(aq) in the solution.
   
   (e) Calculate the pH of the solution.
Advanced Placement Chemistry

1987 Free Response Questions

1) \(\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-\)

Ammonia is a weak base that dissociates in water as shown above. At 25 °C, the base dissociation constant, \(K_b\), for \(\text{NH}_3\) is \(1.8 \times 10^{-5}\).

(a) Determine the hydroxide ion concentration and the percentage dissociation of a 0.150-molar solution of ammonia at 25 °C.

(b) Determine the pH of a solution prepared by adding 0.0500 mole of solid ammonium chloride to 100. milliliters of a 0.150-molar solution of ammonia.

(c) If 0.0800 mole of solid magnesium chloride, MgCl₂, is dissolved in the solution prepared in part (b) and the resulting solution is well-stirred, will a precipitate of Mg(OH)₂ form? Show calculation to support your answer. (Assume the volume of the solution is unchanged. The solubility product constant for Mg(OH)₂ is \(1.5 \times 10^{-11}\)).

2) \(2 \text{HgCl}_2\text{(aq)} + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{Cl}^- + 2 \text{CO}_2\text{(g)} + \text{Hg}_2\text{Cl}_2\text{(s)}\)

The equation for the reaction between mercuric chloride and oxalate ion in hot aqueous solution is shown above. The reaction rate may be determined by measuring the initial rate of formation of chloride ion, at constant temperature, for various initial concentrations of mercuric chloride and oxalate as shown in the following table.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial ([\text{HgCl}_2])</th>
<th>Initial ([\text{C}_2\text{O}_4^{2-}])</th>
<th>Initial Rate of formation of Cl⁻ (mole/liter-min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>0.0836 M</td>
<td>0.202 M</td>
<td>0.52 \times 10^{-4}</td>
</tr>
<tr>
<td>(2)</td>
<td>0.0836 M</td>
<td>0.404 M</td>
<td>2.08 \times 10^{-4}</td>
</tr>
<tr>
<td>(3)</td>
<td>0.0418 M</td>
<td>0.404 M</td>
<td>1.06 \times 10^{-4}</td>
</tr>
<tr>
<td>(4)</td>
<td>0.0316 M</td>
<td>?</td>
<td>1.27 \times 10^{-4}</td>
</tr>
</tbody>
</table>

(a) According to the data shown, what is the rate law for the reaction above?

(b) On the basis of the rate law determined in part (a), calculate the specific rate constant. Specify the units.
1. A pure 14.85 g sample of the weak base ethylamine, C$_2$H$_5$NH$_2$, is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the C$_2$H$_5$NH$_2$ in the solution.

The aqueous ethylamine reacts with water according to the equation below.

\[ \text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^- (\text{aq}) \]

(b) Write the equilibrium-constant expression for the reaction between C$_2$H$_5$NH$_2$(aq) and water.

(c) Of C$_2$H$_5$NH$_2$(aq) and C$_2$H$_5$NH$_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.

(d) A different solution is made by mixing 500. mL of 0.500 $M$ C$_2$H$_5$NH$_2$ with 500. mL of 0.200 $M$ HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

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

(ii) Write the net-ionic equation that represents the reaction that occurs when the C$_2$H$_5$NH$_2$ solution is mixed with the HCl solution.

(iii) Calculate the molar concentration of the C$_2$H$_5$NH$_3^+(aq)$ that is formed in the reaction.

(iv) Calculate the value of $K_b$ for C$_2$H$_5$NH$_2$. 

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**AP® Chemistry 2000 — Scoring Standards**

**Question 1**
(10 points)

(a) \[ K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} \quad \text{or} \quad K_c = \frac{(H_2)^2(S_2)}{(H_2S)^2} \]

1 pt.

• No point earned for a \( K_p \) expression or if an exponent is incorrectly used

(b) (i) \[ [H_2] = 2 [S_2] = \frac{(2.0)(3.72 \times 10^{-2} \text{ mol})}{1.25 \text{ L}} = 5.95 \times 10^{-2} M \]

1 pt.

(ii) \[ [H_2S] = \frac{0.10 \text{ mol} - (2.0)(3.72 \times 10^{-2} \text{ mol})}{1.25 \text{ L}} = 2.05 \times 10^{-2} M \]

or

\[ [H_2S] = 0.0800 M - 0.0595 M = 0.0205 M \]

2 pts.

Notes: One point is earned for getting the correct number of moles of \( H_2S \); second point is earned for dividing by 1.25 L and getting a consistent answer. Although not correct, one point may be earned for calculating the initial \([H_2S]\) (see below) and using that value as the equilibrium \( H_2S \) concentration.

\[ [H_2S] = \frac{3.40 \text{ g}}{341 \text{ g mol}^{-1}} = 0.0798 M \]

(c) \[ K_c = \frac{(5.95 \times 10^{-2})^2 \left(\frac{3.72 \times 10^{-2}}{1.25}\right)}{(2.05 \times 10^{-2})^2} = \frac{(5.95 \times 10^{-2})^2(0.0298)}{(2.05 \times 10^{-2})^2} = 0.250 \]

2 pts.

Notes: One point is earned for correctly using the molarity of the \( S_2 \) (dividing the number of moles by the volume). The second point is earned by correctly using the numbers generated in (b) in the expression shown in (a) and getting the appropriate answer.
Question 1

(d) \[ P = \frac{nRT}{V} = \frac{(3.72 \times 10^{-2} \text{ mol})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(483 \text{ K})}{1.25 \text{ L}} = 1.18 \text{ atm} \]

or

\[ P = [S_2]RT = (0.02976 \text{ mol L}^{-1})(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}) (483 \text{ K}) = 1.18 \text{ atm} \]

Note: The first point is earned for correctly setting up either of these expressions. The second point is earned for the correct answer (or an answer consistent with the numbers used). Also, combining \[ P_{\text{total}} V = n_{\text{total}} RT \] with \[ P_{S_2} = X_{S_2} P_{\text{total}} \], where \( X_{S_2} \) is the mole fraction of \( S_2 \), can earn the points.

(e) \[ K'_{c} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{0.250}} = 2.00 \]

Notes: One point is earned for recognizing that \( K'_{c} \) must be an inverse related to \( K_c \). A second point is earned for recognizing that the square root of \( K_c \) is involved. Only one point can be earned for the expression below, or for correctly calculating just the inverse of \( K_c \) or just \( \sqrt{K_c} \).

\[ K_c = \frac{[H_2S]}{[H_2][S_2]^{1/2}} \]
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.

$$U_3O_8(s) + 3 Cl_2(g) \rightleftharpoons 3 UO_2Cl_2(g) + O_2(g) \quad K_p = \frac{(P_{UO_2Cl_2})^3(P_{O_2})}{(P_{Cl_2})^3}$$

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 $9.734 \times 10^{-4}$ atm.

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

<table>
<thead>
<tr>
<th>I</th>
<th>?</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>1.007 atm</td>
<td>$9.734 \times 10^{-4}$ atm</td>
<td>?</td>
</tr>
</tbody>
</table>

$$9.734 \times 10^{-4} \text{ atm } UO_2Cl_2(g) \times \frac{(1 \text{ mol } O_2)}{(3 \text{ mol } UO_2Cl_2)} = 3.245 \times 10^{-4} \text{ atm } O_2(g)$$

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

$$K_p = \frac{(P_{UO_2Cl_2})^3(P_{O_2})}{(P_{Cl_2})^3} = \frac{(9.734 \times 10^{-4})^3(3.245 \times 10^{-4})}{(1.007)^3} = 2.931 \times 10^{-13}$$

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

$$\Delta G^\circ = -RT \ln K_p$$

$$= (-8.31 \text{ J mol}^{-1} \text{ K}^{-1})((862+273) \text{ K})(\ln (2.931 \times 10^{-13}))$$

$$= 272,000 \text{ J mol}^{-1} = 272 \text{ kJ mol}^{-1}$$
(d) State whether the entropy change, $\Delta S^\circ$, for the reaction at 862°C is positive, negative, or zero. Justify your answer.

$\Delta S^\circ$ is positive because four moles of gaseous products are produced from three moles of gaseous reactants.

One point is earned for the correct explanation.

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

Both $\Delta G^\circ$ and $\Delta S^\circ$ are positive, as determined in parts (c) and (d). Thus, $\Delta H^\circ$ must be positive because $\Delta H^\circ$ is the sum of two positive terms in the equation $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$.

One point is earned for the correct sign.
One point is earned for a correct explanation.

(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.

The mass of $U_3O_8(s)$ will increase because the reaction is at equilibrium, and the addition of a product creates a “stress” on the product (right) side of the reaction. The reaction will then proceed from right to left to reestablish equilibrium so that some $O_2(g)$ is consumed (tending to relieve the stress) as more $U_3O_8(s)$ is produced.

One point is earned for a correct explanation.
Question 1

Answer the following questions relating to the solubilities of two silver compounds, \( \text{Ag}_2\text{CrO}_4 \) and \( \text{Ag}_3\text{PO}_4 \).

Silver chromate dissociates in water according to the equation shown below.

\[
\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \quad K_{sp} = 2.6 \times 10^{-12} \text{ at } 25^\circ\text{C}
\]

(a) Write the equilibrium-constant expression for the dissolving of \( \text{Ag}_2\text{CrO}_4(s) \).

\[
K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]
\]

1 point for correct expression

(b) Calculate the concentration, in mol L\(^{-1}\), of \( \text{Ag}^+(aq) \) in a saturated solution of \( \text{Ag}_2\text{CrO}_4 \) at 25°C.

\[
\begin{align*}
\text{Ag}_2\text{CrO}_4(s) & \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq) \\
\text{I} & \quad - \quad 0 \quad 0 \\
\text{C} & \quad - \quad +2x \quad +x \\
\text{F} & \quad - \quad 0 + 2x \quad 0 + x
\end{align*}
\]

1 point for correct stoichiometry of \( \text{Ag}^+(aq) \) and \( \text{CrO}_4^{2-}(aq) \)

\[
\begin{align*}
2.6 \times 10^{-12} & = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \\
2.6 \times 10^{-12} & = [2x]^2[x] = 4x^3 \\
8.7 \times 10^{-5} & = x = [\text{CrO}_4^{2-}] \\
[\text{Ag}^+] & = 2x = 2 \times (8.7 \times 10^{-5} \text{ M}) = 1.7 \times 10^{-4} \text{ M}
\end{align*}
\]

1 point for substituting and calculating \([\text{Ag}^+]\)

(c) Calculate the maximum mass, in grams, of \( \text{Ag}_2\text{CrO}_4 \) that can dissolve in 100. mL of water at 25°C.

\[
\begin{align*}
\frac{8.7 \times 10^{-5} \text{ mole} \text{Ag}_2\text{CrO}_4}{1 \text{ L}} \times \frac{331.7 \text{ g}}{1 \text{ mole} \text{Ag}_2\text{CrO}_4} & = \frac{0.029 \text{ g} \text{Ag}_2\text{CrO}_4}{1 \text{ L}} \\
\frac{0.029 \text{ g} \text{Ag}_2\text{CrO}_4}{1 \text{ L}} \times 0.100 \text{ L} & = 0.0029 \text{ g} \text{Ag}_2\text{CrO}_4
\end{align*}
\]

1 point for molar mass of \( \text{Ag}_2\text{CrO}_4 \)

1 point for mass of \( \text{Ag}_2\text{CrO}_4 \) in 100 mL
AP® CHEMISTRY
2004 SCORING GUIDELINES

Question 1 (cont’d.)

(d) A 0.100 mol sample of solid AgNO₃ is added to a 1.00 L saturated solution of Ag₂CrO₄. Assuming no volume change, does [CrO₄²⁻] increase, decrease, or remain the same? Justify your answer.

| The [CrO₄²⁻] will decrease. Adding [Ag⁺] will make Q (nonequilibrium reaction quotient) greater than K. To re-establish equilibrium, the reaction goes from right to left, decreasing the quotient to return to equilibrium. | 1 point for correct prediction and explanation in terms of Q or LeChâtelier’s principle |

In a saturated solution of Ag₃PO₄ at 25°C, the concentration of Ag⁺(aq) is 5.3 × 10⁻⁵ M. The equilibrium-constant expression for the dissolving of Ag₃PO₄(s) in water is shown below.

\[ K_{sp} = [Ag⁺]^3[PO₄^{3-}] \]

(e) Write the balanced equation for the dissolving of Ag₃PO₄ in water.

| Ag₃PO₄(s) → 3 Ag⁺(aq) + PO₄^{3-}(aq) | 1 point for correct, balanced chemical equation |

(f) Calculate the value of \( K_{sp} \) for Ag₃PO₄ at 25°C.

\[
[Ag⁺] = 5.3 \times 10^{-5} \, M \\
[PO₄^{3-}] = 5.3 \times 10^{-5} \, M \, Ag^+ \times \frac{1 \, mol \, PO₄^{3-}}{3 \, mol \, Ag^+} = 1.8 \times 10^{-5} \, M \\
K_{sp} = [Ag⁺]^3[PO₄^{3-}] = (5.3 \times 10^{-5})^3(1.8 \times 10^{-5}) = 2.6 \times 10^{-18} \]

1 point for correct \([PO₄^{3-}]\)

1 point for \( K_{sp} \)

(g) A 1.00 L sample of saturated Ag₃PO₄ solution is allowed to evaporate at 25°C to a final volume of 500. mL. What is \([Ag⁺]\) in the solution? Justify your answer.

| \[Ag⁺] = 5.3 \times 10^{-5} \, M \] The \([Ag⁺]\) in a saturated solution of Ag₃PO₄ is independent of the volume of the solution. | 1 point for correct \([Ag⁺]\) and explanation |

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Question 1

(10 points)

(a)  (i)  AgCl(s) → Ag⁺(aq) + Cl⁻(aq)  
         1 point
         •  Correct charges needed to earn credit.
         •  Phases not necessary to earn credit.

     (ii)  \( \frac{8.9 \times 10^{-5} \text{ g}}{143.32 \text{ g/mol}} = 6.2 \times 10^{-7} \text{ mol} \) (in 100 mL)  
             1 point
             \( (6.2 \times 10^{-7} \text{ mol/100 mL}) (1,000 \text{ mL}/1.000 \text{ L}) = 6.2 \times 10^{-6} \text{ mol/L} \)  
             1 point
             Note: The first point is earned for the correct number of moles; the second point is earned for the conversion from moles to molarity.

     (iii)  \( K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = (6.2 \times 10^{-6})^2 = 3.8 \times 10^{-11} \)  
              1 point
              Note: Students earn one point for squaring their result for molarity in (a) (ii).

(b)  (i)  \( n_{\text{Cl}^-} = (0.060 \text{ L})(0.040 \text{ mol/L}) = 0.0024 \text{ mol} \)  
              1 point
              \( [\text{Cl}^-] = (0.0024 \text{ mol})/(0.120 \text{ L}) = 0.020 \text{ mol/L} = 0.020 \text{ M} \)

     \( n_{\text{Pb}^{2+}} = (0.060 \text{ L})(0.030 \text{ mol/L}) = 0.0018 \text{ mol} \)

     \( [\text{Pb}^{2+}] = (0.0018 \text{ mol})/(0.120 \text{ L}) = 0.015 \text{ mol/L} = 0.015 \text{ M} \)

     \( Q = [\text{Pb}^{2+}] [\text{Cl}^-]^2 = (0.015)(0.020)^2 = 6.0 \times 10^{-6} \)  
              1 point
              \( Q < K_{sp} \), therefore no precipitate forms  
              1 point
              Note: One point is earned for calculating the correct molarities; one point is earned for calculating \( Q \); one point is earned for determining whether or not a precipitate will form.

     (ii)  \( [\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{Cl}^-]^2} = \frac{1.6 \times 10^{-5}}{(0.25)^2} = 2.6 \times 10^{-4} \text{ M} \)  
               1 point
Question 1 (cont.)

(iii) for AgCl solution:  \[ [\text{Cl}^-] = \frac{K_{\text{AgCl}}^{sp}}{[\text{Ag}^+]^2} = \frac{1.8 \times 10^{-10}}{0.120} = 1.5 \times 10^{-9} \text{ M} \quad 1 \text{ point} \]

for PbCl₂ solution:  \[ [\text{Cl}^-] = \sqrt{\frac{K_{\text{PbCl}_2}^{sp}}{[\text{Pb}^{2+}]}} = \sqrt{\frac{1.6 \times 10^{-5}}{0.150}} = 1.0 \times 10^{-2} \text{ M} \]

The [Cl⁻] will reach a concentration of 1.5 x 10⁻⁹ M before it reaches a concentration of 1.0 x 10⁻² M, (or 1.5 x 10⁻⁹ << 1.0 x 10⁻²), therefore AgCl(s) will precipitate first.

Note: One point is earned for calculating [Cl⁻] in saturated solutions with the appropriate Ag⁺ and Pb²⁺ concentrations; one point is earned for concluding which salt will precipitate first, based on the student’s calculations.
1. Lactic acid, HC₃H₅O₃, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M HC₃H₅O₃(aq) at 298 K. For parts (a) through (d) below, assume the temperature remains at 298 K.

(a) Write the expression for the acid-dissociation constant, $K_a$, for lactic acid and calculate its value.

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

$$0.50 \times 0.0166 = 0.0083 \ M = x$$

<table>
<thead>
<tr>
<th></th>
<th>HC₃H₅O₃(aq)</th>
<th>H⁺(aq)</th>
<th>C₃H₅O₃⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.50</td>
<td>~0</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>–x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>E</td>
<td>0.50 – x</td>
<td>+x</td>
<td>+x</td>
</tr>
</tbody>
</table>

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{[0.0083][0.0083]}{[0.50 - 0.0083]}$$

$$K_a = 1.4 \times 10^{-4}$$

(b) Calculate the pH of 0.50 M HC₃H₅O₃.

From part (a):

$$[H^+] = 0.0083 \ M$$

$$pH = –\log [H^+] = –\log (0.0083) = 2.08$$
Question 1 (cont’d.)

(c) Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, \( \text{NaC}_3\text{H}_5\text{O}_3 \), in 250. mL of 0.50 \( M \) \( \text{HC}_3\text{H}_5\text{O}_3 \). Assume that volume change is negligible.

\[
\begin{align*}
\frac{0.045 \text{ mol NaC}_3\text{H}_5\text{O}_3}{0.250 \text{ L}} &= 0.18 \text{ M C}_3\text{H}_5\text{O}_3^- \\
\text{HC}_3\text{H}_5\text{O}_3(aq) &\rightarrow \text{H}^+(aq) + \text{C}_3\text{H}_5\text{O}_3^-(aq) \\
\text{I} & \quad 0.50 \quad \sim 0 \quad 0.18 \\
\text{C} & \quad -x \quad +x \quad +x \\
\text{E} & \quad 0.50 - x \quad +x \quad 0.18 + x \\
K_a &= \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{[x][0.18 + x]}{[0.50 - x]} \\
\text{Assume that } x &\ll 0.18 \text{ M} \\
K_a &= 1.4 \times 10^{-4} = \frac{[x][0.18]}{[0.50]} \\
x &= 3.9 \times 10^{-4} \text{ M} = [\text{H}^+] \\
pH &= -\log [\text{H}^+] = -\log (3.9 \times 10^{-4}) = 3.41 \\
\text{OR} \\
pH &= pK_a + \log \frac{0.18}{0.045} = 3.41 \\
&\quad \frac{0.50}{0.125} \\
\end{align*}
\]

1 point earned for \([\text{C}_3\text{H}_5\text{O}_3^-]\) 
(or 0.250 L \times 0.50 mol/L = 0.125 mol \text{HC}_3\text{H}_5\text{O}_3 and 0.045 mol \text{C}_3\text{H}_5\text{O}_3^-)

1 point earned for \([\text{H}^+]\) 
(set up and calculation)

1 point earned for calculating the value of pH
(d) A 100. mL sample of 0.10 \( M \) HCl is added to 100. mL of 0.50 \( M \) HC\(_3\)H\(_5\)O\(_3\). Calculate the molar concentration of lactate ion, C\(_3\)H\(_5\)O\(_3\)^{–}, in the resulting solution.

\[
\begin{align*}
0.50 \, M \, HC\(_3\)H\(_5\)O\(_3\) & \left( \frac{100 \, mL}{200 \, mL} \right) = 0.25 \, M \, HC\(_3\)H\(_5\)O\(_3\) \\
0.10 \, M \, HCl & \left( \frac{100 \, mL}{200 \, mL} \right) = 0.050 \, M \, H^+
\end{align*}
\]

\[
HC\(_3\)H\(_5\)O\(_3\)(aq) \rightarrow H^+(aq) + C\(_3\)H\(_5\)O\(_3\)^{–}(aq)
\]

| \( I \) | 0.25 | 0.050 | 0 |
| \( C \) | \( -x \) | \( +x \) | \( +x \) |
| \( E \) | 0.25 \( - x \) | 0.050 + \( x \) | \( +x \) |

\[
K_a = \frac{[H^+][C\(_3\)H\(_5\)O\(_3\)^{–}]}{[HC\(_3\)H\(_5\)O\(_3\)]} = \frac{[0.050 + x][x]}{[0.25 - x]}
\]

Assume \( x \ll 0.050 \, M \)

\[
K_a = 1.4 \times 10^{-4} = \frac{[0.050][x]}{[0.25]} \Rightarrow x = 7.0 \times 10^{-4} \, M = [C\(_3\)H\(_5\)O\(_3\)^{–}]
\]
Question 1

\[ \text{HF(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq) \quad K_a = 7.2 \times 10^{-4} \]

Hydrofluoric acid, HF(aq), dissociates in water as represented by the equation above.

(a) Write the equilibrium-constant expression for the dissociation of HF(aq) in water.

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \]

One point is earned for the correct expression.

(b) Calculate the molar concentration of H$_3$O$^+$ in a 0.40 M HF(aq) solution.

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.40 - x} = 7.2 \times 10^{-4} \]

Assume \( x \ll 0.40 \), then \( x^2 = (0.40)(7.2 \times 10^{-4}) \)

\[ x = [\text{H}_3\text{O}^+] = 0.017 \text{ M} \]

One point is earned for the correct setup (or the setup consistent with part (a)).

One point is earned for the correct concentration.

HF(aq) reacts with NaOH(aq) according to the reaction represented below.

\[ \text{HF(aq)} + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O(l)} + \text{F}^-(aq) \]

A volume of 15 mL of 0.40 M NaOH(aq) is added to 25 mL of 0.40 M HF(aq) solution. Assume that volumes are additive.

(c) Calculate the number of moles of HF(aq) remaining in the solution.

\[ \text{mol HF(aq)} = \text{initial mol HF(aq)} - \text{mol NaOH(aq) added} \]

\[ = (0.025 \text{ L})(0.40 \text{ mol L}^{-1}) - (0.015 \text{ L})(0.40 \text{ mol L}^{-1}) \]

\[ = 0.010 \text{ mol} - 0.0060 \text{ mol} = 0.004 \text{ mol} \]

One point is earned for determining the initial number of moles of HF and OH$^-$.

One point is earned for setting up and doing correct subtraction.

(d) Calculate the molar concentration of F$^-(aq)$ in the solution.

\[ \text{mol F}^-(aq) \text{ formed} = \text{mol NaOH(aq) added} = 0.0060 \text{ mol F}^-(aq) \]

\[ \frac{0.0060 \text{ mol F}^-(aq)}{(0.015 + 0.025) \text{ L of solution}} = 0.15 \text{ M F}^-(aq) \]

One point is earned for determining the number of moles of F$^-(aq)$.

One point is earned for dividing the number of moles of F$^-(aq)$ by the correct total volume.
(e) Calculate the pH of the solution.

\[
\text{[HF]} = \frac{0.004 \text{ mol HF}}{0.040 \text{ L}} = 0.10 M \text{ HF}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \quad \Rightarrow \quad \frac{[\text{HF}] \times K_a}{[\text{F}^-]} = [\text{H}_3\text{O}^+]
\]

\[
\Rightarrow \frac{0.10 M (7.2 \times 10^{-4})}{0.15 M} = 4.8 \times 10^{-4}
\]

\[
\Rightarrow \text{pH} = -\log (4.8 \times 10^{-4}) = 3.32
\]

OR

\[
\text{pH} = pK_a + \log \frac{[\text{F}^-]}{[\text{HF}]}
\]

\[
= -\log (7.2 \times 10^{-4}) + \log \frac{0.15 M}{0.10 M}
\]

\[
= 3.14 + 0.18
\]

\[
= 3.32
\]

One point is earned for indicating that the resulting solution is a buffer (e.g., by showing a ratio of \([\text{F}^-]\) to \([\text{HF}]\) or moles of \(\text{F}^-\) to \(\text{HF}\)).

One point is earned for the correct calculation of pH.
Advanced Placement Chemistry

1987 Free Response Answers

Notes

- \[\delta\], \[\sigma\] and \[\gamma\] are used to indicate the appropriate Greek letters.
- \[\sqrt{\text{square root}}\] applies to the numbers enclosed in parenthesis immediately following
- All simplifying assumptions are justified within 5%.
- One point deduction for a significant figure or math error, applied only once per problem.
- No credit earned for numerical answer without justification.

Return to Questions

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1)

a) three points

\[\text{[NH}_4^-\text{]} = \text{[OH}^-\text{]} = x\]

\[\text{[NH}_3\text{]} = 0.150 \text{ mol/L} - x\]

\[K_b = (\text{[NH}_4^+\text{]}\text{[OH}^-\text{]})) \div [\text{NH}_3]\]

\[1.8 \times 10^{-5} = [(x)(x)] \div (0.150 - x)\]

approximately equals \[x^2 \div 0.150\]

\[x = [\text{OH}^-] = 1.6 \times 10^{-3} \text{ mol/L}\]

\% diss = \[\frac{(1.6 \times 10^{-3})}{(0.150)}\times 100\% = 1.1\%

b) three points

\[\text{[NH}_4^+\text{]} = 0.0500 \text{ mol} / 0.100 \text{ L} = 0.500 \text{ mol/L NH}_4^+\]

\[\text{[NH}_3\text{]} = 0.150 \text{ mol/L}\]

OR

\[\text{mol NH}_4^+ = 0.0500 \text{ mol NH}_4^+\]

\[\text{mol NH}_3 = 0.150 \text{ mol/L} \times 0.100 \text{ L} = 0.0150 \text{ mol}\]

THEN
1.8 \times 10^{-5} = [(0.500) (x)] ÷ (0.150)

OR

pOH = 4.74 + \log (0.500 / 0.150)

THEN

x = [OH^-] = 5.4 \times 10^{-6} \text{ mol/L}

pOH = 5.27

pH = 14.00 - 5.27 = 8.73

c) three points

Mg(OH)_2(s) \rightleftharpoons Mg^{2+} + OH^-

[\text{Mg}^{2+}] = 0.0800 \text{ mol} / 0.100 \text{ L} = 0.800 \text{ mol/L} (0.800 \pm x = \text{no credit})

([OH^-] = 5.4 \times 10^{-6} \text{ mol/L from b.})

Q= [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.800) (5.4 \times 10^{-6})^2

Q = 2.3 \times 10^{-11}

K_{sp} = 1.5 \times 10^{-11}

since Q > K_{sp}, \text{Mg(OH)}_2 \text{ precipitates}

(Q \text{ must be defined in the same way as } K_{sp})

OR

K_{sp} = 1.5 \times 10^{-11} = (0.800)[\text{OH}^-]^2

[\text{OH}^-] = 4.3 \times 10^{-6} \text{ mol/L}

since 5.4 \times 10^{-6} > 4.3 \times 10^{-6} \text{ mol/L, then Mg(OH)}_2 \text{ precipitates}

2)

a) three points; one each for form of rate law, HgCl_2 exponent, C_2O_4^{2-} exponent

Rate = k [\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2
A pure 14.85 g sample of the weak base ethylamine, \( \text{C}_2\text{H}_5\text{NH}_2 \), is dissolved in enough distilled water to make 500. mL of solution.

(a) Calculate the molar concentration of the \( \text{C}_2\text{H}_5\text{NH}_2 \) in the solution.

\[
\begin{align*}
n_{\text{C}_2\text{H}_5\text{NH}_2} &= 14.85 \text{ g C}_2\text{H}_5\text{NH}_2 \times \frac{1 \text{ mol C}_2\text{H}_5\text{NH}_2}{45.09 \text{ g C}_2\text{H}_5\text{NH}_2} \\
&= 0.3293 \text{ mol C}_2\text{H}_5\text{NH}_2 \\
M_{\text{C}_2\text{H}_5\text{NH}_2} &= \frac{0.3293 \text{ mol C}_2\text{H}_5\text{NH}_2}{0.500 \text{ L}} = 0.659 \text{ M}
\end{align*}
\]

The aqueous ethylamine reacts with water according to the equation below.

\[
\text{C}_2\text{H}_5\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

(b) Write the equilibrium-constant expression for the reaction between \( \text{C}_2\text{H}_5\text{NH}_2(\text{aq}) \) and water.

\[
K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]}
\]

(c) Of \( \text{C}_2\text{H}_5\text{NH}_2(\text{aq}) \) and \( \text{C}_2\text{H}_5\text{NH}_3^+(\text{aq}) \), which is present in the solution at the higher concentration at equilibrium? Justify your answer.

\[ \text{C}_2\text{H}_5\text{NH}_2 \] is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small \( K_b \) value. Therefore only partial dissociation of \( \text{C}_2\text{H}_5\text{NH}_2 \) occurs in water, and \( [\text{C}_2\text{H}_5\text{NH}_3^+] \) is thus less than \( [\text{C}_2\text{H}_5\text{NH}_2] \).
Question 1 (continued)

(d) A different solution is made by mixing 500. mL of 0.500 M \( \text{C}_2\text{H}_5\text{NH}_2 \) with 500. mL of 0.200 M \( \text{HCl} \). Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

(i) Calculate the concentration of \( \text{OH}^- \text{(aq)} \) in the solution.

\[
\begin{align*}
\text{pH} &= -\log[H^+] \\
[H^+] &= 10^{-10.93} = 1.17 \times 10^{-11} \\
[\text{OH}^-] &= \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{1.17 \times 10^{-11}} = 8.5 \times 10^{-4} \text{ M}
\end{align*}
\]

OR

\[
\begin{align*}
\text{pOH} &= 14 - \text{pH} = 14 - 10.93 = 3.07 \\
[\text{OH}^-] &= 10^{-3.07} = 8.5 \times 10^{-4} \text{ M}
\end{align*}
\]

One point is earned for the correct concentration.

(ii) Write the net-ionic equation that represents the reaction that occurs when the \( \text{C}_2\text{H}_5\text{NH}_2 \) solution is mixed with the \( \text{HCl} \) solution.

\[
\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O}
\]

One point is earned for the correct equation.

(iii) Calculate the molar concentration of the \( \text{C}_2\text{H}_5\text{NH}_3^+(aq) \) that is formed in the reaction.

\[
\begin{align*}
\text{moles of} \ \text{C}_2\text{H}_5\text{NH}_2 &= 0.500 \text{ L} \times \frac{0.500 \text{ mol}}{1.00 \text{ L}} = 0.250 \text{ mol} \\
\text{moles of} \ \text{H}_3\text{O}^+ &= 0.500 \text{ L} \times \frac{0.200 \text{ mol}}{1.00 \text{ L}} = 0.100 \text{ mol}
\end{align*}
\]

\[
\begin{array}{c|c|c|c}
 & [\text{C}_2\text{H}_5\text{NH}_2] & [\text{H}_3\text{O}^+] & [\text{C}_2\text{H}_5\text{NH}_3^+] \\
\hline
\text{initial value} & 0.250 & 0.100 & \sim 0 \\
\text{change} & -0.100 & -0.100 & +0.100 \\
\text{final value} & 0.150 & \sim 0 & 0.100
\end{array}
\]

\[
[\text{C}_2\text{H}_5\text{NH}_3^+] = \frac{0.100 \text{ mol} \times \text{C}_2\text{H}_5\text{NH}_3^+}{1.00 \text{ L}} = 0.100 \text{ M}
\]

One point is earned for the correct number of moles of \( \text{C}_2\text{H}_5\text{NH}_2 \) and \( \text{H}_3\text{O}^+ \).

One point is earned for the correct concentration.
(iv) Calculate the value of $K_b$ for $C_2H_5NH_2$.

\[
[C_2H_5NH_2] = \frac{0.150 \text{ mol } C_2H_5NH_2}{1.00 \text{ L}} = 0.150 \text{ M}
\]

\[
K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(0.100)(8.5 \times 10^{-4})}{0.150} = 5.67 \times 10^{-4}
\]

One point is earned for the correct calculation of the molarity of $C_2H_5NH_2$ after neutralization.

One point is earned for the correct value.