CollegeBoard
Advanced Placement
Program

AP® Chemistry
2007 Scoring Guidelines

Question 1

$$HF(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + F^-(aq) \qquad K_a = 7.2 \times 10^{-4}$$

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.

$K_a = \frac{[H_3O^+][F^-]}{[HF]}$	One point is earned for the correct expression.

(b) Calculate the molar concentration of H_3O^+ in a 0.40 M $HF(aq)$ solution.

$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{0.40 - x} = 7.2 \times 10^{-4}$	One point is earned for the correct setup (or the setup consistent with part (a)).
Assume $x << 0.40$, then $x^2 = (0.40)(7.2 \times 10^{-4})$ $x = [H_3O^+] = 0.017\ M$	One point is earned for the correct concentration.

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

$$HF(aq) + OH^-(aq) \rightarrow H_2O(l) + F^-(aq)$$

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.

mol $HF(aq)$ = initial mol $HF(aq)$ − mol $NaOH(aq)$ added = $(0.025\ L)(0.40\ mol\ L^{-1}) - (0.015\ L)(0.40\ mol\ L^{-1})$ = 0.010 mol − 0.0060 mol = 0.004 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.

mol $F^-(aq)$ formed = mol $NaOH(aq)$ added = 0.0060 mol $F^-(aq)$ $\frac{0.0060\ mol\ F^-(aq)}{(0.015 + 0.025)\ L\ of\ solution} = 0.15\ M\ F^-(aq)$	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.

Question 1 (continued)

(e) Calculate the pH of the solution.

$[HF] = \frac{0.004 \text{ mol HF}}{0.040 \text{ L}} = 0.10\ M \text{ HF}$ $K_a = \frac{[H_3O^+][F^-]}{[HF]} \Rightarrow \frac{[HF] \times K_a}{[F^-]} = [H_3O^+]$ $\Rightarrow \frac{0.10\ M\ (7.2 \times 10^{-4})}{0.15\ M} = 4.8 \times 10^{-4}$ $\Rightarrow \text{pH} = -\log(4.8 \times 10^{-4}) = 3.32$	One point is earned for indicating that the resulting solution is a buffer (e.g., by showing a ratio of $[F^-]$ to $[HF]$ or moles of F^- to HF).
OR	
$\text{pH} = \text{p}K_a + \log \frac{[F^-]}{[HF]}$ $= -\log(7.2 \times 10^{-4}) + \log \frac{0.15\ M}{0.10\ M}$ $= 3.14 + 0.18$ $= 3.32$	One point is earned for the correct calculation of pH.

Question 2

$$N_2(g) + 3\ F_2(g) \rightarrow 2\ NF_3(g) \qquad \Delta H^\circ_{298} = -264\ \text{kJ mol}^{-1};\ \Delta S^\circ_{298} = -278\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The following questions relate to the synthesis reaction represented by the chemical equation in the box above.

(a) Calculate the value of the standard free energy change, ΔG°_{298}, for the reaction.

$\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$ $= -264\ \text{kJ mol}^{-1} - (298\ \text{K})(-0.278\ \text{kJ mol}^{-1}\ \text{K}^{-1})$ $= -181\ \text{kJ mol}^{-1}$	One point is earned for correct substitution. One point is earned for the value of ΔG°_{298} (including kJ or J).

(b) Determine the temperature at which the equilibrium constant, K_{eq}, for the reaction is equal to 1.00. (Assume that ΔH° and ΔS° are independent of temperature.)

When $K_{eq} = 1$, then $\Delta G^\circ_T = -RT\ln(1) = 0$ If $\Delta G^\circ_T = 0$, then $0 = \Delta H^\circ - T\Delta S^\circ \Rightarrow$ $T = \dfrac{\Delta H^\circ_{298}}{\Delta S^\circ_{298}}$ $T = \dfrac{-264\ \text{kJ mol}^{-1}}{-0.278\ \text{kJ K}^{-1}\text{mol}^{-1}} = 950.\ \text{K}$	One point is earned for indicating that if $K_{eq} = 1$, then $\Delta G^\circ_T = 0$. One point is earned for the answer (including the unit K).

(c) Calculate the standard enthalpy change, ΔH°, that occurs when a 0.256 mol sample of $NF_3(g)$ is formed from $N_2(g)$ and $F_2(g)$ at 1.00 atm and 298 K.

$0.256\ \text{mol}\ NF_3(g) \times \dfrac{-264\ \text{kJ}}{2.00\ \text{mol}\ NF_3(g)} = -33.8\ \text{kJ}$	One point is earned for multiplying ΔH°_{298} by the number of moles of NF_3 formed. One point is earned for recognizing that 2.00 mol of NF_3 are produced for the reaction as it is written. One point is earned for the answer (including kJ or J).

Question 2 (continued)

The enthalpy change in a chemical reaction is the difference between energy absorbed in breaking bonds in the reactants and energy released by bond formation in the products.

(d) How many bonds are formed when two molecules of NF_3 are produced according to the equation in the box above?

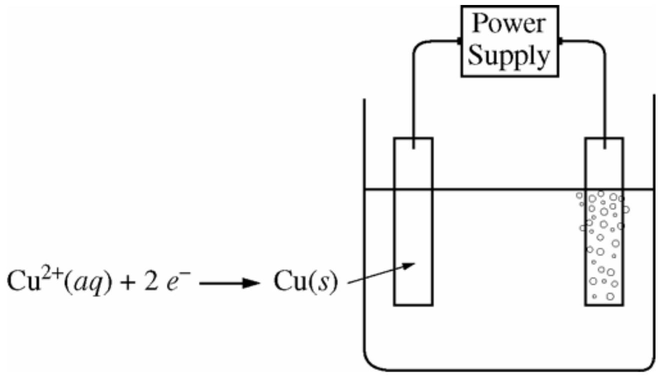
There are six N–F bonds formed.	One point is earned for the correct answer.

(e) Use both the information in the box above and the table of average bond enthalpies below to calculate the average enthalpy of the F – F bond.

Bond	Average Bond Enthalpy (kJ mol^{-1})
N≡N	946
N–F	272
F – F	?

$\Delta H^\circ_{298} = \Sigma E_{bonds\ broken} - \Sigma E_{bonds\ formed} = -264$ kJ mol^{-1} $= [BE_{N\equiv N} + (3 \times BE_{F\text{-}F})] - (6 \times BE_{N\text{-}F})$ $= [946$ kJ $mol^{-1} + (3 \times BE_{F\text{-}F})] - 6(272$ kJ $mol^{-1})$ $= -264$ kJ mol^{-1} $\Rightarrow$ 3 mol $BE_{F\text{-}F} = (-264 - 946 + 1{,}632)$ kJ mol^{-1} $\Rightarrow BE_{F\text{-}F} = 141$ kJ mol^{-1}	One point is earned for the correct number of bonds in all three compounds multiplied by the average bond enthalpies. One point is earned for the answer (including kJ or J). <u>Note:</u> A total of one point is earned if an incorrect number of bonds is substituted in a correct equation and the answer is reasonable (i.e., positive).

Question 3



An external direct-current power supply is connected to two platinum electrodes immersed in a beaker containing 1.0 *M* $CuSO_4(aq)$ at 25°C, as shown in the diagram above. As the cell operates, copper metal is deposited onto one electrode and $O_2(g)$ is produced at the other electrode. The two reduction half-reactions for the overall reaction that occurs in the cell are shown in the table below.

Half-Reaction	$E°$(V)
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23
$Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$	+0.34

(a) On the diagram, indicate the direction of electron flow in the wire.

The electron flow in the wire is from the right toward the left (counterclockwise).	One point is earned for the correct direction.

(b) Write a balanced net ionic equation for the electrolysis reaction that occurs in the cell.

$2\,H_2O(l) + 2\,Cu^{2+}(aq) \rightarrow 4\,H^+(aq) + 2\,Cu(s) + O_2(g)$	One point is earned for all three products. One point is earned for balancing the equation.

(c) Predict the algebraic sign of $\Delta G°$ for the reaction. Justify your prediction.

The sign of $\Delta G°$ would be positive because the reaction is NOT spontaneous.	One point is earned for indicating that $\Delta G°$ is greater than zero <u>and</u> supplying a correct explanation.

Question 3 (continued)

(d) Calculate the value of $\Delta G°$ for the reaction.

$E° = -1.23\text{ V} + 0.34\text{ V} = -0.89\text{ V} = -0.89\text{ J C}^{-1}$ $\Delta G° = -n\mathcal{F}E° = -4\,(96{,}500\text{ C mol}^{-1})(-0.89\text{ J C}^{-1})$ $= +340{,}000\text{ J mol}^{-1} = +340\text{ kJ mol}^{-1}$	One point is earned for calculating $E°$. One point is earned for calculating $\Delta G°$ (consistent with the calculated $E°$).

An electric current of 1.50 amps passes through the cell for 40.0 minutes.

(e) Calculate the mass, in grams, of the Cu(*s*) that is deposited on the electrode.

$q = (1.50\text{ C s}^{-1})(40.0\text{ min}) \times \frac{60\text{ s}}{1\text{ minute}} = 3{,}600\text{ C}$ $\text{mass Cu} = (3{,}600\text{ C}) \times \frac{1\text{ mol } e^-}{96{,}500\text{ C}} \times \frac{1\text{ mol Cu}}{2\text{ mol } e^-} \times \frac{63.55\text{ g Cu}}{1\text{ mol Cu}}$ $= 1.19\text{ g Cu}$	One point is earned for calculating q. One point is earned for calculating the mass of copper deposited. ***OR*** Two points are earned for calculating the mass of copper in one step.

(f) Calculate the dry volume, in liters measured at 25°C and 1.16 atm, of the $O_2(g)$ that is produced.

$n_{O_2} = (1.19\text{ g Cu}) \times \frac{1\text{ mol Cu}}{63.55\text{ g Cu}} \times \frac{1\text{ mol } O_2}{2\text{ mol Cu}} = 0.00936\text{ mol } O_2$ $V = \frac{nRT}{P} = \frac{(0.00936\text{ mol})(0.0821\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})}{1.16\text{ atm}}$ $= 0.197\text{ L}$	One point is earned for calculating the number of moles of O_2. One point is earned for calculating V (consistent with previous calculations).

Question 4

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.

(a) A solution of sodium hydroxide is added to a solution of lead(II) nitrate.

(i) Balanced equation: $2\ OH^- + Pb^{2+} \rightarrow Pb(OH)_2$	One point is earned for the correct reactants. Two points are earned for the correct product. One point is earned for balancing the equation for mass and charge.

(ii) If 1.0 L volumes of 1.0 *M* solutions of sodium hydroxide and lead(II) nitrate are mixed together, how many moles of product(s) will be produced? Assume the reaction goes to completion.

A total of 0.5 mol of $Pb(OH)_2$ will be produced.	One point is earned for the correct number of moles.

(b) Excess nitric acid is added to solid calcium carbonate.

(i) Balanced equation: $2\ H^+ + CaCO_3 \rightarrow Ca^{2+} + H_2O + CO_2$	One point is earned for the correct reactants. Two points are earned for all three of the correct products; one point is earned for any one or two of the three. One point is earned for balancing the equation for mass and charge.

(ii) Briefly explain why statues made of marble (calcium carbonate) displayed outdoors in urban areas are deteriorating.

The H^+ ions in acid rain react with the marble statues and the soluble compounds of Ca that are formed wash away.	One point is earned for a correct answer involving acid precipitation.

Question 4 (continued)

(c) A solution containing silver(I) ion (an oxidizing agent) is mixed with a solution containing iron(II) ion (a reducing agent).

(i) Balanced equation: $Ag^{+} + Fe^{2+} \rightarrow Ag + Fe^{3+}$	One point is earned for the correct reactants. One point is earned for each of the two correct products. One point is earned for balancing the equation for mass and charge.

(ii) If the contents of the reaction mixture described above are filtered, what substance(s), if any, would remain on the filter paper?

The precipitated solid silver will remain on the filter paper.	One point is earned for the correct substance.

Question 5

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

The mass percent of iron in a soluble iron(II) compound is measured using a titration based on the balanced equation above.

(a) What is the oxidation number of manganese in the permanganate ion, $MnO_4^-(aq)$?

+7	One point is earned for the correct oxidation number.

(b) Identify the reducing agent in the reaction represented above.

$Fe^{2+}(aq)$	One point is earned for the correct iron ion.

The mass of a sample of the iron(II) compound is carefully measured before the sample is dissolved in distilled water. The resulting solution is acidified with $H_2SO_4(aq)$. The solution is then titrated with $MnO_4^-(aq)$ until the end point is reached.

(c) Describe the color change that occurs in the flask when the end point of the titration has been reached. Explain why the color of the solution changes at the end point.

The solution in the flask changes from colorless to faint purple-pink at the endpoint of the titration.	One point is earned for stating that a faint pink color appears (unless indication of acid-base reaction).
At the endpoint there is no $Fe^{2+}(aq)$ left in the flask to reduce the colored permanganate ion, so when a small amount of permanganate ion is added after the endpoint, the unreacted permanganate ion present in the solution colors the solution faint purple/pink.	One point is earned for a correct explanation involving excess MnO_4^- after all Fe^{2+} has reacted.

(d) Let the variables g, M, and V be defined as follows:

g = the mass, in grams, of the sample of the iron(II) compound

M = the molarity of the $MnO_4^-(aq)$ used as the titrant

V = the volume, in liters, of $MnO_4^-(aq)$ added to reach the end point

In terms of these variables, the number of moles of $MnO_4^-(aq)$ added to reach the end point of the titration is expressed as $M \times V$. Using the variables defined above, the molar mass of iron (55.85 g mol^{-1}), and the coefficients in the balanced chemical equation, write the expression for each of the following quantities.

Question 5 (continued)

(i) The number of moles of iron in the sample

$\text{mol Fe}^{2+} = 5 \times M \times V$ **OR** $\text{mol Fe}^{2+} = \dfrac{5 \text{ mol Fe}^{2+}}{1 \text{ mol MnO}_4^-} \times M \times V$	One point is earned for either expression.

(ii) The mass of iron in the sample, in grams

$\text{mass Fe} = 5 \times M \times V \times 55.85 \text{ g mol}^{-1}$ **OR** $\text{mass Fe} = \text{mol Fe}^{2+} \times 55.85 \text{ g mol}^{-1}$	One point is earned for the answer in part (d)(i) multiplied by 55.85.

(iii) The mass percent of iron in the compound

$\text{mass \% Fe} = \dfrac{5 \times M \times V \times 55.85}{g} \times 100$ **OR** $\text{mass \% Fe} = \dfrac{\text{mass Fe}}{g} \times 100$	One point is earned for the answer in part (d)(ii) divided by g. One point is earned for converting to percent.

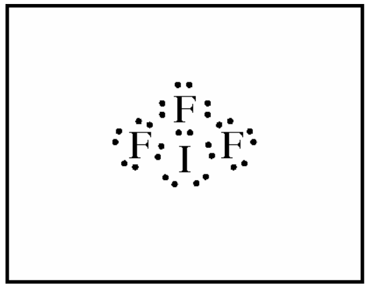
(e) What effect will adding too much titrant have on the experimentally determined value of the mass percent of iron in the compound? Justify your answer.

The experimentally determined mass percent of iron in the compound will be too large. V is too large $\Rightarrow$ expression in (d)(iii) above is too large	One point is earned for stating that the mass percent is too large, with justification.

Question 6

Answer the following questions, which pertain to binary compounds.

(a) In the box provided below, draw a complete Lewis electron-dot diagram for the IF_3 molecule.

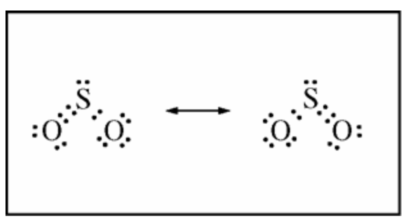


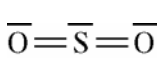
One point is earned for a correct Lewis diagram (can be done with dots or lines).

(b) On the basis of the Lewis electron-dot diagram that you drew in part (a), predict the molecular geometry of the IF_3 molecule.

T-shaped	One point is earned for the molecular geometry consistent with the Lewis diagram in part (a).

(c) In the SO_2 molecule, both of the bonds between sulfur and oxygen have the same length. Explain this observation, supporting your explanation by drawing in the box below a Lewis electron-dot diagram (or diagrams) for the SO_2 molecule.



<table>
<tr><td colspan="2">One point is earned for a correct diagram (can be done with dots or lines).
One point is earned for some indication or discussion of resonance (but the point is <u>not</u> earned for a description of resonance as a dynamic process).
OR</td></tr>
<tr><td>
The bonds are the same length because they are both double bonds.</td><td>One point is earned for a correct diagram (can be done with dots or lines).
One point is earned for stating that both bonds are double bonds.</td></tr>
</table>

Question 6 (continued)

(d) On the basis of your Lewis electron-dot diagram(s) in part (c), identify the hybridization of the sulfur atom in the SO_2 molecule.

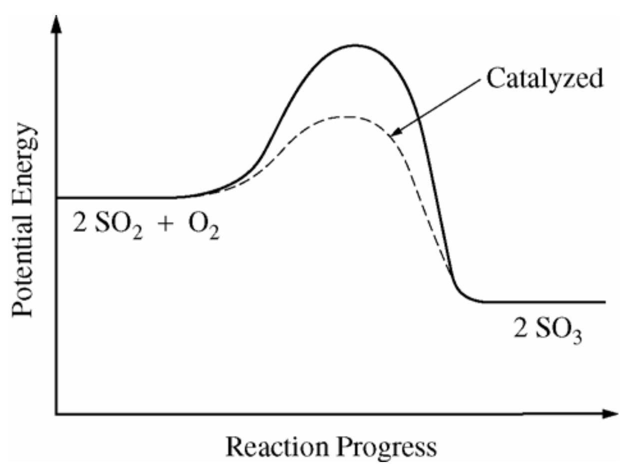
sp^2	One point is earned for hybridization consistent with part (c).

The reaction between $SO_2(g)$ and $O_2(g)$ to form $SO_3(g)$ is represented below.

$$2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$$

The reaction is exothermic. The reaction is slow at 25°C; however, a catalyst will cause the reaction to proceed faster.

(e) Using the axes provided below, draw the complete potential-energy diagram for both the catalyzed and uncatalyzed reactions. Clearly label the curve that represents the catalyzed reaction.



One point is earned for an uncatalyzed reaction curve that must show that $E_a > 0$ and $\Delta H < 0$.
One point is earned for a catalyzed reaction curve that must show $E_a <$ uncatalyzed E_a, must be clearly labeled, and must begin and end at the same energies as the uncatalyzed curve.

Question 6 (continued)

(f) Predict how the ratio of the equilibrium pressures, $\frac{p_{SO_2}}{p_{SO_3}}$, would change when the temperature of the uncatalyzed reaction mixture is increased. Justify your prediction.

The ratio $\frac{p_{SO_2}}{p_{SO_3}}$ would increase as the temperature increases. Because the reaction is exothermic ($\Delta H < 0$), as the temperature is raised the reaction shifts to the left.	One point is earned for the correct answer and explanation.

(g) How would the presence of a catalyst affect the change in the ratio described in part (f)? Explain.

The catalyst would not affect the value of the two equilibrium ratios but would increase the rate of the shifting of the system to the new equilibrium position. The catalyst does this by providing an alternate path with a lower activation energy.	One point is earned for the correct answer and explanation.