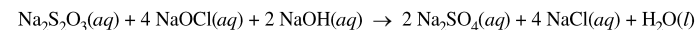


AP Chemistry

Scoring Guidelines

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Question 1



A student performs an experiment to determine the value of the enthalpy change, $\Delta H_{\text{rxn}}^\circ$, for the oxidation-reduction reaction represented by the balanced equation above.

(a) Determine the oxidation number of Cl in NaOCl.

+1	1 point is earned for the correct answer.
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(b) Calculate the number of grams of $\text{Na}_2\text{S}_2\text{O}_3$ needed to prepare 100.00 mL of 0.500 *M* $\text{Na}_2\text{S}_2\text{O}_3(aq)$.

$100.00 \text{ mL} \times \frac{0.500 \text{ mol Na}_2\text{S}_2\text{O}_3}{1000 \text{ mL}} \times \frac{158.10 \text{ g Na}_2\text{S}_2\text{O}_3}{1 \text{ mol Na}_2\text{S}_2\text{O}_3}$ $= 7.90 \text{ g Na}_2\text{S}_2\text{O}_3$	1 point is earned for the correct number of moles of $\text{Na}_2\text{S}_2\text{O}_3$ (may be implicit). 1 point is earned for the correct calculation of mass of $\text{Na}_2\text{S}_2\text{O}_3$ consistent with the number of moles.
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In the experiment, the student uses the solutions shown in the table below.

Solution	Concentration (<i>M</i>)	Volume (mL)
$\text{Na}_2\text{S}_2\text{O}_3(aq)$	0.500	5.00
$\text{NaOCl}(aq)$	0.500	5.00
$\text{NaOH}(aq)$	0.500	5.00

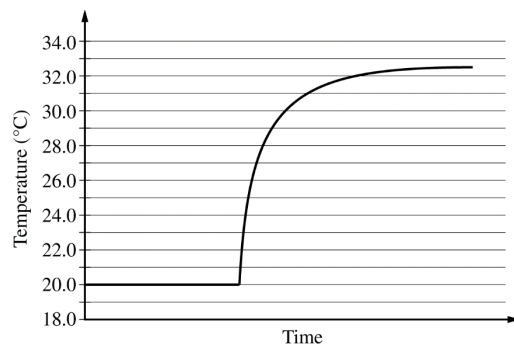
(c) Using the balanced equation for the oxidation-reduction reaction and the information in the table above, determine which reactant is the limiting reactant. Justify your answer.

NaOCl is the limiting reactant. Given that equal numbers of moles of each reactant were present initially, it follows from the coefficients of the reactants in the balanced equation that NaOCl will be depleted first.	1 point is earned for identifying the limiting reactant <u>and</u> providing a valid justification.
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Question 1 (continued)

The solutions, all originally at 20.0°C, are combined in an insulated calorimeter. The temperature of the reaction mixture is monitored, as shown in the graph below.



(d) According to the graph, what is the temperature change of the reaction mixture?

From the graph the final temperature is 32.5°C.
 $\Delta T = T_f - T_i = 32.5^\circ\text{C} - 20.0^\circ\text{C} = 12.5^\circ\text{C}$

1 point is earned for the correct value of ΔT .

(e) The mass of the reaction mixture inside the calorimeter is 15.21 g.

(i) Calculate the magnitude of the heat energy, in joules, that is released during the reaction. Assume that the specific heat of the reaction mixture is 3.94 J/(g·°C) and that the heat absorbed by the calorimeter is negligible.

$$q = mc\Delta T$$

$$= (15.21 \text{ g})(3.94 \text{ J/(g}\cdot^\circ\text{C)})(12.5^\circ\text{C}) = 749 \text{ J}$$

1 point is earned for the correct calculation of q consistent with the ΔT value from part (d).

(ii) Using the balanced equation for the oxidation-reduction reaction and your answer to part (c), calculate the value of the enthalpy change of the reaction, $\Delta H_{\text{rxn}}^\circ$, in kJ/mol_{rxn}. Include the appropriate algebraic sign with your answer.

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Question 1 (continued)

$$n_{\text{NaOCl}} = 5.00 \text{ mL} \times \frac{0.500 \text{ mol NaOCl}}{1000 \text{ mL NaOCl}} = 0.00250 \text{ mol NaOCl}$$

$$n_{\text{rxn}} = 0.00250 \text{ mol NaOCl} \times \frac{1 \text{ mol}_{\text{rxn}}}{4 \text{ mol NaOCl}} = 0.000625 \text{ mol}_{\text{rxn}}$$

$$\Delta H_{\text{rxn}}^\circ = \frac{-0.749 \text{ kJ}}{0.000625 \text{ mol}_{\text{rxn}}} = -1.20 \times 10^3 \text{ kJ/mol}_{\text{rxn}}$$

1 point is earned for correctly calculating the value of mol_{rxn} consistent with the limiting reactant in part (c).

1 point is earned for a negative $\Delta H_{\text{rxn}}^\circ$ obtained by dividing the calculated value of q by the calculated value of mol_{rxn}.

The student repeats the experiment, but this time doubling the volume of each of the reactants, as shown in the table below.

Solution	Concentration (M)	Volume (mL)
Na ₂ S ₂ O ₃ (aq)	0.500	10.0
NaOCl(aq)	0.500	10.0
NaOH(aq)	0.500	10.0

(f) The magnitude of the enthalpy change, $\Delta H_{\text{rxn}}^\circ$, in kJ/mol_{rxn}, calculated from the results of the second experiment is the same as the result calculated in part (e)(ii). Explain this result.

By doubling the volumes, the number of moles of the reactants are doubled, which doubles the amount of energy produced. Therefore the amount of heat per mole will remain the same.

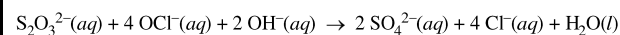
OR

$$\text{In the second experiment, } \Delta H_{\text{rxn}}^\circ = \frac{2mc\Delta T}{2n} = \frac{mc\Delta T}{n} = \Delta H_{\text{rxn}}^\circ.$$

Thus the magnitude is the same as calculated in the first experiment.

1 point is earned for a valid explanation.

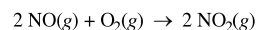
(g) Write the balanced net ionic equation for the given reaction.



1 point is earned for the correct net ionic equation.

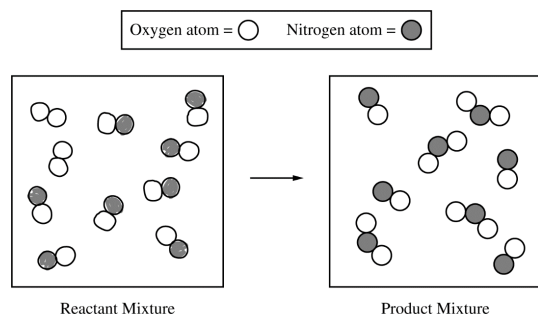
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Question 2



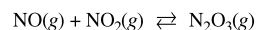
A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of NO(g) and NO₂(g), which the student produces by using the reaction represented above.

- (a) The particle-level representation of the equimolar mixture of NO(g) and NO₂(g) in the flask at the completion of the reaction between NO(g) and O₂(g) is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of NO(g) and O₂(g) that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



See sample student response above. (8 molecules of NO and 2 molecules of O ₂)	1 point is earned for correctly representing molecules of NO and O ₂ . 1 point is earned for correctly representing atom conservation.
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The student reads in a reference text that NO(g) and NO₂(g) will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{rxn}$	$-138.5 \text{ J/(K}\cdot\text{mol}_{rxn})$	$0.87 \text{ kJ/mol}_{rxn}$

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Question 2 (continued)

- (b) The student begins with an equimolar mixture of NO(g) and NO₂(g) in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

- (i) Calculate the value of the equilibrium constant, K , for the reaction at 298 K.

$\Delta G^\circ = -RT \ln K$ $K = e^{-\Delta G^\circ / RT}$ $K = e^{-\frac{870 \text{ J/mol}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}}$ $K = 0.70$	1 point is earned for a correct calculation of K .
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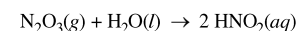
- (ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

No, the pressure will not equal 1.0 atm. $P_{\text{N}_2\text{O}_3}$ would only equal 1.0 atm if the reaction goes to completion. OR The value of K indicates that a substantial amount of reactants will be present at equilibrium.	1 point is earned for a correct choice and valid justification based on the value of K .
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- (c) The student hypothesizes that increasing the temperature will increase the amount of N₂O₃(g) in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

Disagree. Because the reaction is exothermic, increasing the temperature of the reaction will favor the formation of the reactants (according to Le Chatelier's principle).	1 point is earned for the correct choice <u>and</u> a correct justification.
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N₂O₃(g) reacts with water to form nitrous acid, HNO₂(aq), a compound involved in the production of acid rain. The reaction is represented below.



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Question 2 (continued)

- (d) The skeletal structure of the HNO_2 molecule is shown in the box below.
- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

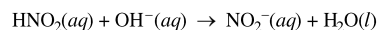


See sample response above. (Line segments can be used to represent electron pairs.)	1 point is earned for a valid diagram.
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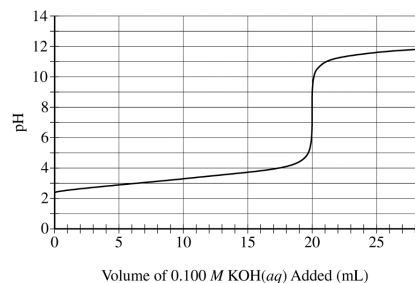
- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

sp^2	1 point is earned for the correct answer.
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To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



The following titration curve shows the change in pH of the solution during the titration.



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Question 2 (continued)

- (e) Use the titration curve and the information above to
- (i) determine the initial concentration of the $\text{HNO}_2(aq)$ solution

$20. \text{ mL KOH} \times \frac{0.100 \text{ mol KOH}}{1000 \text{ mL KOH}} = 0.0020 \text{ mol KOH added}$ $\Rightarrow 0.0020 \text{ mol HNO}_2 \text{ in } 100. \text{ mL of solution because the stoichiometry of the neutralization reaction is 1 to 1.}$ $\frac{0.0020 \text{ mol HNO}_2}{0.100 \text{ L}} = 0.020 \text{ M HNO}_2$	1 point is earned for the correct calculation of the initial concentration.
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- (ii) estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$

The value of $\text{p}K_a$ is about 3.4.	1 point is earned for an acceptable estimate for the value of $\text{p}K_a$.
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- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

$\text{NO}_2^-(aq)$ The titration is past the half-equivalence point; therefore, there will be more conjugate base present than acid.	1 point is earned for the correct choice <u>and</u> a valid justification.
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Question 3

Answer the following questions relating to Fe and its ions, Fe²⁺ and Fe³⁺.

(a) Write the ground-state electron configuration of the Fe²⁺ ion.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ OR $[\text{Ar}] 3d^6$	1 point is earned for a correct electron configuration.
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Ion	Ionic Radius (pm)
Fe ²⁺	92
Fe ³⁺	79

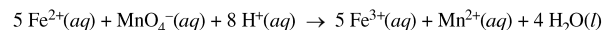
(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe²⁺ ion is larger than the radius of the Fe³⁺ ion.

Both ions have the same nuclear charge; however, the greater number of electrons in the outermost shell of Fe ²⁺ results in greater electron-electron repulsion within that shell, leading to a larger radius.	1 point is earned for a valid explanation.
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(c) Fe³⁺ ions interact more strongly with water molecules in aqueous solution than Fe²⁺ ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

Coulomb's law: $F \propto \frac{q_1 q_2}{r^2}$ (need not be explicitly stated) In comparison to the Fe²⁺ ion, the Fe³⁺ ion has a higher charge. OR The smaller size of Fe³⁺ allows it to get closer to a water molecule.	1 point is earned for a valid explanation.
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A student obtains a solution that contains an unknown concentration of Fe²⁺(aq). To determine the concentration of Fe²⁺(aq) in the solution, the student titrates a sample of the solution with MnO₄[−](aq), which converts Fe²⁺(aq) to Fe³⁺(aq), as represented by the following equation.



(d) Write the balanced equation for the half-reaction for the oxidation of Fe²⁺(aq) to Fe³⁺(aq).

$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e^{-}$	1 point is earned for the correct half-reaction.
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Question 3 (continued)

(e) The student titrates a 10.0 mL sample of the Fe²⁺(aq) solution. Calculate the value of [Fe²⁺] in the solution if it takes 17.48 mL of added 0.0350 M KMnO₄(aq) to reach the equivalence point of the titration.

$17.48 \text{ mL} \times \frac{0.0350 \text{ mol KMnO}_4}{1000 \text{ mL}} = 0.000612 \text{ mol KMnO}_4$ $0.000612 \text{ mol KMnO}_4 \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol KMnO}_4} = 0.003059 \text{ mol Fe}^{2+}$ $\frac{0.003059 \text{ mol Fe}^{2+}}{0.0100 \text{ L}} = 0.306 \text{ M Fe}^{2+}$	1 point is earned for calculating the number of moles of KMnO₄ (may be implicit). 1 point is earned for the correct concentration of Fe²⁺(aq).
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To deliver the 10.0 mL sample of the Fe²⁺(aq) solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

(f) Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the Fe²⁺(aq) solution.

The volumetric flask is designed to contain only 25.00 mL precisely.	1 point is earned for a valid explanation.
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Question 3 (continued)

In a separate experiment, the student is given a sample of powdered Fe(s) that contains an inert impurity. The student uses a procedure to oxidize the Fe(s) in the sample to Fe₂O₃(s). The student collects the following data during the experiment.

Mass of Fe(s) with inert impurity	6.724 g
Mass of Fe ₂ O ₃ (s) produced	7.531 g

(g) Calculate the number of moles of Fe in the Fe₂O₃(s) produced.

$7.531 \text{ g Fe}_2\text{O}_3 \times \frac{1 \text{ mol Fe}_2\text{O}_3}{159.70 \text{ g Fe}_2\text{O}_3} = 0.04716 \text{ mol Fe}_2\text{O}_3$ $0.04716 \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} = 0.09431 \text{ mol Fe}$	1 point is earned for correct calculation.
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(h) Calculate the percent by mass of Fe in the original sample of powdered Fe(s) with the inert impurity.

$0.09431 \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{1 \text{ mol}} = 5.267 \text{ g Fe}$ $\frac{5.267 \text{ g Fe}}{6.724 \text{ g sample}} \times 100 = 78.33\%$	1 point is earned for correct calculation of the mass percent based on the answer to part (g).
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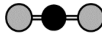
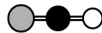
(i) If the oxidation of the Fe(s) in the original sample was incomplete so that some of the 7.531 g of product was FeO(s) instead of Fe₂O₃(s), would the calculated mass percent of Fe(s) in the original sample be higher, lower, or the same as the actual mass percent of Fe(s)? Justify your answer.

The calculated mass percent of Fe would be lower than the actual mass percent of Fe. A sample that contains any FeO (rather than Fe₂O₃) will have a higher <u>actual</u> mass percent of Fe than a completely oxidized sample would have. Therefore, when the moles of Fe are calculated (assuming all the mass of the sample is Fe₂O₃) the <u>calculated</u> number of moles of Fe, and hence the <u>calculated</u> mass percent of Fe, will be lower.	1 point is earned for the correct answer and a valid explanation.
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Question 4

Sulfur atom = 	Carbon atom = 	Oxygen atom = 
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Compound	Molecular Structure	Boiling Point at 1 atm (K)
CS ₂		319
COS		223

The table above gives the molecular structures and boiling points for the compounds CS₂ and COS.

(a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of CS₂(l) is higher than that of COS(l).

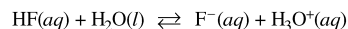
CS₂ has only London dispersion forces, while COS has London dispersion forces and dipole-dipole forces. The London dispersion forces in CS₂ are stronger than the combination of London dispersion forces and dipole-dipole forces in COS.	1 point is earned for correctly identifying all of the intermolecular forces in both molecules. 1 point is earned for a valid explanation.
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(b) A 10.0 g sample of CS₂(l) is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the CS₂(l) has vaporized. What is the pressure in the container once all of the CS₂(l) has vaporized?

$10.0 \text{ g CS}_2 \times \frac{1 \text{ mol CS}_2}{76.13 \text{ g CS}_2} = 0.131 \text{ mol CS}_2$ $P = \frac{nRT}{V} = \frac{(0.131 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(325 \text{ K})}{5.0 \text{ L}}$ $= 0.70 \text{ atm}$	1 point is earned for the correct number of moles of CS₂. 1 point is earned for the correct calculation of pressure with appropriate units.
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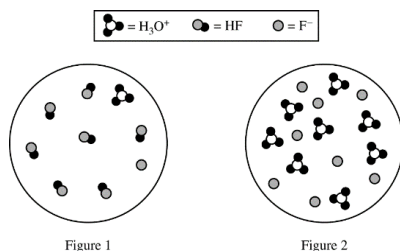
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Question 5



The ionization of $\text{HF}(aq)$ in water is represented by the equation above. In a 0.0350 M $\text{HF}(aq)$ solution, the percent ionization of HF is 13.0 percent.

- (a) Two particulate representations of the ionization of HF molecules in the 0.0350 M $\text{HF}(aq)$ solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)



HF is a weak acid and is only partially ionized. This fact is consistent with Figure 1, which shows that one out of eight (~13%) HF molecules is ionized (to form one H_3O^+ and one F^-).

OR

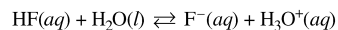
Figure 2 cannot represent HF because it represents 100% ionization of the acid.

1 point is earned for a valid explanation.

- (b) Use the percent ionization data above to calculate the value of K_a for HF .

Assume $[\text{H}_3\text{O}^+] = [\text{F}^-]$ in $\text{HF}(aq)$.

$$\frac{[\text{H}_3\text{O}^+]}{0.0350\text{ M}} = 0.130 \Rightarrow [\text{H}_3\text{O}^+] = 0.00455\text{ M}$$



I	0.0350	0	~0
C	-0.00455	+0.00455	+0.00455
E	0.0304	0.00455	0.00455

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(0.00455)^2}{(0.0304)} = 6.81 \times 10^{-4}$$

1 point is earned for the correct calculation of $[\text{H}_3\text{O}^+]$.

1 point is earned for a value of K_a consistent with the calculated value of $[\text{H}_3\text{O}^+]$.

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Question 5 (continued)

- (c) If 50.0 mL of distilled water is added to 50.0 mL of 0.035 M $\text{HF}(aq)$, will the percent ionization of $\text{HF}(aq)$ in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation.

The percent ionization of HF in the solution would increase.

Doubling the volume of the solution decreases the initial concentration of each species by one-half; therefore,

$$Q = \frac{(\frac{1}{2}[\text{H}_3\text{O}^+]_i)(\frac{1}{2}[\text{F}^-]_i)}{\frac{1}{2}[\text{HF}]_i} = \frac{1}{2}K_a \Rightarrow Q < K_a.$$

Consequently the equilibrium position will shift toward the products and increase the percent ionization.

OR

New volume = twice original volume, thus new $[\text{HF}]_i = \frac{0.035}{2} = 0.0175\text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = 6.81 \times 10^{-4} \text{ (value from part (b))}$$

Let $[\text{H}_3\text{O}^+] = [\text{F}^-] = x$

$$\text{Then } 6.81 \times 10^{-4} = \frac{(x)(x)}{(0.0175 - x)} \approx \frac{x^2}{(0.0175)} \Rightarrow x \approx 0.00345\text{ M}$$

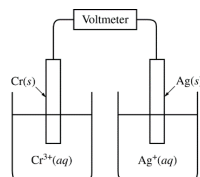
$$\text{Percent ionization} = \frac{0.00345\text{ M}}{0.0175\text{ M}} \times 100 = 20.0\%$$

20.0% > 13.0%; therefore, the percent ionization increases.

1 point is earned for a correct answer and a valid explanation or calculation.

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Question 6



A student sets up a galvanic cell at 298 K that has an electrode of Ag(s) immersed in a 1.0 M solution of Ag⁺(aq) and an electrode of Cr(s) immersed in a 1.0 M solution of Cr³⁺(aq), as shown in the diagram above.

- (a) The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

The salt bridge is missing. The salt bridge allows for the migration of ions to maintain charge balance in each half-cell.

1 point is earned for the correct answer and a valid explanation.

Half-Reaction	E° (V)
$\text{Ag}^+(\text{aq}) + e^- \rightarrow \text{Ag}(\text{s})$	+ 0.80
$\text{Cr}^{3+}(\text{aq}) + 3 e^- \rightarrow \text{Cr}(\text{s})$	?

- (b) The student adds the missing component to the cell and measures E°_{cell} to be +1.54 V. As the cell operates, Ag⁺ ions are reduced. Use this information and the information in the table above to do the following.

- (i) Calculate the value of E° for the half-reaction $\text{Cr}^{3+}(\text{aq}) + 3 e^- \rightarrow \text{Cr}(\text{s})$.

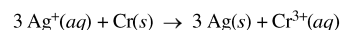
$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

$$+1.54 \text{ V} = +0.80 \text{ V} - x$$

$$x = +0.80 \text{ V} - (+1.54 \text{ V}) = -0.74 \text{ V}$$

1 point is earned for a correct calculation of E°_{red} .

- (ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.



1 point is earned for the correctly balanced equation.

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Question 6 (continued)

- (iii) Calculate the value of ΔG° for the overall cell reaction in J/mol_{rxn}.

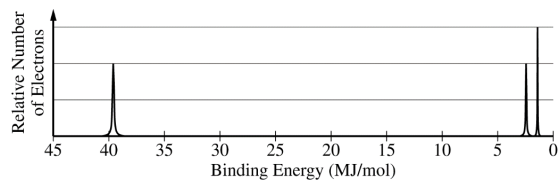
$$\Delta G^\circ = -nFE^\circ = -\left(\frac{3 \text{ mol } e^-}{1 \text{ mol}_{\text{rxn}}}\right)\left(96,485 \frac{\text{C}}{\text{mol } e^-}\right)\left(1.54 \frac{\text{J}}{\text{C}}\right)$$

$$= -4.46 \times 10^5 \text{ J/mol}_{\text{rxn}}$$

1 point is earned for the correct calculation of the value of ΔG° .

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Question 7



The complete photoelectron spectrum of an element is represented above.

(a) Identify the element.

The element is nitrogen, N.	1 point is earned for correctly identifying the element.
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A radioactive isotope of the element decays with a half-life of 10. minutes.

(b) Calculate the value of the rate constant, k , for the radioactive decay. Include units with your answer.

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10. \text{ min}} = 0.069 \text{ min}^{-1}$	1 point is earned for the correct numerical answer. 1 point is earned for the correct unit.
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(c) If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

$64 \rightarrow 32 \rightarrow 16 \rightarrow 8 \rightarrow 4 \rightarrow 2 \rightarrow 1$ 6 half-lives are required. $6 \times 10. \text{ min} = 60. \text{ min}$ OR $\ln[A]_t - \ln[A]_0 = -kt$ $t = \frac{\ln(1) - \ln(64)}{-0.069 \text{ min}^{-1}} = 60. \text{ min}$	1 point is earned for the correct answer <u>and</u> a valid method.
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