AP[°]

AP[®] Chemistry 2012 Scoring Guidelines

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Question 1 (10 points)

A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

Volume of 0.250 <i>M</i> NaOH Added (mL)	pH of Titrated Solution
0.00	?
10.0	3.72
20.0	4.20
30.0	?
40.0	8.62
50.0	12.40

(a) Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.

The pH at the equivalence point is above 7, which indicates that HA is a weak acid.	1 point is earned for the correct explanation.
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(b) Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

$\mathrm{HA}(aq) + \mathrm{OH}^{-}(aq) \rightarrow \mathrm{A}^{-}(aq) + \mathrm{H}_{2}\mathrm{O}(l)$	1 point is earned for writing the net-ionic equation balanced for mass and charge.
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(c) Calculate the number of moles of HA that were titrated.

At the equivalence point, the number of moles of base added equals the number of moles of acid initially present.	1 point is earned for the correct
$0.0400 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} = 0.0100 \text{ mol HA}$	number of moles.

Question 1 (continued)

(d) Calculate the molar mass of HA.

$MM = \frac{\text{mass of acid}}{\text{moles of acid}} = \frac{1.22 \text{ g}}{0.0100 \text{ mol}} = 122 \text{ g/mol}$	1 point is earned for the correct molar mass.
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The equation for the dissociation reaction of HA in water is shown below.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
 $K_a = 6.3 \times 10^{-5}$

(e) Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 *M*. Determine the pH of the initial HA solution.

$K_{a} = \frac{[\text{H}_{3}\text{O}^{+}][\text{A}^{-}]}{[\text{HA}]}$ 6.3×10 ⁻⁵ = $\frac{(x)(x)}{(0.200 - x)}$; assume that x << 0.200 M. $x = [\text{H}_{3}\text{O}^{+}] = 3.5 \times 10^{-3} M$ pH = $-\log[\text{H}_{3}\text{O}^{+}] = -\log(3.5 \times 10^{-3}) = 2.45$	 point is earned for the appropriate substitution into the <i>K_a</i> expression. point is earned for the correct [H₃O⁺]. point is earned for the calculation of pH.
pii $\log[11_{30}] = \log(5.5 \times 10^{\circ}) = 2.45^{\circ}$	

(f) Calculate the value of $[H_3O^+]$ in the solution after 30.0 mL of NaOH solution is added and the total volume of the solution is 80.0 mL.

$\mathrm{HA} \ + \ \mathrm{OH}^{-} \rightarrow \ \mathrm{A}^{-} \ + \ \mathrm{H}_{2}\mathrm{O}$	
mol before rxn: 0.0100 0.00750 0.00000	
mol after rxn: 0.00250 0.00000 0.00750	1 point is earned for the correct calculation of moles of A^- and HA after the reaction.
$[\text{HA}] = \frac{0.00250 \text{mol}}{0.0800 \text{L}} = 3.13 \times 10^{-2} M$	of moles of A ⁻ and TIA and the reaction.
$[A^{-}] = \frac{0.00750 \text{mol}}{0.0800 \text{L}} = 9.38 \times 10^{-2} M$	
$K_a = \frac{[\mathrm{H}_3\mathrm{O}^+][\mathrm{A}^-]}{[\mathrm{HA}]}$	
$6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2} + x)}{(3.13 \times 10^{-2} - x)}$	1 point is earned for the appropriate substitution into the equilibrium expression.
Assume that $x \ll 9.38 \times 10^{-2} M$ and $3.13 \times 10^{-2} M$,	
then $6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2})}{(3.13 \times 10^{-2})}$	1 point is earned for the correct calculation of $[H_3O^+]$.
$x = [H_3O^+] = 2.10 \times 10^{-5} M.$	

Question 2 (10 points)

A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127°C.

(a) Calculate the number of moles of the hydrocarbon in the vessel.

$n = \frac{PV}{RT} = \frac{(0.200 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(400. \text{ K})}$	1 point is earned for the setup.
$n = 6.09 \times 10^{-3} \text{ mol}$	1 point is earned for the numerical answer.

(b) $O_2(g)$ is introduced into the same vessel containing the hydrocarbon. After the addition of the $O_2(g)$, the total pressure of the gas mixture in the vessel is 1.40 atm at 127°C. Calculate the partial pressure of $O_2(g)$ in the vessel.

$P_{\rm O_2} = 1.40 \text{ atm} - 0.200 \text{ atm} = 1.20 \text{ atm}$	1 point is earned for the correct pressure.	
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The mixture of the hydrocarbon and oxygen is sparked so that a complete combustion reaction occurs, producing $CO_2(g)$ and $H_2O(g)$. The partial pressures of these gases at 127°C are 0.600 atm for $CO_2(g)$ and 0.800 atm for $H_2O(g)$. There is $O_2(g)$ remaining in the container after the reaction is complete.

(c) Use the partial pressures of $CO_2(g)$ and $H_2O(g)$ to calculate the partial pressure of the $O_2(g)$ consumed in the combustion.

Question 2 (continued)

(d) On the basis of your answers above, write the balanced chemical equation for the combustion reaction and determine the formula of the hydrocarbon.

The partial pressures occur in the same proportions as the number of moles. $P_{\text{hydrocarbon}}$: P_{O_2} : P_{CO_2} : $P_{\text{H}_2\text{O}}$ 0.200 atm : 1.00 atm : 0.600 atm : 0.800 atm	
$ = 1 : 5 : 3 : 4 C_{3}H_{8} + 5O_{2} \rightarrow 3CO_{2} + 4H_{2}O OR $	1 point is earned for the formula of the hydrocarbon.
$n_{H_2O} = \frac{PV}{RT} = \frac{(0.800 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(400. \text{ K})} = 0.0244 \text{ mol} \text{ H}_2\text{O} \times \frac{2 \text{ mol} \text{ H}}{1 \text{ mol} \text{ H}_2\text{O}}$ = 0.0487 mol H $n_{CO_2} = \frac{PV}{RT} = \frac{(0.600 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(400. \text{ K})} = 0.0183 \text{ mol} \text{ CO}_2 \times \frac{1 \text{ mol} \text{ C}}{1 \text{ mol} \text{ CO}_2}$ = 0.0183 mol C $\frac{0.0487 \text{ mol} \text{ H}}{0.0183 \text{ mol} \text{ C}} = \left(\frac{2.66 \text{ mol} \text{ H}}{1 \text{ mol} \text{ C}}\right) \left(\frac{3}{3}\right) = \frac{8 \text{ mol} \text{ H}}{3 \text{ mol} \text{ C}} \Rightarrow \text{C}_3\text{H}_8$ $\text{C}_3\text{H}_8 + 5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 4 \text{ H}_2\text{O}$	1 point is earned for a balanced equation with the correct proportions among reactants and products.

(e) Calculate the mass of the hydrocarbon that was combusted.

mass = (number of moles)(molar mass)	1 point is earned for using the number of moles combusted from part (a).
$= (6.09 \times 10^{-3} \text{ mol})(44.1 \text{ g/mol}) = 0.269 \text{ g}$	1 point is earned for the calculated mass.

(f) As the vessel cools to room temperature, droplets of liquid water form on the inside walls of the container. Predict whether the pH of the water in the vessel is less than 7, equal to 7, or greater than 7. Explain your prediction.

The pH will be less than 7 because CO_2 is soluble	1 point is earned for the correct choice and explanation.
in water, with which it reacts to form H^+ ions.	F

Ouestion 3 (9 points) $H \stackrel{H}{-} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{-} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{\stackrel{H}{-} \stackrel{H}{\longrightarrow} \stackrel{H}{\rightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\rightarrow$

A sample of $CH_3CH_2NH_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, <i>S</i> °, in J/(mol·K) at 298 K
$CH_3CH_2NH_2(g)$	284.9
$CH_2CH_2(g)$	219.3
$NH_3(g)$	192.8

(a) Using the data in the table above, calculate the value, in $J/(mol_{rxn} \cdot K)$, of the standard entropy change, ΔS° , for the reaction at 298 K.

$\Delta S_{rxn}^{\circ} = \Sigma S_{products}^{\circ} - \Sigma S_{reactants}^{\circ}$	
$\Delta S_{rxn}^{\circ} = [(219.3 + 192.8) - 284.9] \text{ J/(mol}_{rxn} \cdot \text{K})$	1 point is earned for the correct ΔS° .
$= 127.2 \text{ J/(mol}_{rxn} \cdot \text{K})$	

(b) Using the data in the table below, calculate the value, in kJ/mol_{*rxn*}, of the standard enthalpy change, ΔH° , for the reaction at 298 K.

Bond	C–C	C = C	С-Н	C–N	N-H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

 $\Delta H^{\circ} = \text{enthalpy of bonds broken - enthalpy of bonds formed}$ $\Delta H^{\circ} = [5(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}}) + 2(\Delta H_{\text{N-H}})] - [4(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C=C}}) + 3(\Delta H_{\text{N-H}})]$ $= [5(413) + 293 + 348 + 2(391)] - [4(413) + 614 + 3(391)] = 49 \text{ kJ/mol}_{rxn}$ OR $\Delta H^{\circ} = [(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}})] - [(\Delta H_{\text{C=C}}) + (\Delta H_{\text{N-H}})]$ $= [413 + 293 + 348] \text{ kJ/mol} - [614 + 391] \text{ kJ/mol} = 49 \text{ kJ/mol}_{rxn}$

Question 3 (continued)

(c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

The temperature of the contents should decrease because the reaction is endothermic, as indicated by the positive ΔH° .	1 point is earned for the correct choice with explanation.
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An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of CH₃CH₂NH₂ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the CH₃CH₂NH₂ is found to be 3.60×10^{-4} mol/L.

(d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.

$\ln[A]_t - \ln[A]_o = -kt$	1 point is earned for the initial concentration of $CH_3CH_2NH_2$.
$\ln(3.60 \times 10^{-4} \text{ mol/L}) - \ln\left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right) = -k(20.0 \text{ min})$ -7.929 - (-6.053) = -k(20.0 min)	1 point is earned for the correct setup of the first order integrated rate law equation.
$k = 9.38 \times 10^{-2} \mathrm{min}^{-1}$	1 point is earned for the calculated result with unit.

(e) Calculate the initial rate, in $M \min^{-1}$, of the reaction at 773 K.

initial rate =
$$k[CH_3CH_2NH_2] = (9.38 \times 10^{-2} \text{ min}^{-1}) \left(\frac{4.70 \times 10^{-3} \text{ mol}}{2.00 \text{ L}}\right)$$
 1 point is earned for the calculated result.

(f) If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

The plot would produce a curve; had the reaction been second order	1 point is earned for the correct
the plot would have been a straight line. A plot of ln[CH ₃ CH ₂ NH ₂]	choice with explanation.
vs. t would have yielded a straight line.	*

Question 4 (15 points)

(a) A piece of solid strontium carbonate is dropped into a 0.1 M solution of hydrochloric acid.

(i) Balanced equation:	1 point is earned for the correct reactants.
$2 \text{ H}^+ + \text{SrCO}_3 \rightarrow \text{Sr}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	2 points are earned for the correct products.
OR, H ⁺ + SrCO ₃ \rightarrow Sr ²⁺ + HCO ₃ ⁻	1 point is earned for correctly balancing the equation for mass and charge.

(ii) Indicate one thing that would be observed as the reaction occurs.

The solid dissolves OR a gas is given off.	1 point is earned for either observation.
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(b) Magnesium metal is strongly heated in oxygen gas.

(i) Balanced equation:	2 points are earned for the correct reactants.
$2 \text{ Mg} + \text{O}_2 \rightarrow 2 \text{ MgO}$	 point is earned for the correct product. point is earned for correctly balancing the equation for mass and charge.

(ii) What is the oxidation number of magnesium before the reaction occurs, and what is the oxidation number of magnesium after the reaction is complete?

Oxidation number before = 0 . Oxidation number after = $+2$.	1 point is earned for two correct responses.
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Question 4 (continued)

(c) A solution of nickel(II) chloride is added to a solution of sodium hydroxide, forming a precipitate.

(i) Balanced equation:	2 points are earned for the correct reactants.
$Ni^{2+} + 2 OH^{-} \rightarrow Ni(OH)_{2}$	1 point is earned for the correct product.
	1 point is earned for correctly balancing the equation for mass and charge.

(ii) If equal volumes of 1.0 M nickel (II) chloride and 1.0 M sodium hydroxide are used, what ion is present in the solution in the highest concentration after the precipitate forms?

The chloride ion	1 point is earned for the correct ion.
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Question 5 (8 points)

Process	$\Delta H^{\circ} (\text{kJ/mol}_{rxn})$
$\operatorname{Br}_2(l) \to \operatorname{Br}_2(g)$	30.91
$I_2(s) \rightarrow I_2(g)$	62.44

At 298 K and 1 atm, the standard state of Br_2 is a liquid, whereas the standard state of I_2 is a solid. The enthalpy changes for the formation of $Br_2(g)$ and $I_2(g)$ from these elemental forms at 298 K and 1 atm are given in the table above.

(a) Explain why ΔH° for the formation of $I_2(g)$ from $I_2(s)$ is larger than ΔH° for the formation of $Br_2(g)$ from $Br_2(l)$. In your explanation identify the type of particle interactions involved and a reason for the difference in magnitude of those interactions.

Two reasons may be given. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar	1 point is earned for identifying London dispersion forces.
molecules, will be stronger in I_2 because of its greater number of electrons and larger size. The second reason is that since ΔH of sublimation is approximately ΔH of fusion plus ΔH of vaporization, $I_2(g)$ should have a larger ΔH° of formation since it involves sublimation, whereas $Br_2(g)$ formation involves only vaporization.	1 point is earned for either of the following: explaining the reason for the greater LDFs in I ₂ OR stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.

(b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.

$I_2(s) \rightarrow I_2(g)$ should have the greater change in entropy. The sublimation of I_2 may be thought of as a combination of fusion and vaporization. The conversion from solid to liquid would involve an increase in entropy, as would the conversion from liquid to gas. Br ₂ is only undergoing the liquid to gas conversion and so will undergo a smaller entropy increase.	1 point is earned for the correct choice with a correct explanation.
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Question 5 (continued)

(c) $I_2(s)$ and $Br_2(l)$ can react to form the compound IBr(l). Predict which would have the greater molar enthalpy of vaporization, IBr(l) or $Br_2(l)$. Justify your prediction.

IBr(l). Two reasons may be given. First, IBr is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, IBr should have stronger London dispersion forces because of the greater number of electrons in the larger IBr molecule.	1 point is earned for the correct choice with either or both of the acceptable reasons.
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An experiment is performed to compare the solubilities of $I_2(s)$ in different solvents, water and hexane (C_6H_{14}). A student adds 2 mL of H_2O and 2 mL of C_6H_{14} to a test tube. Because H_2O and C_6H_{14} are immiscible, two layers are observed in the test tube. The student drops a small, purple crystal of $I_2(s)$ into the test tube, which is then corked and inverted several times. The C_6H_{14} layer becomes light purple, while the H_2O layer remains virtually colorless.

(d) Explain why the hexane layer is light purple while the water layer is virtually colorless. Your explanation should reference the relative strengths of interactions between molecules of I_2 and the solvents H_2O and C_6H_{14} , and the reasons for the differences.

The hexane layer is purple because most of the I_2 is dissolved in it. The entrance of the I_2 into water requires disruption of the hydrogen bonds in water, which are much stronger than the London dispersion forces in hexane. Meanwhile, the London dispersion forces between I_2 and hexane would be stronger than the London dispersion forces between I_2 and water. (Water and I_2 can also interact through a dipole-induced dipole force, but this attraction is insufficient to overcome the other differences noted above.)	 point is earned for recognizing from the experimental observations that the iodine dissolved in the hexane. point is earned for a correct explanation referencing the differences between water and hexane in their interactions with I₂.
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- (e) The student then adds a small crystal of KI(s) to the test tube. The test tube is corked and inverted several times. The I⁻ ion reacts with I₂ to form the I₃⁻ ion, a linear species.
 - (i) In the box below, draw the complete Lewis electron-dot diagram for the I_3^- ion.

Question 5 (continued)

(ii) In which layer, water or hexane, would the concentration of I_3^- be higher? Explain.

I_3^- would be more soluble in water because of the ion-dipole interactions that would occur between the ions and the polar water	1 point is earned for the correct choice and explanation.	
molecules. No such interactions are possible in the nonpolar hexane.	enoice and explanation.	

Question 6 (9 points)

In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

- Observation 1: $Pb(s) + X^{2+}(aq) \rightarrow Pb^{2+}(aq) + X(s)$ Observation 2: $Q(s) + X^{2+}(aq) \rightarrow$ no reaction Observation 3: $Pb(s) + Q^{2+}(aq) \rightarrow Pb^{2+}(aq) + Q(s)$
- (a) On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to most reactive on the lines provided below.

Q,X	, <u>Pb</u>
least reactive metal	most reactive metal
Q, X, Pb	2 points are earned for the correctly ordered relationship.
	(1 point earned for Q, Pb, X or X, Q, Pb)

Question 6 (continued)

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of $1.0 M Pb(NO_3)_2(aq)$ and an electrode made of metal X immersed in 100. mL of $1.0 M X(NO_3)_2(aq)$. A salt bridge containing saturated aqueous KNO₃ connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.



(b) Write the equation for the half-reaction that occurs at the anode.

$Pb(s) \rightarrow Pb^{2+}(aq) + 2 e^{-}$	1 point is earned for the correct equation.	
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- (c) The value of the standard potential for the cell, E° , is 0.47 V.
 - (i) Determine the standard reduction potential for the half-reaction that occurs at the cathode.

 $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$ $E_{cathode}^{\circ} = E_{cell}^{\circ} + E_{anode}^{\circ}$ $E_{cathode}^{\circ} = 0.47 + (-0.13) = 0.34 \text{ V}$ 1 point is earned for the calculated reduction potential with mathematical justification.

Question 6 (continued)

(ii) Determine the identity of metal X.

The metal is copper.	1 point is earned for identification of the metal.

(d) Describe what happens to the mass of each electrode as the cell operates.

The mass of the Pb electrode decreases and the mass of the Cu electrode increases.	1 point is earned for <u>both</u> descriptions.
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- (e) During a laboratory session, students set up the electrochemical cell shown above. For each of the following three scenarios, choose the correct value of the cell voltage and justify your choice.
 - (i) A student bumps the cell setup, resulting in the salt bridge losing contact with the solution in the cathode compartment. Is V equal to 0.47 or is V equal to 0? Justify your choice.

(ii) A student spills a small amount of $0.5 M \text{ Na}_2\text{SO}_4(aq)$ into the compartment with the Pb electrode, resulting in the formation of a precipitate. Is V less than 0.47 or is V greater than 0.47 ? Justify your choice.

V > 0.47 V. The sulfate ion will react with the Pb ²⁺ ion to form a precipitate. This results in a thermodynamically favored anode half-cell reaction and hence a larger potential difference. The choice may also be justified using the Nernst equation. $E_{cell} = E_{cell}^{\circ} - \left(\frac{RT}{nF}\right) \ln \frac{[Pb^{2+}]}{[Cu^{2+}]}$	1 point is earned for the correct choice with an appropriate explanation.
Decreasing the $[Pb^{2+}]$ will increase the cell voltage.	

(iii) After the laboratory session is over, a student leaves the switch closed. The next day, the student opens the switch and reads the voltmeter. Is V less than 0.47 or is V equal to 0.47? Justify your choice.

$V < 0.47 V$. Over time, $[Pb^{2+}]$ increases and $[Cu^{2+}]$ decreases, making both half-cell reactions less thermodynamically favorable. The choice may also be justified using the Nernst equation. Increasing $[Pb^{2+}]$ and decreasing $[Cu^{2+}]$ decreases the cell voltage. The choice may also be justified by stating that the voltage is zero as a result of the establishment of equilibrium.	1 point is earned for the correct choice with an appropriate explanation.
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