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.

<table>
<thead>
<tr>
<th>Volume of 0.250 M NaOH Added (mL)</th>
<th>pH of Titrated Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>?</td>
</tr>
<tr>
<td>10.0</td>
<td>3.72</td>
</tr>
<tr>
<td>20.0</td>
<td>4.20</td>
</tr>
<tr>
<td>30.0</td>
<td>?</td>
</tr>
<tr>
<td>40.0</td>
<td>8.62</td>
</tr>
<tr>
<td>50.0</td>
<td>12.40</td>
</tr>
</tbody>
</table>

(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. One point is earned for the correct explanation.

(b) Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

HA(aq) + OH⁻(aq) → A⁻(aq) + H₂O(l) One point is earned for the correct equation.

(c) Calculate the number of moles of HA that were titrated.

At the equivalence pt., moles of base added equals moles of acid initially present.
Moles of acid = moles of base = M x V = (0.250M)(0.0400L)

\[ n_A = n_B = 0.0100 \text{ moles} \]

One point is earned for the correct number of moles calculated.

(d) Calculate the molar mass of HA.

molar mass = \frac{\text{mass of acid}}{n_A} = \frac{1.22 \text{ g}}{0.0100 \text{ mol}} = 122 \text{ g/mol} One point is earned for the correctly calculated molar mass.
Question 1 (continued)

The equation for the dissociation reaction of HA in water is shown below.

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \quad K_a = 6.3 \times 10^{-5}
\]

(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.

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = 6.3 \times 10^{-5}
\]

\[
x = [\text{H}_3\text{O}^+] = [\text{A}^-] = 0.200 - x
\]

\[
K_a = \frac{(x)(x)}{(0.200 - x)}; \text{ assume } x << 0.200
\]

\[
6.3 \times 10^{-5} = \frac{x^2}{0.200}; x = 3.5 \times 10^{-3} \text{M}
\]

\[
pH = - \log [\text{H}_3\text{O}^+] = - \log (3.5 \times 10^{-3}) = 2.45
\]

(f) Calculate the value of [H₃O⁺] in the solution after 30.0 mL of NaOH solution is added and the total volume of the solution is 80.0 mL.

\[
\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}
\]

moles before rctn.: 0.0100 (.0300L)(0.250M)

0.00750

moles after rctn: 0.0025 0 0.0075

Concentrations after establishment of equilibrium:

\[
[\text{H}_3\text{O}^+] = x; \quad [\text{HA}] = \frac{(0.0025 \text{ mol})}{(0.080 \text{ L})} - x; \quad [\text{A}^-] = \frac{(0.0075 \text{ mol})}{(0.080 \text{ L})} + x
\]

Assume x << (0.0025/0.080)

\[
[\text{HA}] = 3.1 \times 10^{-2} \text{M}; \quad [\text{A}^-] = 9.4 \times 10^{-2} \text{M}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = 6.3 \times 10^{-5} = \frac{(x)(9.4 \times 10^{-2} \text{M})}{(3.1 \times 10^{-2} \text{M})}
\]

\[
x = 2.1 \times 10^{-5} \text{M}
\]
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.

\[
\text{n} = \frac{\text{PV}}{\text{RT}} = \frac{(0.200 \text{ atm})(1.00 \text{ L})}{(0.0821 \text{ L-atm/K-mol})(400 \text{ K})} = 6.09 \times 10^{-3} \text{ mol}
\]

One point is earned for the setup.  
One point is earned for numerical answer.

(b) \( \text{O}_2(\text{g}) \) is introduced into the same vessel containing the hydrocarbon. After the addition of the \( \text{O}_2(\text{g}) \), the total pressure of the gas mixture in the vessel is 1.40 atm at 127°C. Calculate the partial pressure of \( \text{O}_2(\text{g}) \) in the vessel.

\[
\text{P}_{\text{O}_2} = (1.40 - 0.20) \text{ atm} = 1.20 \text{ atm}
\]

One point is earned for correct pressure.

The mixture of the hydrocarbon and oxygen is sparked so that a complete combustion reaction occurs, producing \( \text{CO}_2(\text{g}) \) and \( \text{H}_2\text{O}(\text{g}) \). The partial pressures of these gases at 127°C are 0.600 atm for \( \text{CO}_2(\text{g}) \) and 0.800 atm for \( \text{H}_2\text{O}(\text{g}) \). There is \( \text{O}_2(\text{g}) \) remaining in the container after the reaction is complete.

(c) Use the partial pressures of \( \text{CO}_2(\text{g}) \) and \( \text{H}_2\text{O}(\text{g}) \) to calculate the partial pressure of the \( \text{O}_2(\text{g}) \) consumed in the combustion.

\[
\begin{align*}
? \ C_x\text{H}_y + ? \ \text{O}_2 & \rightarrow \ ? \ \text{CO}_2 + ? \ \text{H}_2\text{O} \\
\text{Before rctn.} & \ 0.200 \text{ atm} \quad 1.20 \text{ atm} \quad - \quad - \\
\text{After rctn.} & \ 0 \quad ? \quad 0.600 \text{ atm} \quad 0.800 \text{ atm} \\
\end{align*}
\]

\[
\begin{align*}
0.600 \text{ atm} \ \text{CO}_2 \left( \frac{1 \ \text{ atm} \ \text{O}_2}{1 \ \text{ atm} \ \text{CO}_2} \right) &= 0.600 \text{ atm} \ \text{O}_2 \\
0.800 \text{ atm} \ \text{H}_2\text{O} \left( \frac{1 \ \text{ atm} \ \text{O}_2}{2 \ \text{ atm} \ \text{H}_2\text{O}} \right) &= 0.400 \text{ atm} \ \text{O}_2 \\
\end{align*}
\]

\[
\text{Total O}_2 \ \text{consumed} = 1.000 \text{ atm}
\]

One point is earned for correct stoichiometry in \( \text{O}_2 \) consumption.  
One point is earned for the calculated result.
(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.

\[ \frac{P_{\text{hydrocarb}}}{P_{\text{O}_2}} : \frac{P_{\text{CO}_2}}{P_{\text{H}_2}\text{O}} = \frac{0.200 \text{ atm}}{1.00 \text{ atm}} : \frac{0.600 \text{ atm}}{0.800 \text{ atm}} = 1 : 5 : 3 : 4 \]

\[ \text{C}_3\text{H}_8 + 5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 4 \text{ H}_2\text{O} \]

One point is earned for the formula for the hydrocarbon.
One point is earned for a balanced equation with the right proportions among reactants and products.

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

\[ \text{mass} = (\text{no. of moles}) \times (\text{molar mass}) \]
\[ = (6.09 \times 10^{-3} \text{ mol}) \times (44.0 \text{ g/mol}) = 0.268 \text{ g} \]

One point is earned for the molar mass of the hydrocarbon.
One 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.

pH will be less than 7 because \( \text{CO}_2 \) is soluble in water and is a weak acid.

One point is earned for the correct choice and explanation.
Question 3
(9 points)

A sample of CH₃CH₂NH₂ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

(a) Using the data in the table above, calculate the value, in J/(mol_rxn·K), of the standard entropy change, ΔS°, for the reaction at 298 K.

\[ \Delta S^\circ_{\text{rxn}} = \Sigma S^\circ_{\text{prod}} - \Sigma S^\circ_{\text{react}} \]
\[ \Delta S^\circ_{\text{rxn}} = [(219.3 + 192.8) - 284.9] \text{ J/(mol}_{rxn}\text{-K)} \]
\[ = 127.2 \text{ J/(mol}_{rxn}\text{-K)} \]

(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.

\[ \Delta H^\circ = \text{enthalpy of bonds broken} - \text{enthalpy of bond formed.} \]
\[ \Delta H^\circ = [5(\Delta H_{C-H}) + (\Delta H_{C-N}) + (\Delta H_{C=C}) + 2(\Delta H_{N-H})] - [4(\Delta H_{C-H}) + (\Delta H_{C=C}) + 3(\Delta H_{N-H})] \]

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\[
\Delta H^\circ = \left[(\Delta H_{\text{C-H}}) + (\Delta H_{\text{C-N}}) + (\Delta H_{\text{C-C}})\right] - \left[(\Delta H_{\text{C=C}}) + (\Delta H_{\text{N-H}})\right]
\]

= 49 kJ/mol

\[
\text{rxn count and calculated } \Delta H^\circ.
\]

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 \(\Delta H_{\text{rxn}}\).

An experiment is carried out to measure the rate of the reaction, which is first order. A \(4.70 \times 10^{-3}\) mol sample of \(\text{CH}_3\text{CH}_2\text{NH}_2\) is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the \(\text{CH}_3\text{CH}_2\text{NH}_2\) is found to be \(3.60 \times 10^{-4}\) mol/L.

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

\[
\ln [A]_t - \ln [A]_o = -kt
\]

\[
\ln (3.60 \times 10^{-4} \text{ mol/L}) - \ln (4.70 \times 10^{-3} \text{ mol/2.0 L}) = -k(20.0 \text{ min})
\]

\[
-7.929 - (-6.053) = -k(20.0 \text{ min})
\]

\[
k = 9.38 \times 10^{-2} \text{ min}^{-1}
\]

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

\[
\text{Rate} = k[C_2\text{H}_5\text{NH}_2] = (9.38 \times 10^{-2} \text{ min}^{-1})(4.70 \times 10^{-3} \text{ mol/2.0L})
\]

\[
= 2.20 \times 10^{-4} \text{mol/L} - \text{min}
\]

(f) If \(\frac{1}{[\text{CH}_3\text{CH}_2\text{NH}_2]}\) 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.

A curve. Had the reaction been second order the plot would have been a straight line. A plot of \(\ln[C_2\text{H}_5\text{NH}_2]\) vs. \(t\) would
have yielded a straight line.

**Question 4**
(15 points)

For each of the following three reactions, write a balanced equation for the reaction in part (i) and answer the question about the reaction in part (ii). 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 scored.

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

(i) Balanced equation:

\[
2 \text{H}^+ + \text{SrCO}_3 \rightarrow \text{Sr}^{2+} + \text{CO}_2 + \text{H}_2\text{O}
\]

One point is earned for the correct reactants.

Two points are earned for the correct products.

One point is earned for correctly balancing (mass and charge) the equation.

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

The solid dissolves. A gas is given off. One point is earned for either observation.

(b) Magnesium metal is strongly heated in oxygen gas.

(i) Balanced equation:

\[
\text{Mg} + \text{O}_2 \rightarrow 2 \text{MgO}
\]

One point is earned for the correct reactants.

Two points are earned for the correct product.

One point is earned for correctly balancing (mass and charge) the equation.

(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. One point is earned for two correct responses.
(c) A solution of nickel(II) chloride is added to a solution of sodium hydroxide, forming a precipitate.

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

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

The chloride ion. One point is earned for the correct ion.
At 298 K and 1 atm, the standard state of \( \text{Br}_2 \) is a liquid, whereas the standard state of \( \text{I}_2 \) is a solid. The enthalpy changes for the formation of \( \text{Br}_2(g) \) and \( \text{I}_2(g) \) from these elemental forms at 298 K and 1 atm are given in the table above.

(a) Explain why \( \Delta H^\circ \) for the formation of \( \text{I}_2(g) \) from \( \text{I}_2(s) \) is larger than \( \Delta H^\circ \) for the formation of \( \text{Br}_2(g) \) from \( \text{Br}_2(l) \). 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. Since \( \Delta H \) of sublimation = \( \Delta H \) of fusion plus \( \Delta H \) of vaporization, \( \text{I}_2 \) (g) should have a larger \( \Delta H^\circ \) of formation since it involves sublimation whereas \( \text{Br}_2 \) (g) formation involves only vaporization. The second reason is that the London dispersion forces, the only intermolecular forces involved for both of these non-polar molecules, will be stronger in \( \text{I}_2 \) because of its greater number of electrons and larger size. 

One point is earned for either of the reasons.

One point is earned for identification of the type of intermolecular force involved and explanation of the difference in strength of the force.

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

\( \text{I}_2(s) \rightarrow \text{I}_2(g) \) should have the greater change in entropy. The sublimation of \( \text{I}_2 \) 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. \( \text{Br}_2 \) is only undergoing the liquid to gas conversion hence will undergo a smaller entropy increase.

One point is earned for the correct choice with a correct explanation.

(c) \( \text{I}_2(s) \) and \( \text{Br}_2(l) \) can react to form the compound \( \text{IBr}(l) \). Predict which would have the greater molar enthalpy of vaporization, \( \text{IBr}(l) \) or \( \text{Br}_2(l) \). Justify your prediction.

\( \text{IBr}(l) \). Two reasons may be given. First, \( \text{IBr} \) is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, \( \text{IBr} \) should have stronger London dispersion forces because of the greater number of electrons and larger I atom.

One point is earned for the correct choice with either or both of the acceptable reasons.
Question 5 (continued)

An experiment is performed to compare the solubilities of I\(_2\)(s) in different solvents, water and hexane (C\(_6\)H\(_{14}\)).

A student adds 2 mL of H\(_2\)O and 2 mL of C\(_6\)H\(_{14}\) to a test tube. Because H\(_2\)O and C\(_6\)H\(_{14}\) 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\(_6\)H\(_{14}\) layer becomes light purple, while the H\(_2\)O 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\(_2\)O and C\(_6\)H\(_{14}\), and the reasons for the differences.

The hexane layer is purple because most of the I\(_2\) is dissolved in it. The London dispersion forces between I\(_2\) and C\(_6\)H\(_{14}\) should be much stronger than those between I\(_2\) and H\(_2\)O. Furthermore, entry of the I\(_2\) into water requires disruption of the hydrogen bonds in water, which are relatively stronger than the London dispersion forces in the hexane, which must be overcome to allow I\(_2\) to enter the hexane.

<table>
<thead>
<tr>
<th>Why hexane layer is purple</th>
<th>Why water layer is colorless</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most of I(_2) dissolved in hexane</td>
<td>Disruption of hydrogen bonds in water required</td>
</tr>
</tbody>
</table>

One point is earned for recognizing that the iodine has dissolved in the hexane.

One point is earned for a correct explanation referencing the differences between water and hexane in its interaction with I\(_2\).

(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 I\(_2\) to form the I\(_3^-\) ion, a linear species.

(i) In the box below, draw the complete Lewis electron-dot diagram for the I\(_3^-\) ion.

\[
\begin{array}{c}
\text{I} \\
\vdots \\
\text{I} \\
\vdots \\
\text{I} \\
\vdots \\
\text{I} \\
\end{array}
\]

One point is earned for the correct Lewis diagram.

(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 interaction that would occur between the ion and the polar water. No such interaction is possible in the non-polar hexane.

<table>
<thead>
<tr>
<th>Solubility in water</th>
<th>Solubility in hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Higher</td>
<td>Lower</td>
</tr>
</tbody>
</table>

One point is earned for the correct choice 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: \(\text{Pb}(s) + X^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + X(s)\)
Observation 2: \(\text{Q}(s) + X^{2+}(aq) \rightarrow \text{no reaction}\)
Observation 3: \(\text{Pb}(s) + Q^{2+}(aq) \rightarrow \text{Pb}^{2+}(aq) + \text{Q}(s)\)

(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.

\[
\begin{array}{ccc}
\text{Q} & , & \text{X} & , & \text{Pb} \\
\text{least reactive metal} & , & \text{middle metal} & , & \text{most reactive metal}
\end{array}
\]

One or two points may be earned according to the following scheme:
There are three relationships - Q vs. X, Q vs. Pb and X vs. Pb. If all the relationships are correct, the right order is obtained. Two points are earned. If one relationship is wrong, only one point is earned. If two or three relationships are wrong, no point is earned.

Possibilities:
- Q, X, Pb 2 pts.
- Q, Pb, X 1 pt.
- X, Q, Pb 1 pt.
- All other possibilities are worth 0 pts.

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100 mL of 1.0 M \(\text{Pb(NO}_3\text{)}_2(aq)\) and an electrode made of metal X immersed in 100 mL of 1.0 M \(\text{X(NO}_3\text{)}_2(aq)\). A salt bridge containing saturated aqueous KNO\(_3\) 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.

\[ \text{Pb}(s) \rightarrow \text{Pb}^{2+}(aq) + 2\ e^- \]

One point is earned for the correct equation.

(c) The value of the standard potential for the cell, \( E^\circ \), is 0.47 V.

(i) Determine the standard reduction potential for the half-reaction that occurs at the cathode.

\[
E^\circ_{\text{cell}} = E^\circ_{\text{red,cath}} + E^\circ_{\text{ox,anode}} = E^\circ_{\text{red,cath}} - E^\circ_{\text{red,anode}}
\]

\[
E^\circ_{\text{red,anode}} = E^\circ_{\text{red,Pb}} = -0.13V
\]

\[
E^\circ_{\text{cell}} = 0.47V = E^\circ_{\text{red,cath}} - (-0.13V)
\]

\[
E^\circ_{\text{red,cath}} = 0.34V
\]

One point is earned for the calculated reduction potential.

(ii) Determine the identity of metal X.

The metal is copper.

One 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 decreases while the mass of Cu increases.  
One point is earned for both descriptions being correct.

(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.

$V = 0$. If the circuit is broken, no voltage difference is measurable.  
One point is earned for the correct choice with explanation.

(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.

$V$ is greater than 0.47V. Precipitation lowers $[\text{Pb}^{2+}]$, resulting in a thermodynamically more favorable anode reaction, hence a larger potential difference.  
One point is earned for the correct choice with explanation.

(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.

$V$ is less than 0.47V. As current is drawn, $[\text{Pb}^{2+}]$ increases making the anode reaction less favorable, and $[\text{Cu}^{2+}]$ decreases making the cathode reaction less favorable. Both factors would decrease the potential difference. The choice may also be justified using the Nernst equation:

$$E_{\text{cell}} = E_{\text{o cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]}$$

Increasing $[\text{Pb}^{2+}]$ and decreasing $[\text{Cu}^{2+}]$ both decrease $E_{\text{cell}}$. (Nernst may also be used in (ii).)  
One point is earned for the correct choice with either explanation.