A student investigates the enthalpy of solution, \( \Delta H_{\text{soln}} \), for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of \( \pm 0.1 \text{ g} \), and a thermometer with a precision of \( \pm 0.1 \text{°C} \).

(a) To measure \( \Delta H_{\text{soln}} \) for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl\(_{(s)}\), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C.

(i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is 4.18 J/(g·°C). Include units with your answer.

\[
q = mc\Delta T = (110.0 \text{ g})(4.18 \text{ J/(g·°C)})(35.6\text{°C} - 15.0\text{°C})
\]

\[
= 9,470 \text{ J} = 9.47 \text{ kJ}
\]

(ii) Determine the value of \( \Delta H_{\text{soln}} \) for LiCl in kJ/mol\(_{\text{rxn}} \).

\[
\frac{10.0 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}}}{0.236 \text{ mol LiCl}} = -40.1 \text{ kJ/mol}_{\text{rxn}}
\]

To explain why \( \Delta H_{\text{soln}} \) for NaCl is different than that for LiCl, the student investigates factors that affect \( \Delta H_{\text{soln}} \), and finds that ionic radius and lattice enthalpy (which can be defined as the \( \Delta H \) associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ionic Radius (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>76</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>102</td>
</tr>
</tbody>
</table>

(b) Write the complete electron configuration for the Na\(^+\) ion in the ground state.

\[1s^2 \ 2s^2 \ 2p^6\]
(c) Using principles of atomic structure, explain why the Na\(^+\) ion is larger than the Li\(^+\) ion.

| The valence electrons in the Na\(^+\) ion are in a higher principal energy level than the valence electrons in the Li\(^+\) ion. Electrons in higher principal energy levels are, on average, farther from the nucleus. | 1 point is earned for a correct explanation based on occupied principal energy levels. |

(d) Which salt, LiCl or NaCl, has the greater lattice enthalpy? Justify your answer.

| LiCl. Because the Li\(^+\) ion is smaller than the Na\(^+\) ion, the Coulombic attractions between ions in LiCl are stronger than in NaCl. This results in a greater lattice enthalpy. | 1 point is earned for the correct choice and justification. |

(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li\(^+\) or Cl\(^-\)) in the boxes below.

See diagram above. 1 point is earned for both identifications.

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the exothermic dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

| There are interactions between Li\(^+\) ions and polar water molecules and between Cl\(^-\) ions and polar water molecules. These are ion-dipole interactions. | 1 point is earned for identifying the particles that interact. 1 point is earned for correctly identifying the type of interaction. |
(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li⁺ or Cl⁻) in the boxes below.

![Diagram of LiCl crystal representation]

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

\[ \Delta H_{\text{fus}} = n \Delta fH_{\text{m}} \]

\[ \Delta H_{\text{fus}} = 110 \cdot 4.18 \frac{J}{g \cdot ^\circ C} \cdot 20.6 ^\circ C \]

\[ 9.47 \text{ KJ} \]

\[ \frac{10.03 \text{ g LiCl}}{1 \text{ mol LiCl}} = 42.94 \text{ g LiCl} = 0.236 \text{ mol LiCl} \]

\[ \frac{9.47 \text{ KJ}}{0.236 \text{ mol LiCl}} = 40.1 \text{ KJ/mol LiCl} \]

\[ \Delta H_{\text{fus}} = 40.1 \text{ KJ/mol LiCl} \]

(g) The Na⁺ ion has a full 2nd energy level, in addition to its 1st. Li⁺ only has 1 energy level. The extra "shell" of electrons makes the atomic radius of Na⁺ much bigger than that of Li⁺.

(h) LiCl has greater lattice enthalpy because the relatively small radius of Li⁺ means the Coulombic attractions between Li⁺ and Cl⁻ are greater than those of NaCl. It takes more energy to separate Li⁺ and Cl⁻ than Na⁺ and Cl⁻.

(i) When LiCl dissolves in water, first, Li⁺ and Cl⁻...
must break the electrostatic attractions between them, their lattice bonds. This is an endothermic process. Next, H₂O molecules must stretch the inter-molecular forces between them, primarily hydrogen bonding, to "make room" for Li⁺ or Cl⁻ ions. This is also endothermic. Finally, the Li⁺ & Cl⁻ are surrounded by H₂O molecules, with the oxygens pointed towards Li⁺ and the hydrogens pointed towards Cl⁻. The strong ion-dipole attractions between water, with a permanent dipole, and Li⁺ or Cl⁻ with charges, causes the formation of new inter-molecular ion-dipole forces. This process is highly exothermic, and releases more energy than is required in the first endothermic steps, which makes dissolution of LiCl exothermic overall.
(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li⁺ or Cl⁻) in the boxes below.

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

1. a) i) \( (100.0 \, \text{g} + 10.0 \, \text{g}) \left( \frac{1.18 \, \text{J/g°C}}{100 \, \text{J/K}} \right) \left( \frac{35.6°C - 15.0°C}{1000 \, \text{J/K}} \right) = 9.47 \, \text{kJ} \)
   
   ii) \(-9.47 \, \text{kJ} / (10.0 \, \text{g} \, \text{LiCl}, 1 \, \text{mol} \, \text{LiCl}, 42.4 \, \text{g}) = -40.2 \, \text{kJ/mol} \approx \Delta H_{\text{soln}}\)

b) Na⁺ = [Ne] = 1s² 2s² 2p⁶

c) The Na⁺ ion is larger than the Li⁺ ion because Na⁺ has more electrons and more energy levels than Li⁺ has, therefore the ion has a greater size.

d) LiCl has a greater lattice enthalpy than NaCl because Li⁺ has a smaller atomic radius, meaning that the Li and Cl atoms are closer together and so are their nuclei, resulting in greater attraction than if the radius was greater and there was a longer distance between the anion and cation.

e) Shown in the diagram.

f) When LiCl dissolves, the positive dipole of H₂O molecules around the hydrogen atoms are attracted to negatively charged Cl⁻ ions, causing London dispersion forces and dipole-dipole interactions. The negative dipole of H₂O molecules around the oxygen atom result in attraction to the Li⁺ ion, forming ionic bonds.
(e) Below is a representation of a portion of a crystal of LiCl. Identify the ions in the representation by writing the appropriate formulas (Li⁺ or Cl⁻) in the boxes below.

[f] The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

(a) \[ \Delta H = q \]
\[ = 110g \left( \frac{4.18 \text{ J}}{\text{g} \cdot \text{K}} \right) (35.6 - 15.6^\circ \text{C}) \]
\[ = 947.8 \text{ J} \leq 9.47 \text{ kJ} \]

(ii) Negative \( \Delta H \), the temperature increases, so more heat is released than absorbed, meaning the reaction is exothermic (heat is a product in exothermic reactions).

(b) \( 1s^22s^22p^6 \)

(c) The Na⁺ ion is larger than the Li⁺ ion because it has more energy levels which causes electron shielding (repulsive forces between electrons) and therefore increases the distance between them.

(d) NaCl has a greater lattice enthalpy due to its larger molar mass. This makes it more polarizable and therefore has stronger IMFs.

(f) LiCl dissociates into its ions Li⁺ and Cl⁻. H₂O is a polar molecule and therefore forms ion-dipole interactions with Li⁺ and Cl⁻ (attracted to O and it respectively). These are strong and in addition with LDFs found between all molecules, the energy released is greater than the energy absorbed by the system when dissociating salts.
AP® CHEMISTRY
2016 SCORING COMMENTARY

Overview

This question assessed the students’ understanding of a range of chemical concepts concerning the physical properties of ionic compounds. The students were asked to comment on a series of scenarios that dealt with a single ionic compound (LiCl), as well as compare/contrast the physical properties of different cations (Li+ vs. Na+) or ionic compounds (LiCl vs. NaCl). In part (a) students were presented with experimental calorimeter data, obtained from the dissolution of LiCl in water, and asked to calculate the magnitude of the heat flowing between the system and its surroundings. With the calculated value for heat energy, students were then asked to calculate the change in enthalpy of solution of LiCl ($\Delta H_{\text{soln}}$) in units of kJ/mol. In part (b) students were asked to write out the complete electron configuration for sodium ion (Na+). In part (c) students were asked to explain why the ionic radius of Na+ is greater than that of Li+. In part (d) students were asked to determine which salt, LiCl or NaCl, has the greater lattice enthalpy and to justify their selection. In part (e) students were provided a diagram of a typical three-dimensional lattice structure composed of small and large ions (represented as black and gray circles, respectively). Students were asked to label each type of circle with the correct ions, either Li+ or Cl−. In part (f) students were presented with a dissolution scenario that offered some information about the thermodynamic properties involved in such a physical change. The students were then asked to identify the particles that are primarily involved in the exothermic process of dissolution and to identify the primary type of interaction that occurs between the particles.

Sample: 1A

Score: 10

This response earned 10 out of 10 possible points. The student earned both points in part (a)(i) for correctly setting up and calculating the amount of heat, with the correct units, absorbed during the dissolution process (inserting a value for $\Delta T$, rather than showing the subtraction of $T_f - T_i$ is accepted). In part (a)(ii) the student correctly calculated the number of moles of LiCl dissolved in water and then used that quantity, along with the value of $q$ from part (a)(i), to correctly calculate the value for $\Delta H_{\text{soln}}$. To complete the second point in part (a)(ii) the student indicated that the dissolution process was exothermic by including the negative sign in $\Delta H_{\text{soln}}$. The student earned the point in part (b) for giving the complete electron configuration for Na+. The point in part (c) was earned by indicating that the sodium ion has a full (occupied) second energy level, whereas the lithium ion only has one energy level. The second sentence of the response for part (c) is not required to earn the point. In part (d) the student correctly identified LiCl as having the larger lattice enthalpy. The point was then earned for a discussion of the smaller lithium ion radius that results in a greater Coulombic attraction between lithium and chloride ions relative to the attractions between sodium and chloride ions, and that more energy is therefore required to separate LiCl into its ions. The point in part (e) was earned for placing Cl− in the box with the arrow pointing toward the large gray circle and Li+ in the box with the arrow pointing toward the small black circle. Although the student goes into great detail about the various interactions (both endothermic and exothermic) associated with dissolution, the student earned 1 point in part (f) by stating that the lithium and chloride ions are surrounded by water molecules with the “oxygens pointed towards Li++” and the “hydrogens pointed towards Cl−.” The second point was earned for stating that ion-dipole attractions are the intermolecular force between the ions and water.
Sample: 1B
Score: 8

This response earned 8 out of 10 possible points. The student earned both points in part (a)(i) for correctly setting up the heat equation and for obtaining the correct value, with proper units, for the heat absorbed. Although the student did not explicitly report a value for the number of moles of LiCl in part (a)(ii), the setup of the mole calculation within the calculation for $\Delta H_{\text{soln}}$ is correct, so the first point was earned. To earn the second point in part (a)(ii) the student calculated the value of $\Delta H_{\text{soln}}$ and indicated that the dissolution process was exothermic by including the negative sign in $\Delta H_{\text{soln}}$. The student earned the point in part (b) for writing the complete electron configuration for Na$. The student did not earn the point in part (c). The argument that Na$ has “more” electrons or “more” energy levels is not sufficient to justify the sodium ion’s larger radius. The student earned the point in part (d) for indicating that there is a greater attraction between lithium and chloride ions because they are closer together due to lithium’s smaller radius. The point in part (e) was earned for placing Cl$ in the box with an arrow pointing toward the large gray circle and Li$ in the box with the arrow pointing toward the small black circle. The student earned the first point in part (f) for naming the particles that are interacting with one another. The second point was not earned because the student identifies the particle interactions as being either dipole-dipole forces or ionic bonds.

Sample: 1C
Score: 6

This response earned 6 out of 10 possible points. The student earned both points in part (a)(i) for correctly setting up the heat equation and for obtaining the correct value, with proper units, for the heat absorbed. The student did not earn either point in part (a)(ii) for stating that the dissolution is exothermic. The point for the electron configuration in part (b) was earned. In part (c) the student explains the larger radius of Na$ by stating that it has “more” energy levels (than Li$) without emphasizing the electron occupation of those energy levels; therefore, the point was not earned. The point in part (d) was not earned for the “larger molar mass” argument. The point in part (e) was earned for placing Cl$ in the box with an arrow pointing toward the large gray circle and for placing Li$ in the box with an arrow pointing toward the small black circle. Both points were earned for the student’s response in part (f). The particles of interest are listed as H$O, Li$, and Cl$, and the primary intermolecular force is identified as ion-dipole.