

**AP<sup>®</sup> CHEMISTRY**  
**2012 SCORING GUIDELINES**

**Question 5**  
**(8 points)**

| Process                                     | $\Delta H^\circ$ (kJ/mol <sub>rxn</sub> ) |
|---------------------------------------------|-------------------------------------------|
| $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$ | 30.91                                     |
| $\text{I}_2(s) \rightarrow \text{I}_2(g)$   | 62.44                                     |

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. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar molecules, will be stronger in $\text{I}_2$ because of its greater number of electrons and larger size. The second reason is that since $\Delta H$ of sublimation is approximately $\Delta H$ 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. | <p>1 point is earned for identifying London dispersion forces.</p> <p>1 point is earned for either of the following:<br/> explaining the reason for the greater LDFs in <math>\text{I}_2</math></p> <p style="text-align: center;">OR</p> <p>stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.</p> |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

- (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 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)  $\text{I}_2(s)$  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 in the larger $\text{IBr}$ molecule. | 1 point is earned for the correct choice with either or both of the acceptable reasons. |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------|

An experiment is performed to compare the solubilities of  $\text{I}_2(s)$  in different solvents, water and hexane ( $\text{C}_6\text{H}_{14}$ ). A student adds 2 mL of  $\text{H}_2\text{O}$  and 2 mL of  $\text{C}_6\text{H}_{14}$  to a test tube. Because  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{14}$  are immiscible, two layers are observed in the test tube. The student drops a small, purple crystal of  $\text{I}_2(s)$  into the test tube, which is then corked and inverted several times. The  $\text{C}_6\text{H}_{14}$  layer becomes light purple, while the  $\text{H}_2\text{O}$  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  $\text{I}_2$  and the solvents  $\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{14}$ , and the reasons for the differences.

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| The hexane layer is purple because most of the $\text{I}_2$ is dissolved in it. The entrance of the $\text{I}_2$ 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 $\text{I}_2$ and hexane would be stronger than the London dispersion forces between $\text{I}_2$ and water. (Water and $\text{I}_2$ can also interact through a dipole-induced dipole force, but this attraction is insufficient to overcome the other differences noted above.) | 1 point is earned for recognizing from the experimental observations that the iodine dissolved in the hexane.<br><br>1 point is earned for a correct explanation referencing the differences between water and hexane in their interactions with $\text{I}_2$ . |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

- (e) The student then adds a small crystal of  $\text{KI}(s)$  to the test tube. The test tube is corked and inverted several times. The  $\text{I}^-$  ion reacts with  $\text{I}_2$  to form the  $\text{I}_3^-$  ion, a linear species.

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

|                                                                      |                                                |
|----------------------------------------------------------------------|------------------------------------------------|
| $\left[ :\ddot{\text{I}}-\ddot{\text{I}}-\ddot{\text{I}}: \right]^-$ | 1 point is earned for a correct Lewis diagram. |
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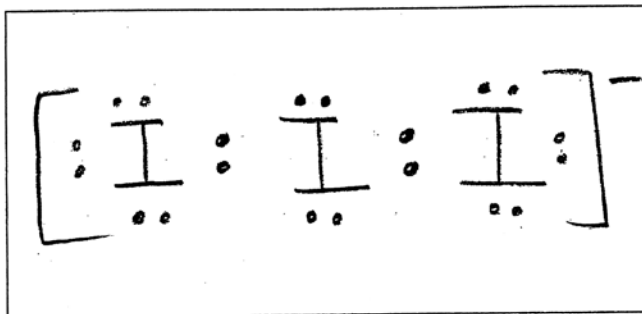
**Question 5 (continued)**

(ii) In which layer, water or hexane, would the concentration of  $\text{I}_3^-$  be higher? Explain.

|                                                                                                                                                                                                                 |                                                           |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| $\text{I}_3^-$ would be more soluble in water because of the ion-dipole interactions that would occur between the ions and the polar water molecules. No such interactions are possible in the nonpolar hexane. | 1 point is earned for the correct choice and explanation. |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|

(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.



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

a) The  $\Delta H^\circ$  for the formation of  $I_2(g)$  from  $I_2(s)$  is larger than  $\Delta H^\circ$  for the formation of  $Br_2(g)$  from  $Br_2(l)$  because of variations in strength of these molecules' London dispersion forces. These dispersion forces create temporary induced dipoles between molecules of  $I_2$  when it is a solid and also between molecules of  $Br_2$  when it is a liquid. The stronger the forces, the more energy needed to overcome the forces keeping the substances from entering their gaseous states. Because  $I_2$  has more electrons than does  $Br_2$ , its London dispersion forces are stronger and it has a greater tendency to stay a solid. Thus its  $\Delta H^\circ$  for the formation of  $I_2(g)$  is greater.

## ADDITIONAL PAGE FOR ANSWERING QUESTION 5

- b)  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$  has a greater change in entropy. Entropy is a measurement of disorder in a system, and solids have less entropy than liquids which have less entropy than gases. Because the initial state of  $\text{Br}_2$  (liquid) already has more entropy than the initial state of  $\text{I}_2$  (solid), the magnitude of the change in entropy for  $\text{I}_2(\text{s})$  to  $\text{I}_2(\text{g})$  must be greater.
- c)  $\text{IBr}(\text{l})$  would have a greater molar heat of vaporization because in its liquid form, it also has dipole-dipole forces keeping its molecules from vaporizing. Dipole-dipole forces are caused from differences in electronegativity and are a stronger intermolecular force than the London dispersion forces with  $\text{Br}_2$ . Thus, the  $\Delta H$  of vaporization for  $\text{IBr}$  must be greater to overcome the stronger forces.
- d) The hexane layer is light purple because some of the  $\text{I}_2$  dissolved into the hexane, a nonpolar solvent.  $\text{I}_2$  is a nonpolar molecule, and the only forces involved with  $\text{I}_2$  are London dispersion forces, which are relatively weak and make  $\text{I}_2$  readily soluble in nonpolar solvents like  $\text{C}_6\text{H}_{14}$ . On the other hand,  $\text{H}_2\text{O}$  is a polar solvent with

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## ADDITIONAL PAGE FOR ANSWERING QUESTION 5

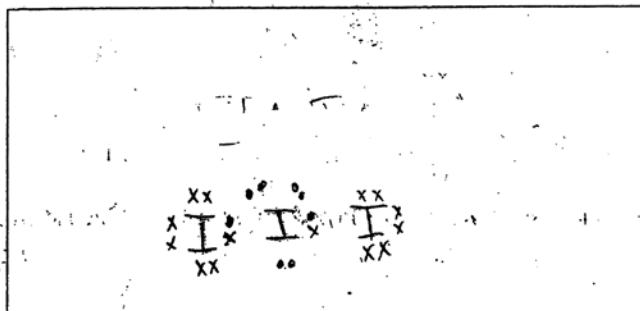
hydrogen bonding b/c of the difference in electronegativity between the O & H atoms in its molecules. Hydrogen bonds are a force of greater strength compared to dispersion forces and therefore, water cannot dissolve  $I_2$ . This explains why the  $H_2O$  remained colorless; the  $H_2O$  nearly repelled the nonpolar  $I_2$ .

e) (ii) The concentration of  $I_3^-$  would be higher in the  $H_2O$  because of  $H_2O$ 's polarity. The water molecule, because of the difference in electronegativity between O & H, is a polar molecule with  $+$  and  $-$  ends. It, as a result, will dissolve more of the negatively charged  $I_3^-$  ion than the nonpolar hexane.

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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  $I_2$  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.



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

a) The enthalpy for the iodine reaction is greater because it jumps two phases. Because it is going from a solid to a gas it requires more heat.  $Br_2$  is only changing to liquid gas from liquid.

b) I believe the  $I_2$  reaction process will have a greater entropy because it starts from a more stable state. It changes from a very orderly state to a chaotic state. The  $Br_2$  changes from an already unorderly state to the chaotic state. The change is more dynamic in the  $I_2$ .

c)  $Br_2$  is a more stable compound and the bonds would require more energy to break giving it a higher enthalpy.

d)  $I_2$  is a symmetrical molecule, making it have no dipole moment.  $I_2$  + hexane are both non-polar. ~~like~~ Non-polar cannot mix with or dissolve into ~~other~~ polar substances.

## ADDITIONAL PAGE FOR ANSWERING QUESTION 5

Water is polar and cannot mix with the hexane or dissolve the  $I_2$ . The Hexane accepts the  $I_2$  + dissolves it because of its non-polarity.

(E)

ii. The conc. of  $I_2$  could be higher in the  $H_2O$  layer because it is Asymmetrical causing it to be polar.  $H_2O$  Dissolves polar substances while Hexane does not.

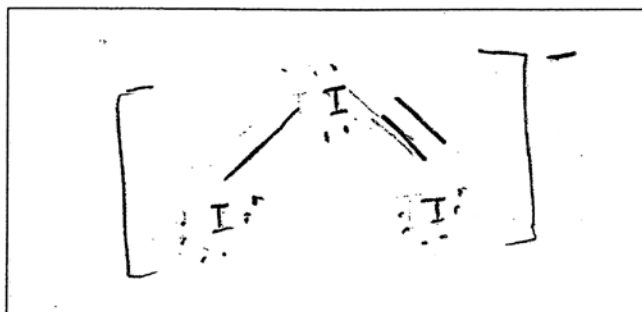
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(e) The student then adds a small crystal of  $KI(s)$  to the test tube. The test tube is corked and inverted several times. The  $I^-$  ion reacts with  $I_2$  to form the  $I_3^-$  ion, a linear species.

(i) In the box below, draw the complete Lewis electron-dot diagram for the  $I_3^-$  ion.

$$7 + 7 + 7 + 1 = 22$$



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

a)  $Br_2$  is vaporizing from a liquid to a gas; in a liquid, the particles are somewhat in motion and apart from one another, so it takes a smaller amount of energy to change the liquid particles into gas particles. The particles of  $I_2$  in a solid state are packed together and are not in much motion; therefore, we need more energy to set those packed particles into fast motion and spread out the particles.

b)  $I_2(s) \rightarrow I_2(g)$  has the greater change of entropy. Entropy measures disorder. A solid has no disorder, while a gas has plenty of disorder, so this change in entropy would be greater than from a liquid, which has some disorder, to a gas.

c)  $IBr(l)$  because it is bigger and more massive than  $Br_2(l)$ ; therefore, more energy is required to set  $IBr$  into fast motion than  $Br_2(l)$ , which is smaller.

## ADDITIONAL PAGE FOR ANSWERING QUESTION 5

d)  $I_2$  and  $C_6H_{14}$  are non polar molecules, so it would easily dissolve in  $C_6H_{14}$ . However, water is nonpolar, so it is difficult to dissolve  $I_2$  into  $H_2O$ .

e) (i) look at box

(ii) water because  $I_3^-$  is polar, so the  $I_3^-$  would dissolve in  $H_2O$  better

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**AP<sup>®</sup> CHEMISTRY**  
**2012 SCORING COMMENTARY**

**Question 5**

**Overview**

This question asked students to explain the behavior of various aggregations of iodine and bromine in terms of enthalpy and entropy changes and solubility tendencies. In addition, they were asked to represent the  $\text{I}_3^-$  ion as a Lewis electron-dot diagram. Part (a) asked students to explain why the enthalpy of formation of  $\text{I}_2(g)$  exceeds that of  $\text{Br}_2(g)$ . They were instructed to identify the type of particle interactions involved and to provide a reason for the difference in magnitude of these interactions. Part (b) asked students to predict which of the two processes in part (a) would have a greater change in entropy and to provide a justification for their prediction. Part (c) asked students to predict whether  $\text{IBr}(l)$  or  $\text{Br}_2(l)$  would have a greater molar enthalpy of vaporization and to justify their predictions. Part (d) described an experimental procedure and observation involving the combination of water, hexane ( $\text{C}_6\text{H}_{14}$ ), and a crystal of solid  $\text{I}_2$ . Students were asked to explain the observation and to reference the relative strengths of interactions between the two solvents and the crystal. In part (e) students were told a small crystal of  $\text{KI}(s)$  was added to the combination of chemicals described in part (d). In part (e)(i) students were asked to draw the complete Lewis electron-dot diagram for the  $\text{I}_3^-$  ion. Finally, in part (e)(ii) they were asked to state which solvent layer would contain the higher concentration of  $\text{I}_3^-$  and to explain why.

**Sample: 5A**  
**Score: 7**

Part (e)(i) did not earn the point because the central iodine atom is missing one lone pair of electrons.

**Sample: 5B**  
**Score: 5**

Part (a) earned 1 point for the statement that the enthalpy change from a solid to a gas requires more energy (heat) than the change from a liquid to a gas. Part (c) did not earn the point because the  $\text{Br}_2$  is incorrectly identified as having a greater molar enthalpy. Part (e)(ii) did not earn the point because the response states that  $\text{I}_3^-$  is a polar species.

**Sample: 5C**  
**Score: 3**

Part (a) earned 1 point for the statement that the vaporization of  $\text{Br}_2$  involves a smaller enthalpy change than the conversion of  $\text{I}_2$  solid to a gas. Part (c) did not earn the point because there is no mention of London dispersion or dipole-dipole forces. Part (d) earned 1 point for indicating that the  $\text{I}_2$  would easily dissolve in the  $\text{C}_6\text{H}_{14}$ . The second point was not earned because the student incorrectly states that water is nonpolar. Part (e)(i) did not earn the point because the Lewis structure includes a double bond where there should not be one. Part (e)(ii) did not earn the point because the  $\text{I}_3^-$  ion is identified as polar.