

**AP<sup>®</sup> CHEMISTRY**  
**2006 SCORING GUIDELINES (Form B)**

**Question 3**

3. Answer the following questions about the thermodynamics of the reactions represented below.



(a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}$ <p>Reaction is spontaneous because <math>\Delta G^\circ &lt; 0</math>.</p>	<p>One point is earned for the correct value of <math>\Delta G^\circ</math>.</p> <p>One point is earned for a correct justification of spontaneity.</p>
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(b) Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction X at 25°C.

$\Delta G^\circ = -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT}$ $\ln K_{eq} = -\frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019$ $K_{eq} = e^{2.019} = (7.5314) = 8$	<p>One point is earned for the correct answer.</p>
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(c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ \Rightarrow \ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ <p>Since <math>\Delta H^\circ</math> is positive, an increase in <math>T</math> will cause <math>-\Delta H^\circ/RT</math> to become a smaller negative number, therefore <math>K_{eq}</math> will increase.</p> <p><b>OR</b></p> <p>The reaction is endothermic (<math>\Delta H = +18 \text{ kJ mol}^{-1}</math>); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of <math>K_{eq}</math>.</p>	<p>One point is earned for the correct choice with a correct explanation.</p>
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**AP<sup>®</sup> CHEMISTRY**  
**2006 SCORING GUIDELINES (Form B)**

**Question 3 (continued)**

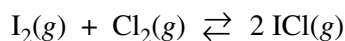
- (d) Explain why the standard entropy change is greater for reaction *Y* than for reaction *X*.

<p>Both reaction <i>X</i> and reaction <i>Y</i> have solid iodine as a reactant, but the second reactant in reaction <i>X</i> is chlorine gas whereas the second reactant in reaction <i>Y</i> is liquid bromine. Liquids have lower entropies than gases, thus in reaction <i>Y</i> the reactants are more ordered (and have lower entropies) than in reaction <i>X</i>. The products of both reaction <i>X</i> and reaction <i>Y</i> have about the same disorder, so the <u>change</u> in entropy from reactants to products is greater in reaction <i>Y</i> than in reaction <i>X</i>.</p>	<p>One point is earned for a correct explanation.</p>
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- (e) Above what temperature will the value of the equilibrium constant for reaction *Y* be greater than 1.0? Justify your answer with calculations.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $K_{eq} = 1 \text{ when } \Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow$ $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K}$ <p>So when <math>T &gt; 330 \text{ K}</math>, <math>\Delta G^\circ &lt; 0 \text{ kJ mol}^{-1} \Rightarrow K_{eq} &gt; 1.0</math></p>	<p>One point is earned for <math>\Delta G^\circ = 0</math>.</p> <p>One point is earned for the correct temperature.</p>
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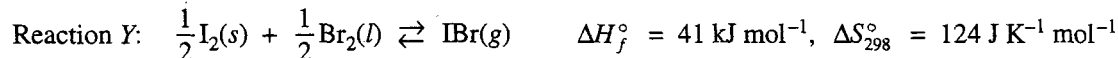
- (f) For the vaporization of solid iodine,  $\text{I}_2(s) \rightarrow \text{I}_2(g)$ , the value of  $\Delta H_{298}^\circ$  is  $62 \text{ kJ mol}^{-1}$ . Using this information, calculate the value of  $\Delta H_{298}^\circ$  for the reaction represented below.



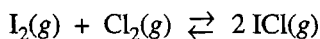
$\begin{array}{l} \text{I}_2(s) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad \Delta H_{298}^\circ = 2 \times 18 \text{ kJ mol}^{-1} \\ \text{I}_2(g) \rightleftharpoons \text{I}_2(s) \quad \Delta H_{298}^\circ = -62 \text{ kJ mol}^{-1} \\ \hline \text{I}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{ICl}(g) \quad \Delta H_{298}^\circ = -26 \text{ kJ mol}^{-1} \end{array}$	<p>One point is earned for <math>\Delta H_{298}^\circ</math> of either the first or second equation.</p> <p>One point is earned for the correct sum of the <math>\Delta H_{298}^\circ</math> values.</p>
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3A1

3. Answer the following questions about the thermodynamics of the reactions represented below.



- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction X at 25°C.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X.
- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.
- (f) For the vaporization of solid iodine,  $\text{I}_2(s) \rightarrow \text{I}_2(g)$ , the value of  $\Delta H_{298}^\circ$  is 62 kJ mol<sup>-1</sup>. Using this information, calculate the value of  $\Delta H_{298}^\circ$  for the reaction represented below.



$$(a) \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = 18 \text{ kJ/mol} - 298 \text{ K} \cdot 78 \text{ J/K} \cdot 10^{-3} \text{ kJ/J}$$

$$= -5.2 \text{ kJ/mol} < 0$$

∴ Since  $\Delta G^\circ < 0$ , it is spontaneous.

$$(b) \Delta G^\circ = -RT \ln K_{eq} = -5.2 \times 10^3 \text{ J/mol}$$

$$\therefore K_{eq} = e^{-\frac{\Delta G^\circ}{RT}} = 8.2$$

(c) Since

$$K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}, \text{ and } \Delta G^\circ < 0, \text{ an increase in } T \text{ would}$$

result in a decrease in  $-\frac{\Delta G^\circ}{RT}$ , which would

result in a smaller  $K_{eq}$ .

(d) In reaction X, gas is present in both the reactants and the products, and the products have 0.5 moles of more gas than reactants.

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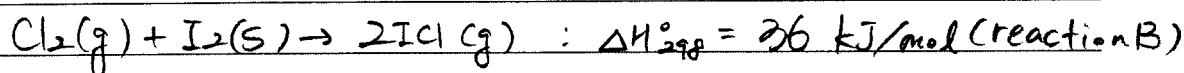
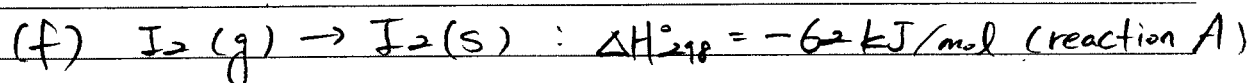
(d) (continued) However, in reaction Y, none of the reactants are at gas phase, and 1 mole of gas are produced after the reaction.

(e) Since  $K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$ ,  $\Delta G^\circ$  must be smaller than zero for  $K_{eq}$  to be greater than 1.0.

$$\therefore \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ < 0$$

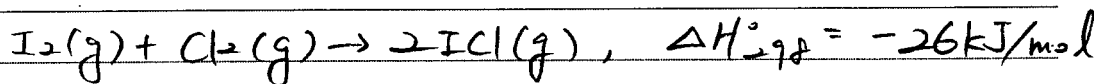
$$41 \text{ kJ/mol} - T \cdot 124 \text{ J/K} \cdot \text{mol} \cdot 10^{-3} \text{ kJ/J} < 0$$

$$\therefore T > 331 \text{ K}$$



Reaction B is derived from reaction X.

add reaction A and reaction B.



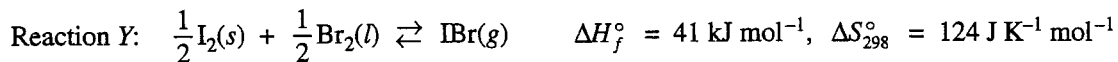
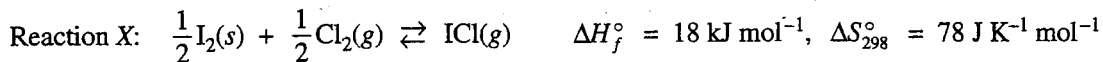
$$\therefore \Delta H_{298}^\circ = -26 \text{ kJ/mol}$$

**STOP**

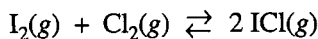
If you finish before time is called, you may check your work on this part only.  
Do not turn to the other part of the test until you are told to do so.

3B<sub>1</sub>

3. Answer the following questions about the thermodynamics of the reactions represented below.



- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction X at 25°C.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X.
- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.
- (f) For the vaporization of solid iodine,  $I_2(s) \rightarrow I_2(g)$ , the value of  $\Delta H_{298}^\circ$  is 62 kJ mol<sup>-1</sup>. Using this information, calculate the value of  $\Delta H_{298}^\circ$  for the reaction represented below.



(a)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
 $T = 298 \text{ K}$

$\therefore \Delta G^\circ = 18000 - 298 \times 78 = -5244 \text{ J}$

Since the Gibbs free energy is negative, reaction X is spontaneous.

(b)  $\Delta G^\circ = -RT \ln K$

$= -8.31 \text{ J/mol K} \times 298 \text{ K} \ln K$

$\Delta G^\circ = (\text{from (a)}) -5244 \text{ J}$

$K_{eq} = \boxed{8.3}$

$K = e^{-\Delta G^\circ / RT} = 8.3112$

(c) increase because increase in temperature will favor forward reaction (since it is endothermic, so it will increase the concentration of ICl. This means that  $K_{eq}$ , which is equal to  $\frac{[ICl]}{[I_2]^{1/2}[Cl_2]^{1/2}}$ , will increase.

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d. Change in entropy means the change in the amount of disorder. In fact compared to the reaction X, which has gaseous reactant and products, the reaction Y only has solid and liquid for its reactants. In fact the change in the entropy would be much greater than that of reaction X.

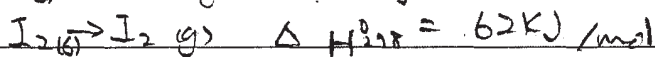
$$e. K_{eq} = e^{-\frac{\Delta G^\circ}{RT}} > 1$$

$$\Rightarrow -\frac{\Delta G^\circ}{RT} > \ln 1 = 0$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 4048 \text{ J}$$

$$-RT > 0$$

Since R is positive, at any temperature, the equilibrium constant for reaction Y will be less than 1.0



$$\therefore \Delta H_f^\circ = 36 \text{ kJ/mol} - 62 \text{ kJ/mol}$$

$$= -26 \text{ kJ/mol}$$

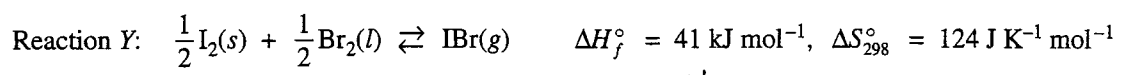
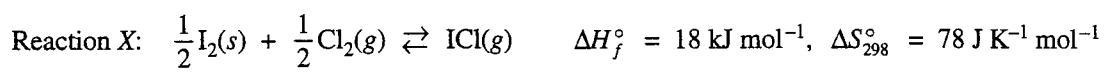
$$\boxed{-26 \text{ kJ/mol}}$$

**STOP**

If you finish before time is called, you may check your work on this part only.  
Do not turn to the other part of the test until you are told to do so.

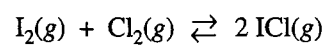
3C1

3. Answer the following questions about the thermodynamics of the reactions represented below.



$\Delta G = H - T\Delta S$

- (a) Is reaction X, represented above, spontaneous under standard conditions? Justify your answer with a calculation.
- (b) Calculate the value of the equilibrium constant,  $K_{eq}$ , for reaction X at 25°C.
- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.
- (d) Explain why the standard entropy change is greater for reaction Y than for reaction X.
- (e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0? Justify your answer with calculations.
- (f) For the vaporization of solid iodine,  $I_2(s) \rightarrow I_2(g)$ , the value of  $\Delta H_{298}^\circ$  is 62 kJ mol<sup>-1</sup>. Using this information, calculate the value of  $\Delta H_{298}^\circ$  for the reaction represented below.



(a)  $\Delta G = H - T\Delta S$ . if  $\Delta G < 0$  it is spontaneous.  
 $= 18 - T \cdot 78$

Because T is positive,  $\Delta G$  is negative. Therefore,  $X_{rec}$  is spontaneous.

(b)  $K_{eq} = \frac{[ICl]^2}{[Cl_2]}$

(c) Because  $\Delta H_f$  is endothermic, ( $\Delta H_f < 0$  Exo,  $\Delta H_f > 0$  Endo)  
increase in temperature will help to make more products.  
Increase in concentration of products increase  $K_{eq}$ . ( $\because K_{eq} = \frac{[ICl]^2}{[Cl_2]}$ )

(d) Entropy means how freely atoms can move.  
In  $X_{rec}$ , gas changes to gas  
 $(Cl_2) \longrightarrow (ICl)$   
In  $Y_{rec}$ , liquid changes to gas.  
 $(Br_2) \longrightarrow (IBr)$

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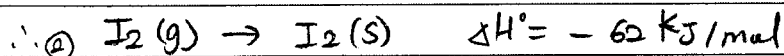
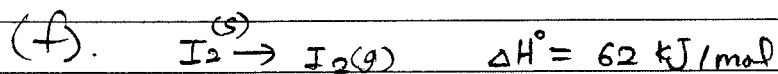
Change of phase increases the entropy more

This is why entropy of  $Y_{rec}$  is greater than that of  $X_{rec}$

(e) To have  $K_{eq}$  greater than 1.0, reactions should shift to right  
In order to make more products compare to reactant.

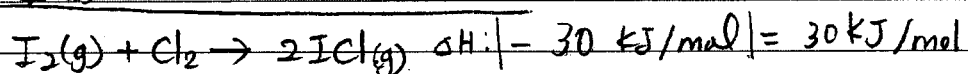
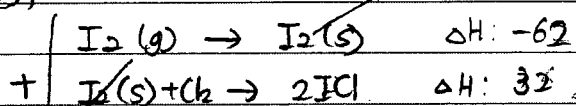
This reaction is also endothermic, which means higher temperature will make more products.

Therefore, temperature should be higher than equilibrium temperature.



To add ① + ②,

we get



**STOP**

If you finish before time is called, you may check your work on this part only.  
Do not turn to the other part of the test until you are told to do so.



AP<sup>®</sup> CHEMISTRY  
2006 SCORING COMMENTARY (Form B)

Question 3

**Sample: 3A**

**Score: 8**

This excellent response earned 8 out of 9 possible points: 2 points for part (a), 1 point for part (b), 1 point for part (d), 2 points for part (e), and 2 points for part (f). The point was not earned in part (c) because  $K_{eq}$  would increase, not decrease; the argument presented is not valid because  $\Delta G$  itself changes with temperature.

**Sample: 3B**

**Score: 6**

The point was not earned in part (a)(i) because the number of significant figures in the calculated value of  $\Delta G^\circ$  is too large by more than one, and the units are incorrect. The points were not earned in part (e).

**Sample: 3C**

**Score: 4**

Only 1 point was earned in part (a) because the justification is not adequate ( $\Delta G$  is not actually calculated). The point was not earned in part (b), nor were the points earned in part (e). In part (f) 1 point was earned for a correct  $\Delta H_{298}^\circ$ , but the second point was not earned because of the math error and incorrect sign.