Question 3

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

Reaction *X*: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftarrows ICl(g)$ $\quad \Delta H_f^\circ = 18 \text{ kJ mol}^{-1}, \ \Delta S_{298}^\circ = 78 \text{ J K}^{-1} \text{ mol}^{-1}$

Reaction *Y*: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftarrows IBr(g)$ $\quad \Delta H_f^\circ = 41 \text{ kJ mol}^{-1}, \ \Delta S_{298}^\circ = 124 \text{ J K}^{-1} \text{ mol}^{-1}$

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ mol}^{-1} \text{ K}^{-1}) = -5 \text{ kJ mol}^{-1}$ Reaction is spontaneous because $\Delta G^\circ < 0$.	One point is earned for the correct value of ΔG°. One point is earned for a correct justification of spontaneity.

(b) Calculate the value of the equilibrium constant, K_{eq}, for reaction *X* at 25°C.

$\Delta G^\circ = -RT \ln K_{eq} \Rightarrow \ln K_{eq} = -\frac{\Delta G^\circ}{RT}$ $\ln K_{eq} = -\frac{(-5 \text{ kJ mol}^{-1})(10^3 \text{ J kJ}^{-1})}{(8.31 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 2.019$ $K_{eq} = e^{2.019} = (7.5314) = 8$	One point is earned for the correct answer.

(c) What effect will an increase in temperature have on the equilibrium constant for reaction *X*? Explain your answer.

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

Question 3 (continued)

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

Both reaction X and reaction Y have solid iodine as a reactant, but the second reactant in reaction X is chlorine gas whereas the second reactant in reaction Y is liquid bromine. Liquids have lower entropies than gases, thus in reaction Y the reactants are more ordered (and have lower entropies) than in reaction X. The products of both reaction X and reaction Y have about the same disorder, so the change in entropy from reactants to products is greater in reaction Y than in reaction X.	One point is earned for a correct explanation.

(e) Above what temperature will the value of the equilibrium constant for reaction Y be greater than 1.0 ? Justify your answer with calculations.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $K_{eq} = 1$ when $\Delta G^\circ = 0 \Rightarrow T\Delta S^\circ = \Delta H^\circ \Rightarrow$ $T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{41 \text{ kJ mol}^{-1}}{0.124 \text{ kJ mol}^{-1}\text{K}^{-1}} = 330 \text{ K}$ So when $T > 330$ K, $\Delta G^\circ < 0$ kJ mol^{-1} $\Rightarrow$ $K_{eq} > 1.0$	One point is earned for $\Delta G^\circ = 0$. One point is earned for the correct temperature.

(f) For the vaporization of solid iodine, $I_2(s) \rightarrow I_2(g)$, the value of ΔH°_{298} is 62 kJ mol^{-1}. Using this information, calculate the value of ΔH°_{298} for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$$

$I_2(s) + Cl_2(g) \rightleftarrows 2\,ICl(g)$	$\Delta H^\circ_{298} = 2 \times 18$ kJ mol^{-1}	One point is earned for ΔH°_{298} of either the first or second equation.
$I_2(g) \rightleftarrows I_2(s)$	$\Delta H^\circ_{298} = -62$ kJ mol^{-1}	
$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$	$\Delta H^\circ_{298} = -26$ kJ mol^{-1}	One point is earned for the correct sum of the ΔH°_{298} values.

3A,

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

Reaction X: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftarrows ICl(g)$ $\quad \Delta H_f^\circ = 18\ \text{kJ mol}^{-1},\ \Delta S_{298}^\circ = 78\ \text{J K}^{-1}\ \text{mol}^{-1}$

Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftarrows IBr(g)$ $\quad \Delta H_f^\circ = 41\ \text{kJ mol}^{-1},\ \Delta S_{298}^\circ = 124\ \text{J K}^{-1}\ \text{mol}^{-1}$

(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 ΔH_{298}° is 62 kJ mol^{-1}. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$$

(a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 18\ \text{kJ/mol} - 298\text{K} \cdot 78\ \text{J/K·mol} \cdot 10^{-3}\ \text{kJ/J}$
$= -5.2\ \text{kJ/mol} < 0$
∴ 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 $K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$, and $\Delta G^\circ < 0$, an increase in T 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 $K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$, ΔG° must be smaller than zero for K_{eq} to be greater than 1.0

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

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

$\therefore T > 331\,K$

(f) $I_2(g) \rightarrow I_2(s)$: $\Delta H^\circ_{298} = -62\,kJ/mol$ (reaction A)

$Cl_2(g) + I_2(s) \rightarrow 2ICl(g)$: $\Delta H^\circ_{298} = 36\,kJ/mol$ (reaction B)

Reaction B is derived from reaction X.

add reaction A and reaction B.

$I_2(g) + Cl_2(g) \rightarrow 2ICl(g)$, $\Delta H^\circ_{298} = -26\,kJ/mol$

$\therefore \Delta H^\circ_{298} = -26\,kJ/mol$

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 1

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

Reaction X: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftarrows ICl(g)$ $\quad \Delta H_f^\circ = 18 \text{ kJ mol}^{-1}, \ \Delta S_{298}^\circ = 78 \text{ J K}^{-1} \text{ mol}^{-1}$

Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftarrows IBr(g)$ $\quad \Delta H_f^\circ = 41 \text{ kJ mol}^{-1}, \ \Delta S_{298}^\circ = 124 \text{ J K}^{-1} \text{ mol}^{-1}$

(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 ΔH_{298}° is 62 kJ mol^{-1}. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$$

(a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$T = 298$ K

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

Since the Gibb's free energy is negative, reaction X is spontaneous.

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

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

ΔG° (from (a)) $= -5244$ J $\quad$ Keq = 8.3

$K = e^{\Delta G^\circ / -RT} = 18.3112$

(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 Keq, which is equal to $\frac{[ICl]}{[I_2]^{\frac{1}{2}}[Cl_2]^{\frac{1}{2}}}$, 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 ligvid for its reactants In fact the change in the entropy would be much greater than that of reaction X.

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

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 4048\,J$

$-RT > 0$

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

f. $I_{2(s)} + Cl_{2(g)} \rightleftharpoons ICl_{(g)} \quad \Delta H^\circ_f = 36\ KJ\ mol$

$I_{2(s)} \rightarrow I_{2(g)} \quad \Delta H^\circ_{rxn} = 62\ KJ/mol$

$\therefore \Delta H^\circ f = 36\ KJ/mol - 62\ KJ/mol$

$= -26\ KJ/mol$

$-26\ KJ/mol$

STOP

If you finish before time is called, you may check your work on this part only.
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3C1

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

Reaction X: $\frac{1}{2}I_2(s) + \frac{1}{2}Cl_2(g) \rightleftarrows ICl(g)$ $\quad \Delta H_f^\circ = 18\ \text{kJ mol}^{-1}$, $\Delta S_{298}^\circ = 78\ \text{J K}^{-1}\text{ mol}^{-1}$

Reaction Y: $\frac{1}{2}I_2(s) + \frac{1}{2}Br_2(l) \rightleftarrows IBr(g)$ $\quad \Delta H_f^\circ = 41\ \text{kJ mol}^{-1}$, $\Delta S_{298}^\circ = 124\ \text{J K}^{-1}\text{ mol}^{-1}$

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

(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 ΔH_{298}° is 62 kJ mol^{-1}. Using this information, calculate the value of ΔH_{298}° for the reaction represented below.

$$I_2(g) + Cl_2(g) \rightleftarrows 2\,ICl(g)$$

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

$= 18 - T \cdot 78$

Because T is positive, ΔG is negative. Therefore, X_{rec} is spontaneous.

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

(c) Because ΔH_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}. ($\because K_{eq} = \frac{[ICl]\uparrow}{[Cl_2]}$)

(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 phrase increases the entropy more
This is why entropy of Y_{rec} is greather 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.

(f). $I_2^{(s)} \rightarrow I_2(g)$ $\Delta H^\circ = 62$ kJ/mol

① $(s)I_2 + Cl_2 \rightarrow 2ICl$ $\Delta H^\circ = 18 \times 2$ kJ/mol

∴ ② $I_2(g) \rightarrow I_2(s)$ $\Delta H^\circ = -62$ kJ/mol

To add ① + ②,

we get

$I_2(g) \rightarrow I_2(s)$ $\Delta H: -62$

$+ \quad I_2(s) + Cl_2 \rightarrow 2ICl$ $\Delta H: 32$

$I_2(g) + Cl_2 \rightarrow 2ICl(g)$ $\Delta H: |-30 \text{ kJ/mol}| = 30$ kJ/mol

STOP

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AP® 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 ΔG 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 $\Delta G°$ 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 (ΔG 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 ΔH°_{298}, but the second point was not earned because of the math error and incorrect sign.