Question 6

Use principles of thermodynamics to answer the following questions.

(a) The gas N₂O₄ decomposes to form the gas NO₂ according to the equation below.

\[
\begin{array}{c}
\text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO}_2
\end{array}
\]

(i) Predict the sign of \(\Delta H^\circ\) for the reaction. Justify your answer.

Bonds are broken when NO₂ molecules form from N₂O₄ molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of \(\Delta H^\circ\) is positive.

One point is earned for the correct sign and a correct explanation.

(ii) Predict the sign of \(\Delta S^\circ\) for the reaction. Justify your answer.

There are two gaseous product molecules for each gaseous reactant molecule, so the product has more entropy than the reactant. The entropy increases as the reaction proceeds, so the sign of \(\Delta S^\circ\) is positive.

One point is earned for the correct sign and a correct explanation.

(b) One of the diagrams below best represents the relationship between \(\Delta G^\circ\) and temperature for the reaction given in part (a). Assume that \(\Delta H^\circ\) and \(\Delta S^\circ\) are independent of temperature.

\[
\begin{array}{c}
\Delta G^\circ \quad \Delta G^\circ \\
\downarrow \quad \downarrow \\
T \quad T
\end{array}
\]

Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\).

The leftmost graph should be circled.

\(\Delta S^\circ\) is positive, so as \(T\) increases, \(T\Delta S^\circ\) becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from \(\Delta H^\circ\) to get \(\Delta G^\circ\), so \(\Delta G^\circ\) decreases with increasing temperature.

One point is earned for the correct graph selection.

One point is earned for the explanation.
(c) A reaction mixture of $\text{N}_2\text{O}_4$ and $\text{NO}_2$ is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of $\text{N}_2\text{O}_4$ decreases.

The reaction is endothermic. For endothermic reactions, increasing the temperature drives the reaction to the right. This increases the equilibrium concentration of $\text{NO}_2$ and decreases the equilibrium concentration of $\text{N}_2\text{O}_4$.

One point is earned for the correct explanation.

(ii) The value of $K_{eq}$ at 25°C is $5.0 \times 10^{-3}$. Will the value of $K_{eq}$ at 100°C be greater than, less than, or equal to this value?

Because the reaction is endothermic, at higher temperatures the reaction goes further to the right. This means that the value of $K_{eq}$ at 100°C will be greater than the value of $K_{eq}$ at 25°C.

One point is earned for the correct choice. (No explanation required.)

(d) Using the value of $K_{eq}$ at 25°C given in part (c)(ii), predict whether the value of $\Delta H^\circ$ is expected to be greater than, less than, or equal to the value of $T\Delta S^\circ$. Explain.

$K_{eq}$ at 25°C is less than 1, hence $\Delta G^\circ$ must be positive. And in order for $\Delta G^\circ$ to be positive, $\Delta H^\circ$ must be greater than $T\Delta S^\circ$.

One point is earned for the correct prediction.

One point is earned for the explanation.
6. Use principles of thermodynamics to answer the following questions.

(a) The gas $\text{N}_2\text{O}_4$ decomposes to form the gas $\text{NO}_2$ according to the equation below.

\[
\text{O} - \text{N} - \text{O} \quad \rightarrow \quad \text{O} - \text{N} + \cdot \text{O} - \text{N} - \text{O}
\]

(i) Predict the sign of $\Delta H^\circ$ for the reaction. Justify your answer.

(ii) Predict the sign of $\Delta S^\circ$ for the reaction. Justify your answer.

(b) One of the diagrams below best represents the relationship between $\Delta G^\circ$ and temperature for the reaction given in part (a). Assume that $\Delta H^\circ$ and $\Delta S^\circ$ are independent of temperature.

\[\begin{array}{c}
\text{Diagram 1} \\
\text{Diagram 2} \\
\text{Diagram 3}
\end{array}\]

Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

(c) A reaction mixture of $\text{N}_2\text{O}_4$ and $\text{NO}_2$ is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of $\text{N}_2\text{O}_4$ decreases.

(ii) The value of $K_{eq}$ at 25°C is $5.0 \times 10^{-3}$. Will the value of $K_{eq}$ at 100°C be greater than, less than, or equal to this value?

(d) Using the value of $K_{eq}$ at 25°C given in part (c)(ii), predict whether the value of $\Delta H^\circ$ is expected to be greater than, less than, or equal to the value of $T\Delta S^\circ$. Explain.

\[\begin{array}{c}
(i) \Delta H^\circ > 0 , \text{ since energy is needed to break bonds the reaction is endothermic.} \\
(ii) \Delta S^\circ > 0 , \text{ since 1 mol of solid gives 2 mol of gas = \text{reaction is random.}}
\end{array}\]
(b) \[ \Delta H > 0, \Delta S > 0 \]

\[ \Delta G^\circ = \Delta H - T \Delta S^\circ \]

As the temperature rises, the product \( T \Delta S \) becomes more negative and at the value gets greater than \( \Delta H \).

\( \Delta G^\circ \) decreases.

\[ \Delta G^\circ (T) = \Delta H \text{ (Lower the same)} - T \Delta S \text{ (Always the same)} \]

\( \Rightarrow \Delta G^\circ \downarrow \) and be (some more negative).

(c) (i) \( N_2 + O_2 \rightarrow 2 NO_2 \) is an endo thermic reaction \( \Delta H > 0 \);

By L. C. P. reaction shift to the right since an increase in temperature favors endothermic reactions.

\( \therefore \Rightarrow [N_2O_4] \downarrow \rightarrow [NO_2] \uparrow \)

(ii) \( K_{eq} = [NO_2]^2 \)

\( \Rightarrow \) Temp \( \uparrow \Rightarrow \) forward reaction is favored

\( \therefore [NO_2]^2 \uparrow \Rightarrow K_{eq} \uparrow \)

(d) \[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

\[ \Delta G^\circ = -RT \ln K = -(8.31)(25 + 273)(0.05 \times 10^{-3}) \]

\( \ln n(x) \) if \( x < 1 \) \( \Rightarrow \ln (x) < 0 \)

\( \Rightarrow \Delta G^\circ > 0 \)

\[ \Delta H^\circ = \Delta G^\circ + T \Delta S^\circ \]

\( \therefore \Delta H^\circ > T \Delta S^\circ \)
6. Use principles of thermodynamics to answer the following questions.

(a) The gas \( \text{N}_2\text{O}_4 \) decomposes to form the gas \( \text{NO}_2 \) according to the equation below.

\[
\text{E} + \text{N} - \text{N} \rightarrow \text{O} \cdot \text{N} + \cdot \text{N} \quad \text{O}
\]

(i) Predict the sign of \( \Delta H^\circ \) for the reaction. Justify your answer.

(ii) Predict the sign of \( \Delta S^\circ \) for the reaction. Justify your answer.

(b) One of the diagrams below best represents the relationship between \( \Delta G^\circ \) and temperature for the reaction given in part (a). Assume that \( \Delta H^\circ \) and \( \Delta S^\circ \) are independent of temperature.

\[
\Delta G^\circ \\
\downarrow \text{T} \quad \Delta G^\circ \;
\downarrow \text{T} \quad \Delta G^\circ \\
\downarrow \text{T}
\]

Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ > 0 \]

(c) A reaction mixture of \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \) is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of \( \text{N}_2\text{O}_4 \) decreases.

(ii) The value of \( K_{eq} \) at 25°C is \( 5.0 \times 10^{-3} \). Will the value of \( K_{eq} \) at 100°C be greater than, less than, or equal to this value?

(d) Using the value of \( K_{eq} \) at 25°C given in part (c)(ii), predict whether the value of \( \Delta H^\circ \) is expected to be greater than, less than, or equal to the value of \( T\Delta S^\circ \). Explain.

\[
\text{a.i.} \quad \Delta H^\circ > 0, \text{ as breaking bonds requires energy}
\]
\[
\text{a.ii.} \quad \Delta S^\circ < 0 \quad \text{as} \quad \Delta S^\circ = \frac{-\Delta H^\circ}{T} \quad \text{and} \quad \Delta H^\circ > 0, \Delta S^\circ \text{ will be negative}
\]

[C.ii] Using Le Chatelier's principle if we want to increase the temperature of the reaction, we would be adding more Energy to the system.

GO ON TO THE NEXT PAGE.
The system is using L.E.P. The system would partially contract the imposed change by following the forward reaction, so decreasing the C(NO₃)₂.

\[ \text{K}_\text{eq} = \frac{[\text{C(NO}_3]^2}{[\text{N}_2\text{O}_4]} \]

Increasing the temperature will increase the C(NO₃)₂ produced and decrease the [N₂O₄] consumed, consequently, the new Kₑq will be greater than the initial Kₑq which was at 25°C.

\[ \Rightarrow \text{K}_\text{eq at } 100°C > \text{K}_\text{eq at } 25°C \]

d. \( \Delta G^° = -RT \ln \text{K}_\text{eq at equilibrium} \)
\[ = -8.31 (25 + 273) \ln (5 \times 10^{-2}) \]
\[ \Rightarrow \Delta G^° < 0 \]

\[ \Delta G^° = \Delta H^° - T \Delta S^° > 0 \]
\[ \text{for } -T \Delta S^° > -\Delta H^° \]
\[ T \Delta S^° < \Delta H^° \]

This is because as the reaction is not spontaneous, \( \Delta G^° < 0 \), so solving the equation, we are able to derive that \( \Delta H^° > T \Delta S^° \).
6. Use principles of thermodynamics to answer the following questions.

(a) The gas \( \text{N}_2\text{O}_4 \) decomposes to form the gas \( \text{NO}_2 \) according to the equation below.

\[
\text{N} = \text{N} + \text{N} \quad \text{O} + \text{O} \]

(i) Predict the sign of \( \Delta H^\circ \) for the reaction. Justify your answer.

(ii) Predict the sign of \( \Delta S^\circ \) for the reaction. Justify your answer.

(b) One of the diagrams below best represents the relationship between \( \Delta G^\circ \) and temperature for the reaction given in part (a). Assume that \( \Delta H^\circ \) and \( \Delta S^\circ \) are independent of temperature.

\[\Delta G^\circ \] vs. \( T \) \[\Delta G^\circ \] vs. \( T \) \[\Delta G^\circ \] vs. \( T \]

Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \).

(c) A reaction mixture of \( \text{N}_2\text{O}_4 \) and \( \text{NO}_2 \) is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of \( \text{N}_2\text{O}_4 \) decreases.

(ii) The value of \( K_{eq} \) at 25°C is \( 5.0 \times 10^{-3} \). Will the value of \( K_{eq} \) at 100°C be greater than, less than, or equal to this value?

(d) Using the value of \( K_{eq} \) at 25°C given in part (c)(ii), predict whether the value of \( \Delta H^\circ \) is expected to be greater than, less than, or equal to the value of \( T\Delta S^\circ \). Explain.

\( \Delta H^\circ \) is negative because the molecules are \underline{decomposing}.

\( \Delta S^\circ \) is positive because the reaction occurs \underline{spontaneously}.

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GO ON TO THE NEXT PAGE.
6) Circled because as temperature gets higher, the substance that gas gets larger. And therefore you are taking more away from DH° so it has a negative linear correlation related to temperature.

d) The concentration of N₂O₄ decreases because when heat is added to solution its equilibrium equation shifts towards the product side.

(i) Greater than because key is concentration products over reactants. And if the products increase with heat and the reactants decrease the ratio will be greater and therefore higher key.
Sample: 6A
Score: 8

This response earned all 8 points: 1 for part (a)(i), 1 for part (a)(ii), 2 for part (b), 1 for part (c)(i), 1 for part (c)(ii), and 2 for part (d). Note: in part (a)(ii) the response incorrectly indicates that solid N₂O₄ goes to 2 moles of NO₂ gas; however, the point was earned on the basis that the response shows the idea of the formation of a greater number of moles of gas.

Sample: 6B
Score: 6

The point was earned in part (a)(i). The point was not earned in part (a)(ii). One of the 2 points was earned in part (b) because the selection is consistent with the incorrect response in part (a)(ii). The points were earned in parts (c)(i), (c)(ii), and (d).

Sample: 6C
Score: 3

The points were not earned in parts (a)(i) and (a)(ii). The points were earned in part (b). The point was not earned in part (c)(i). The point was earned in part (c)(ii) for the correct choice. The points were not earned in part (d).