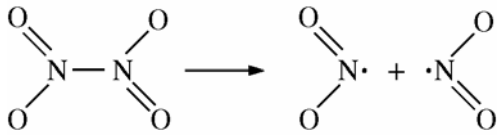
AP® CHEMISTRY
2008 SCORING GUIDELINES (Form B)

Question 6

Use principles of thermodynamics to answer the following questions.

(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



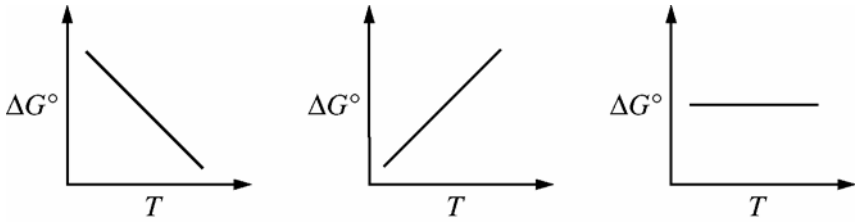
(i) Predict the sign of $\Delta H°$ for the reaction. Justify your answer.

Bonds are broken when NO_2 molecules form from N_2O_4 molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of $\Delta H°$ is positive.	One point is earned for the correct sign and a correct explanation.

(ii) Predict the sign of $\Delta S°$ 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 $\Delta S°$ 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 $\Delta G°$ and temperature for the reaction given in part (a). Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.



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

The leftmost graph should be circled. $\Delta S°$ is positive, so as T increases, $T\Delta S°$ becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from $\Delta H°$ to get $\Delta G°$, so $\Delta G°$ decreases with increasing temperature.	One point is earned for the correct graph selection. One point is earned for the explanation.

Question 6 (continued)

(c) A reaction mixture of N_2O_4 and 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 N_2O_4 decreases.

The reaction is endothermic. For endothermic reactions, increasing the temperature drives the reaction to the right. This increases the equilibrium concentration of NO_2 and decreases the equilibrium concentration of N_2O_4.	One point is earned for the correct explanation.

(ii) The value of K_{eq} at 25°C is 5.0×10^{-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.)

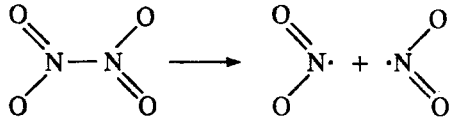
(d) Using the value of K_{eq} at 25°C given in part (c)(ii), predict whether the value of $\Delta H°$ is expected to be greater than, less than, or equal to the value of $T\Delta S°$. Explain.

K_{eq} at 25°C is less than 1, hence $\Delta G°$ must be positive. And in order for $\Delta G°$ to be positive, $\Delta H°$ must be greater than $T\Delta S°$.	One point is earned for the correct prediction. One point is earned for the explanation.

6A1

6. Use principles of thermodynamics to answer the following questions.

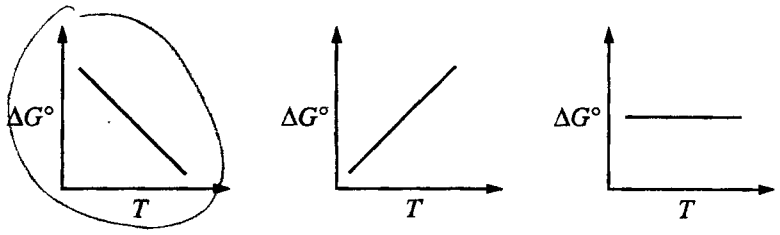
(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



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

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

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



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

(c) A reaction mixture of N_2O_4 and 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 N_2O_4 decreases.

(ii) The value of K_{eq} at 25°C is 5.0×10^{-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 $\Delta H°$ is expected to be greater than, less than, or equal to the value of $T\Delta S°$. Explain.

(a) (i) $\Delta H^\circ > 0$. since energy is needed to break bonds the reaction is endothermic.

(ii) $\Delta S^\circ > 0$ since 1 mole of solid gives 2 mols of gas $\Rightarrow$ reaction is random.

6A2

ADDITIONAL PAGE FOR ANSWERING QUESTION 6

(b) $\Delta H > 0; \Delta S > 0$

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

as the temperature risises. the product $T\Delta S$ becomes more negative and the value gets greater than ΔH.

$\Rightarrow \Delta G^\circ$ decreases.

ΔG (↓) = ΔH (stays the same) − T(↑) ΔS° (stays the same)

$\therefore \Rightarrow \Delta G$ ↓ and be comes more negative

(c) (i) $N_2O_4 \rightarrow 2NO_2$ is an endo thermic reaction $\Delta H > 0$

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

$\therefore \Rightarrow [N_2O_4]$ ↓ $\Rightarrow [NO_2]$ ↑

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

K as Temp ↑ $\Rightarrow$ forward reaction is favoured

$\therefore [NO_2]^2$ ↑ $\Rightarrow$ K_{eq} ↑.

(d) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ 4

$\Delta G^\circ = -RT \ln K = -(8.31)(25+273)(\ln 5 \times 10^{-3})$

$\ln \ln(x)$ if $\alpha x < 1 \Rightarrow \ln(x) < 0$

$\Rightarrow \Delta G^\circ > 0$

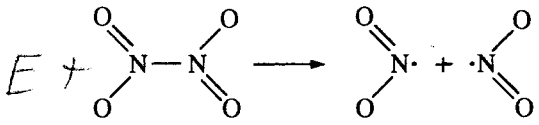
$\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

$\therefore \Delta H^\circ > T\Delta S^\circ$

6B,

6. Use principles of thermodynamics to answer the following questions.

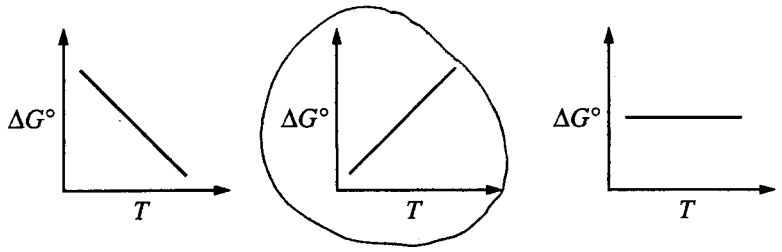
(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



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

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

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



Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G° = \Delta H° - T\Delta S° > 0$

(c) A reaction mixture of N_2O_4 and 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 N_2O_4 decreases.

(ii) The value of K_{eq} at 25°C is 5.0×10^{-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 $\Delta H°$ is expected to be greater than, less than, or equal to the value of $T\Delta S°$. Explain.

a.i.) $\Delta H° > 0$, as breaking bonds requires Energy

ii.) $\Delta S° < 0$, as $\Delta S° = \frac{-\Delta H°}{T}$, & as $\Delta H° > 0$, $\Delta S°$ will be negative

(b. Circled above)

c-i) Using Le Chatelier's Principle, if we were to increase the temperature of the reaction, we would be adding more Energy to the

GO ON TO THE NEXT PAGE.

system, & using LCP, the system would ~~Keq~~ partially counteract the imposed change by following the forward reaction, & so decreasing the $[N_2O_4]$.

(ii.) $K_{eq} = \frac{[NO_2]^2}{N_2O_4}$. Increasing the temperature will increase the $[NO_2]$ produced & decrease the $[N_2O_4]$ consumed, & therefore, the new K_{eq}, at 100°C will be greater than the initial K_{eq} which was at 25°C.

$\Rightarrow K_{eq}$ at 100°C $> K_{eq}$ at 25°C

d. $\Delta G^\circ = -RT \ln K_{eq}$ at equilibrium

$= -8.31(25+273)\ln(5\cdot10^{-2})$ → -ve

$\Rightarrow \Delta G^\circ > 0$

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

$-T\Delta S^\circ > -\Delta H$

$T\Delta S^\circ < \Delta H^\circ$

This is because as the reaction is not spontaneous, $\Delta G^\circ > 0$, & so solving the equation, we are able to derive that $\Delta H^\circ > T\Delta S^\circ$

6C,

6. Use principles of thermodynamics to answer the following questions.

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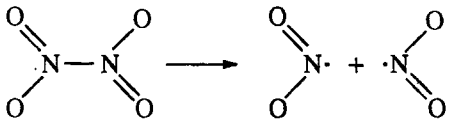
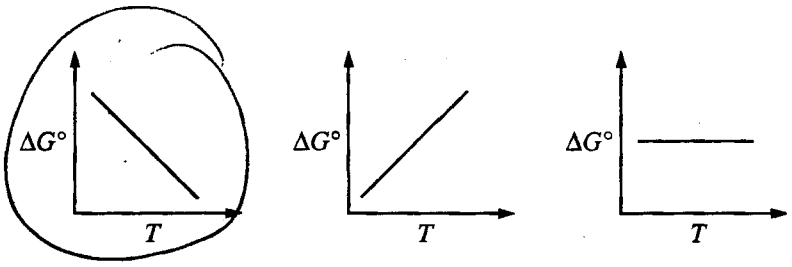


(i) Predict the sign of $\Delta H°$ for the reaction. Justify your answer.

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

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



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

(c) A reaction mixture of N_2O_4 and 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 N_2O_4 decreases.

(ii) The value of K_{eq} at 25°C is 5.0×10^{-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 $\Delta H°$ is expected to be greater than, less than, or equal to the value of $T\Delta S°$. Explain.

a(i) $\Delta H°$ is negative because the molecules are decomposing

a(ii) $\Delta S°$ is positive because the reaction occurs spontaneously

ADDITIONAL PAGE FOR ANSWERING QUESTION 6

6C2

b) Circled because as temperature gets higher the subtrahend $T\Delta S^\circ$ gets larger. And therefore you are taking more away from ΔH° so it has a negative linear correlation related to temperature.

c(i) the concentration of N_2O_4 decreases because when heat is added to solution its ~~saturation~~ equilibrium equation shifts ~~and~~ towards the product side.

c(ii) greater than because Keq is concentration of products over reactants. And if the products increase with heat and the reactants decrease the ratio will be greater and therefore higher Keq.

AP® CHEMISTRY
2008 SCORING COMMENTARY (Form B)

Question 6

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 N_2O_4 goes to 2 moles of NO_2 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).