

AP[®] CHEMISTRY
2009 SCORING GUIDELINES

Question 5 (8 points)

Reaction	Equation	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
X	$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$	+131 kJ mol ⁻¹	+134 J mol ⁻¹ K ⁻¹	+91 kJ mol ⁻¹
Y	$\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$	+41 kJ mol ⁻¹	+42 J mol ⁻¹ K ⁻¹	+29 kJ mol ⁻¹
Z	$2 \text{CO}(g) \rightleftharpoons \text{C}(s) + \text{CO}_2(g)$?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

- (a) For reaction X, write the expression for the equilibrium constant, K_p .

$K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$	One point is earned for the correct expression.
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- (b) For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.

<p>K_p will increase.</p> <p>If the temperature is increased for an endothermic reaction ($\Delta H_{298}^{\circ} = +131 \text{ kJ mol}^{-1}$), then by Le Chatelier's principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of K_p will increase.</p> <p>OR</p> <p>Because $\Delta G^{\circ} = -RT \ln K_p = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ}$,</p> <p>then $\ln K_p = -\frac{\Delta H_{298}^{\circ}}{RT} + \frac{\Delta S_{298}^{\circ}}{R}$.</p> <p>An increase in T for a positive ΔH_{298}° results in an increase in $\ln K_p$ and thus an increase in K_p.</p>	One point is earned for the correct answer with appropriate justification.
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Question 5 (continued)

- (c) For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.

<p>K_p for reaction Y is less than 1.</p> <p>For reaction Y, $\Delta G_{298}^{\circ} = +29 \text{ kJ mol}^{-1}$, a positive number.</p> <p>Because $\Delta G^{\circ} = -RT \ln K$ and ΔG° is positive, then $\ln K_p$ must be negative. This is true when K_p is less than 1.</p> <p>OR</p> <p>A positive ΔG° results in a nonspontaneous reaction under standard conditions. This favors reactants over products as equilibrium is approached starting from standard conditions, resulting in a K_p less than 1.</p>	<p>One point is earned for the correct answer with appropriate justification.</p>
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- (d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

<p>The total bond energy of the reactants is larger.</p> <p>Reaction Y is endothermic ($\Delta H_{298}^{\circ} = +41 \text{ kJ mol}^{-1} > 0$), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.</p>	<p>One point is earned for the correct answer with appropriate explanation.</p>
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- (e) Is the following statement true or false? Justify your answer.

“On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur.”

<p>The statement is false.</p> <p>Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.</p>	<p>One point is earned for the correct answer with appropriate justification.</p>
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Question 5 (continued)

(f) Consider reaction Z at 298 K.

(i) Is ΔS° for the reaction positive, negative, or zero? Justify your answer.

<p>ΔS° for reaction Z is negative.</p> <p>In reaction Z, two moles of gas with relatively high entropy are converted into one mole of solid and one mole of gas, a net loss of one mole of gas and thus a net loss in entropy.</p> <p>OR</p> <p>Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus ΔS° for reaction Z is the sum of two negative numbers and must itself be negative.</p>	<p>One point is earned for the correct answer with an appropriate justification.</p>
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(ii) Determine the value of ΔH° for the reaction.

<p>Add the values of the negatives of ΔH_{298}° for reactions X and Y :</p> <p>$-131 \text{ kJ mol}^{-1} + (-41 \text{ kJ mol}^{-1}) = \mathbf{-172 \text{ kJ mol}^{-1}}$</p>	<p>One point is earned for the correct answer.</p>
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(iii) A sealed glass reaction vessel contains only $\text{CO}(g)$ and a small amount of $\text{C}(s)$. If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

<p>The pressure in the flask decreases.</p> <p>The reaction would proceed to the right, forming more $\text{C}(s)$ and $\text{CO}_2(g)$. Because two moles of $\text{CO}(g)$ would be consumed for every mole of $\text{CO}_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.</p>	<p>One point is earned for the correct answer with an appropriate explanation.</p>
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Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

Reaction	Equation	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
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Y	$\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$	+41 kJ mol ⁻¹	+42 J mol ⁻¹ K ⁻¹	+29 kJ mol ⁻¹
Z	$2 \text{CO}(g) \rightleftharpoons \text{C}(s) + \text{CO}_2(g)$?	?	?

5. Answer the following questions using the information related to reactions X, Y, and Z in the table above.

- For reaction X, write the expression for the equilibrium constant, K_p .
- For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.
- For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.
- For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.
- Is the following statement true or false? Justify your answer.
"On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."
- Consider reaction Z at 298 K.
 - Is ΔS° for the reaction positive, negative, or zero? Justify your answer.
 - Determine the value of ΔH° for the reaction.
 - A sealed glass reaction vessel contains only CO(g) and a small amount of C(s). If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

5. (a) $K_p = \frac{(P(\text{CO}_2))(P(\text{H}_2))}{(P(\text{H}_2\text{O}))}$

(b) K_p will increase. the partial pressures of CO_2 , H_2 , and H_2O will all increase because pressure is directly related to temperature, therefore K_p will increase.

ADDITIONAL PAGE FOR ANSWERING QUESTION 5

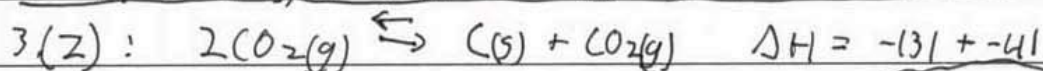
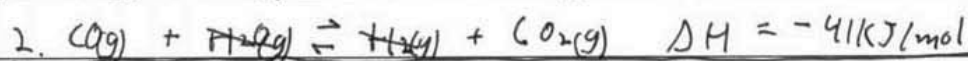
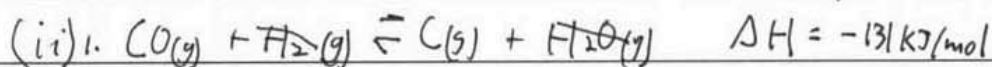
(c) $K_p < 1$ because the reaction is not spontaneous ($\Delta G^\circ > 0$). Therefore reaction favors ~~reactants~~ reactants, and $K_p < 1$.

(d) according to the equation: $\Delta H^\circ = \sum(\text{Bonds broken}) - \sum(\text{Bonds Formed})$, and the fact that $\Delta H^\circ_{\text{rxn}} > 0$, ~~therefore~~ the total bond energy of the reactants is greater.

(e) The statement is false. No value of ΔH , ΔS , or ΔG can determine the rate of reaction. the rate of reaction can only be determined by the rate law, which can only be found experimentally.

(f)

(i) ΔS° for 2 is negative. creating 1 gas molecule from 2 results in a net decrease in entropy.



$= -172 \text{ kJ/mol}$

(iii) If a reaction occurs, then it is proceeding ~~left~~ toward the right. The pressure will decrease because ~~there is~~ one mole of gas is created by 2 mol of gas, and P is directly related to the number of moles of gas present.

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Z	$2 \text{CO(g)} \rightleftharpoons \text{C(s)} + \text{CO}_2\text{(g)}$?	?	?

5. Answer the following questions using the information related to reactions X, Y, and Z in the table above.

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- For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.
- For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.
- For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.
- Is the following statement true or false? Justify your answer.
"On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."
- Consider reaction Z at 298 K.
 - Is ΔS° for the reaction positive, negative, or zero? Justify your answer.
 - Determine the value of ΔH° for the reaction.
 - A sealed glass reaction vessel contains only CO(g) and a small amount of C(s). If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

5a) $K_p = \frac{P_{\text{CO}} \cdot P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$

b.) K_p will increase with increased temperature because the reaction is endothermic and there will be more products as the forward reaction proceeds ~~the~~ to use energy as heat.

ADDITIONAL PAGE FOR ANSWERING QUESTION 5

c.) Less than one, because ΔG is positive, meaning the reaction is not spontaneous and there will be much more reactants than products.

d.) The products, because ΔG is positive and they have more energy free to do work than the reactants.

e.) False, because neither of the will occur at all since neither of them are spontaneous.

f.) i.) Negative, because both the reactions that have been added to form Z have positive ΔS , and both of them has been reversed, requiring a change in the sign.

$$\begin{array}{ll} \text{ii.) } X & + 131 \text{ kJ mol}^{-1} \\ Y & + 41 \text{ kJ mol}^{-1} \end{array}$$

X is reversed

Y is reversed

$$-131 + (-41) = -172 \text{ kJ mol}^{-1} \text{ for Z}$$

iii.) ~~Increase, because the reaction is exothermic and with~~
Decrease, because as the reaction proceeds forward, there will be fewer moles of gas present since the reactants have more moles than the products.

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

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Z	$2 \text{CO(g)} \rightleftharpoons \text{C(s)} + \text{CO}_2\text{(g)}$?	?	?

5. Answer the following questions using the information related to reactions X, Y, and Z in the table above.

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- For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.
- For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.
- For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.
- Is the following statement true or false? Justify your answer.
"On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."
- Consider reaction Z at 298 K.
 - Is ΔS° for the reaction positive, negative, or zero? Justify your answer.
 - Determine the value of ΔH° for the reaction.
 - A sealed glass reaction vessel contains only CO(g) and a small amount of C(s). If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

(a)
$$\frac{[\text{CO(g)}][\text{H}_2\text{(g)}]}{[\text{H}_2\text{O(g)}]}$$

(b) it will increase, because more products will form

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(c) equal, because there are equal volumes of gaseous products and reactants

(d) the energy of the products is greater, because the reaction is endothermic, meaning they require more energy than the reactants

(e) false, because the free energy of Δ is greater, making it react more readily and spontaneously

(H)(i) negative, because there is less gas and a solid being formed

$$(ii) -131 \text{ kJ/mol} - -41 \text{ kJ/mol} = -172 \text{ kJ/mol}$$

(iii) it will increase, because more gas will form

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Question 5

Overview

This question assessed students' conceptual understanding of equilibrium, thermodynamics, and kinetics through a series of questions about three related chemical reactions and their corresponding thermodynamic data. In part (a) students were asked to write the pressure equilibrium expression, which tested the ability to distinguish between pressure equilibria and concentration equilibria. In part (b) students were asked to predict and justify the change in the equilibrium constant when the temperature increases, which tested their skill at applying thermodynamic data to a disturbance in the equilibrium system. Part (c) required students to use the thermodynamic data (Gibbs free energy) to predict and justify the magnitude of K_p relative to 1. Part (d) tested their understanding of the approximate relationship of enthalpy to the mathematical difference between energy of bonds being broken and bonds being formed in a chemical reaction.

Part (e) tested conceptual understanding of both thermodynamics and kinetics by asking if there is any relationship between the two. In part (f)(i) students were asked to predict and justify the sign of ΔS° . This tested their understanding of Hess's Law, since the reverse of reactions X and Y add up to reaction Z. Students could also have answered this question by demonstrating an understanding of the concept of the change of entropy between the reactants and the products in a chemical reaction. For part (f)(ii) students had to find the actual value of ΔH° , so understanding of Hess's Law was vital. Part (f)(iii) required them to predict and explain what would happen to the pressure in a sealed vessel containing the reactant and only one product. Since the system was not at equilibrium, students were expected to predict in which direction the reaction would proceed (not shift) and what effect that process would have on the initial pressure.

Sample: 5A

Score: 7

This response earned 7 of the possible 8 points. In part (b) the point was not earned because the increase in K_p is incorrectly attributed to an increase in pressure resulting from the temperature change.

Sample: 5B

Score: 6

In part (d) the point was not earned because the response states that the bond energy of the products is greater and uses a ΔG_{298}° argument. In part (e) the point was not earned because the student tries to use thermodynamic data from the table to justify why the statement is false.

Sample: 5C

Score: 2

The point was not earned in part (a) because the K_c is given instead of the K_p . In part (b) the response correctly states that K_p "will increase" but does not explain why "more products will form," so the point was not earned. In part (c) the point was not earned because the response assumes the volumes of all the gases are equal and that therefore K_p is equal to 1. The response to part (d) incorrectly states that the bond energy of the products is greater than that of the reactants because of a positive enthalpy, and the point was not earned. In part (e) the response correctly states that the statement is false but then tries to use the thermodynamic data to explain that the opposite of the statement is true,

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Question 5 (continued)

so the point was not earned. The 2 points for parts (f)(i) and (f)(ii) were earned. In part (f)(iii) the response incorrectly states that the pressure will increase as a result of the formation of more gas, so the point was not earned.