AP® CHEMISTRY
2009 SCORING GUIDELINES

Question 5 (8 points)

Reaction	Equation	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
X	$C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$	+131 kJ mol^{-1}	+134 J mol^{-1} K^{-1}	+91 kJ mol^{-1}
Y	$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$	+41 kJ mol^{-1}	+42 J mol^{-1} K^{-1}	+29 kJ mol^{-1}
Z	$2\,CO(g) \rightleftarrows C(s) + CO_2(g)$	?	?	?

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.

$K_p = \dfrac{p_{CO} \times p_{H_2}}{p_{H_2O}}$	One point is earned for the correct expression.

(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.

K_p will increase. If the temperature is increased for an endothermic reaction ($\Delta H^\circ_{298} = +131$ 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. **OR** Because $\Delta G^\circ = -RT \ln K_p = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$, then $\ln K_p = -\dfrac{\Delta H^\circ_{298}}{RT} + \dfrac{\Delta S^\circ_{298}}{R}$. An increase in T for a positive ΔH°_{298} results in an increase in $\ln K_p$ and thus an increase in K_p.	One point is earned for the correct answer with appropriate justification.

AP® CHEMISTRY
2009 SCORING GUIDELINES

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.

K_p for reaction Y is less than 1. For reaction Y, $\Delta G^\circ_{298} = +29$ kJ mol^{-1}, a positive number. 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. **OR** 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.	One point is earned for the correct answer with appropriate justification.

(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.

The total bond energy of the reactants is larger. Reaction Y is endothermic ($\Delta H^\circ_{298} = +41$ 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.	One point is earned for the correct answer with appropriate explanation.

(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."

The statement is false. Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.	One point is earned for the correct answer with appropriate justification.

Question 5 (continued)

(f) Consider reaction Z at 298 K.

(i) Is $\Delta S°$ for the reaction positive, negative, or zero? Justify your answer.

$\Delta S°$ for reaction Z is negative. 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. **OR** Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus $\Delta S°$ for reaction Z is the sum of two negative numbers and must itself be negative.	One point is earned for the correct answer with an appropriate justification.

(ii) Determine the value of $\Delta H°$ for the reaction.

Add the values of the negatives of $\Delta H°_{298}$ for reactions X and Y : $-131\ \text{kJ mol}^{-1} + (-41\ \text{kJ mol}^{-1}) = \mathbf{-172\ kJ\ mol^{-}}$	One point is earned for the correct answer.

(iii) 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.

The pressure in the flask decreases. The reaction would proceed to the right, forming more $C(s)$ and $CO_2(g)$. Because two moles of $CO(g)$ would be consumed for every mole of $CO_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.	One point is earned for the correct answer with an appropriate explanation.