Chemical Thermodynamics and Equilibrium Practice Items

1. Chemical equilibrium occurs when

I. the rate of the forward reaction equals the rate of the reverse reaction.
II. the concentrations of products and reactants attain steady state values.
III. heat flows between the system and environment are reversible.

A. I
B. I and III
C. II and III
D. I, II and III

2. Which of the following is the proper expression of K_c for the following reaction?

$$4NH_3\,(g) + 5O_2\,(g) \rightleftharpoons 4NO\,(g) + 6H_20\,(g)$$

A. $\dfrac{[NH_3]\,[O_2]}{[NO]\,[H_2O]}$

B. $\dfrac{4[NO]\,6[H_2O]}{4[NH_3]\,5[O_2]}$

C. $\dfrac{[NO]^4\,[H_2O]^6}{[NH_3]^4\,[O_2]^5}$

D. $\dfrac{[NH_3]^4\,[O_2]^5}{[NO]^4\,[H_2O]^6}$

3. The reaction of sulfur dioxide with oxygen occurs according to the following stoichiometry:

$$3SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$
$$\Delta H = -197.8\ kJ\ mol^{-1}$$

At 1000°C and 0.3 atm, the equilibrium constant, K_p, is equal to 3.42. Which of the following strategies would be likely to increase the equilibrium yield of sulfur trioxide?

I. Increasing the pressure of the reaction vessel
II. Introducing a catalyst
III. Heating the reaction vessel further

A. I only
B. I and III
C. II and III
D. I, II and III

4. Which of the following will lead to an *increase* in the equilibrium constant?

I. Increasing the temperature of an endothermic reaction
II. Increasing the pressure of a reaction vessel where products represent fewer moles of gas than the reagents
III. Introducing a catalyst

A. I only
B. I and II
C. II and III
D. I, II and III

5. The equilibrium constant under standard conditions for the reaction of SO_2 with O_2 to form SO_3, $K_c = 1.5 \times 10^{-1}\ M^{-1}$

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

If 0.01 mol of each of the three gases are present along with argon in a 1 liter container at STP, which of the following is occurring?

A. The forward reaction occurs at a higher rate than the reverse reaction.
B. The reverse reaction occurs at a higher rate than the forward reaction.
C. The reaction is at equilibrium.
D. Pressure is increasing in the container.

6. Which statement below about standard free energy change, $\Delta G°$, is **untrue**?

A. If $\Delta G°$ for a reaction is large and positive, the equilibrium constant, *K*, is very small.
B. If $\Delta G°$ for a reaction is large and negative, *K* is very large.
C. If $\Delta G°$ is large and negative, the reaction will be spontaneous forward for all concentrations of reagents and products.
D. $\Delta G°$ may be negative even with a positive standard enthalpy change $\Delta H°$.

7. Cyclohexanol inter-converts between axial and equatorial conformations. At 25°C, about 90% exists in the equatorial form with the remainder in the axial form. What is the approximate standard free energy change for with the transformation from equatorial to axial cyclohexanol?

A. -2 kJ mol^{-1}
B. 0.5 kJ mol^{-1}
C. 2 kJ mol^{-1}
D. 5 kJ mol^{-1}

8. $CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)$

$K_c = 4.05$ at 500°C for the above reaction. If 1.0 mole of both carbon monoxide and water vapor are placed in a 2.0 liter container at 500°C, approximately what concentration of carbon monoxide will be in the container at equilibrium?

A. 0.17 M
B. 0.25 M
C. 0.33 M
D. 0.67 M

9. Which of the following is the result when the decomposition of ammonium chloride occurs in an open container at STP?

$$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

A. Decomposition does not occur.
B. All of the ammonium chloride is eventually consumed.
C. The entropy of the system decreases.
D. The system eventually achieves equilibrium as described by K_p for the decomposition of NH_4Cl at STP.

10. The decomposition of solid ammonium carbamate occurs by the following reaction.

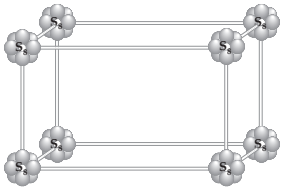
$$(NH_4)(NH_2CO_2)\,(s) \rightleftharpoons 2NH_3\,(g) + CO_2\,(g)$$

When solid ammonium carbamate is introduced into an evacuated flask at 25°C, the total pressure of gas at equilibrium is 0.117 atm. What is the value of K_p at 25°C?

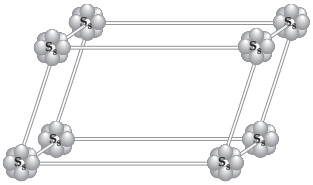
A. 2.4×10^{-4}
B. 3.0×10^{-3}
C. 3.9×10^{-2}
D. 1.2×10^{-1}

The following passage pertains to questions 10-15

Sulfur has various allotropic forms. At room temperature, sulfur exists in yellow crystals consisting of S_8 molecules arranged with rhombic symmetry. The melting point of rhombic sulfur is 113°C. At this temperature, however, the liquid sulfur may be recrystallized to form a monoclinic allotrope, the melting point of which is 119°C. These two crystalline forms are pictured below:



Orthorhombic Sulfur



Monoclinic Sulfur

The table below provides the values of various thermodynamic functions of rhombic and monoclinic sulfur at various temperatures:

		rhombic sulfur			monoclinic sulfur	
T [K]		H $\left[\frac{kJ}{mol}\right]$	S $\left[\frac{J}{K\ mol}\right]$		H $\left[\frac{kJ}{mol}\right]$	S $\left[\frac{J}{K\ mol}\right]$
300		5.5	39.0		5.9	40.1
310		5.7	39.5		6.1	40.6
320		5.9	40.0		6.3	41.1
330		6.1	40.5		6.5	41.6
340		6.3	41.0		6.7	42.1
350		6.5	41.5		6.9	42.6
360		6.7	42.0		7.1	43.1
370		6.9	42.5		7.3	43.6
380		7.1	43.0		7.5	44.1

11. S_8 molecules are held within the crystal lattice of elemental sulfur by

A. strong nuclear forces
B. dipole-dipole interactions
C. Van der Waals forces
D. covalent bonds

12. How many sulfur atoms are in an orthorhombic sulfur unit cell?

A. 6
B. 8
C. 32
D. 64

13. What is the approximate specific heat of rhombic sulfur?

A. 0.8 J g^{-1} K^{-1}
B. 2.0 J g^{-1} K^{-1}
C. 4.8 J g^{-1} K^{-1}
D. 20 J mol^{-1} K^{-1}

14. Which of the following is the correct interpretation of the fact that rhombic sulfur is the lower temperature form and monoclinic sulfur is the higher temperature form?

I. Addition of heat shifts equilibrium to favor the endothermic process.
II. At higher temperatures the change in free energy from the rhombic to the monoclinic form is positive.
III. Enthalpy change favors the rhombic but the entropy change favors the monoclinic.

A. I
B. III
C. I and III
D. I, II, and III

15. Which is the best explanation for why rhombic sulfur possesses a lower melting point (113°C) than monoclinic sulfur (119°C)?

A. In that temperature range, rhombic sulfur has greater free energy.
B. In that temperature range, monoclinic sulfur has less entropy.
C. In that temperature range, monoclinic sulfur has greater free energy.
D. In that temperature range, rhombic sulfur has greater enthalpy.

16. What is the approximate value of the temperature at which, if you cooled molten sulfur, there would be an equal probability of obtaining by crystallization either rhombic or monoclinic sulfur?

A. 310 K
B. 335 K
C. 365 K
D. 400 K