Equilibrium and Chemical Thermodynamics Problem Set

1. Chemical equilibrium occurs when:

   I. The rate of the forward reaction equals the rate of the back reaction
   II. The concentrations of products and reactants attain steady state values.
   III. Energy in the system is distributed in the most probably manner.

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

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

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

3. The reaction for nitrogen fixation reaction resulting in the production of ammonia is as follows:

$$3H_2\,(g) + N_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H = -92.4\ KJ\ mol^{-1}$$

   At 500 ^oC, the equilibrium constant, K_p, is equal to 3.8×10^{-5}. Which of the following strategies would significantly increase the yield of ammonia?

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

   a. I
   b. I and II
   c. II and III
   d. I, II, and III

4. Which of the following statements is *untrue*?

   a. A catalyst increases the rate of both the forward and reverse reaction.
   b. Changing the pressure in gas-phase equilibrium reaction will alter the equilibrium constant.
   c. The equilibrium constant of an exothermic reaction will fall will increasing temperature.
   d. More than one of the above is untrue

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

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

If 0.25 mol of each of the three gases are mixed in a 1 liter container, which of the following occurs?

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 immediately achieves equilibrium.
d. Impossible to determine from given information.

6. For the reaction,

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

The equilibrium constant, K_c = 4.05 at 500 ºC. If 1.0 mole of both carbon monoxide and water vapor are placed in a 2.0 liter container at 500 ºC, approximately what concentration of carbon monoxide will be in the container at equilibrium?

a. .33 M
b. .67 M
c. .17 M
d. .25 M

7. Which of the following statements about the relationship between ΔG^0, the standard free energy change, and K, the thermodynamic equilibrium constant, is *untrue*?

a. When ΔG^0 is large and positive, K is very small.
b. When ΔG^0 is large and negative, K is very large.
c. When ΔG^0 is zero, K = 1.
d. All of the above are true.

8. Which of the following occurs when the decomposition of ammonium chloride, described by the reaction below, occurs in an open container?

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

a. Decomposition does not occur.
b. All of the ammonium chloride is eventually consumed.
c. The entropy of the system remains constant.
d. More than one of the above is correct.

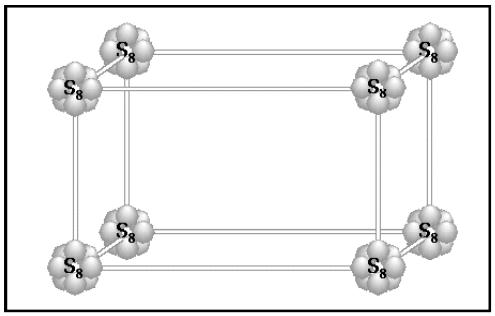
9. Cyclohexanol interconverts between the axial and equatorial conformation. At 25 ºC, about 90% of the the cyclohexanol will exist in the equatorial form with the remainder in the axial form. What is the approximate standard free energy change associated with a transformation from equatorial to axial cyclohexanol? (Remember $\Delta G^0 = -2.303\,RT \log K$)

a. 5 kJ mol^{-1}
b. 2 kJ mol^{-1}
c. -5 kJ mol^{-1}
d. cannot be determined from given information

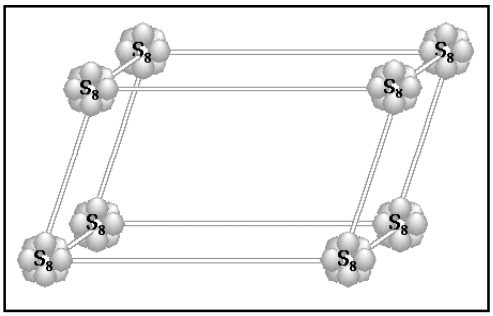
The following passage pertains to questions 10-15

Sulfur has various allotropic forms. At room temperature, sulfur (AN 16, AW 32) exists in yellow crystals consisting of S_8 molecules arranged with rhombic symmetry. The melting point of rhombic sulfur is 113 ^oC. At this temperature, however, the liquid sulfur may be recrystallized to form a monoclinic allotrope, the melting point of which is 119 ^oC. These two crystalline forms are pictured below:

rhombic sulfur



monoclinic sulfur



The tables below gives the values of the thermodynamic functions enthalpy and entropy (for moles of sulfur atoms), of rhombic and monoclinic sulfur at various temperatures:

$T\,[K]$		rhombic sulfur $H\left[\frac{kJ}{mol}\right]$	rhombic sulfur $S\left[\frac{J}{K\,mol}\right]$		monoclinic sulfur $H\left[\frac{kJ}{mol}\right]$	monoclinic sulfur $S\left[\frac{J}{K\,mol}\right]$
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

10. Which of the following hold the S_8 molecules within the crystal lattice of rhombic or monoclinic sulfur?

    a. strong nuclear forces
    b. dipole-dipole interactions
    c. London forces
    d. covalent bonds

11. How many sulfur atoms are in a monoclinic sulfur unit cell?

    a. 64
    b. 8
    c. 32

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

    a. 20 J mol^{-1} K^{-1}
    b. 2.0 kJ g^{-1} K^{-1}
    c. 0.6 J g^{-1} K^{-1}
    d. impossible to determine from given information

13. 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. LeChatelier's principle predicts that, with the addition of heat, equilibrium will shift in the direction favoring the endothermic process.
    II. At higher temperatures the change in free energy from the rhombic to the monoclinic form is positive.
    III. The enthalpy difference favors the rhombic but the entropy difference favors the monoclinic. At increased temperature the entropy difference becomes more important.

    a. I
    b. III
    c. I and III
    d. I, II, and III

14. In thermodynamic terms, which is the best explanation for why rhombic sulfur possesses a lower melting point (113 ^{o}C) than monoclinic sulfur (119 ^{o}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.

15. 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. 390 K
    b. 355 K
    c. 365 K
    d. cannot be determined from given information