Answers to Review #6: Equilibrium Theory

1. Know the meanings of, and be able to apply, the following terms:

enthalpy	Gibb's Free energy	equilibrium
entropy	spontaneous reaction	

2. What are four conditions that must be met in order for equilibrium to be established?
   - the reaction must be reversible
   - the system must be closed
   - the macroscopic properties of the system must be constant
   - the equilibrium must be capable of being reached from either reactants or products

3. For each of the following reactions, identify whether:

i) maximum entropy favours the products or reactants
ii) minimum enthalpy favours the products or reactants
iii) the reaction will be spontaneous at any temperature, non-spontaneous at any temperature, or will form an equilibrium mixture of products and reactants:

a) $H_2SO_4\,(l) + 2\,H_2O\,(l) \leftrightarrow 2\,H_3O^+\,(aq) + SO_4^{2-}\,(aq) + \text{heat}$
   - maximum entropy favours the products
   - minimum enthalpy favours the products
   - the reaction will be spontaneous at all temperatures

b) $C_2H_2\,(g) + 2\,CaO\,(s) \leftrightarrow CaC_2\,(s) + H_2O_2\,(l) + \text{heat}$
   - maximum entropy favours the reactants (because a gas is formed)
   - minimum enthalpy favours the products
   - the reaction is reversible so it will form an equilibrium mixture of reactants and products

c) $3\,O_2\,(g) + \text{energy} \leftrightarrow 2\,O_3\,(g)$
   - maximum entropy favours the reactants
   - minimum enthalpy favours the reactants
   - the reaction (as written) will be non-spontaneous at all temperatures

d) $H_2O\,(l) + \text{heat} \leftrightarrow H_2O\,(g)$
   - maximum entropy favours the products
   - minimum enthalpy favours the reactants
   - the reaction is reversible so it will form an equilibrium mixture of reactants and products

e) $Zn\,(s) + 2\,HCl\,(aq) \leftrightarrow ZnCl_2\,(aq) + H_2\,(g) + \text{heat}$
   - maximum entropy favours the products
   - minimum enthalpy favours the products
   - the reaction is spontaneous at all temperatures

e) $PbI_2\,(s) + \text{heat} + H_2O\,(l) \leftrightarrow Pb^{2+}\,(aq) + 2\,I^{1-}\,(aq)$
   - maximum entropy favours the products
   - minimum enthalpy favours the reactants
   - the reaction is reversible so it will form an equilibrium mixture of reactants and products

4. Which of the following reactions has the greatest increase in entropy?

a) $3\ O_2\ (g) \leftrightarrow\ 2\ O_3\ (g)$

b) $N_2H_4\ (l)\ +\ 2\ H_2O_2\ (l) \leftrightarrow\ N_2\ (g)\ +\ 4\ H_2O\ (g)$

c) $H_2O\ (l)\ +\ \frac{1}{2}\ O_2\ (g) \leftrightarrow\ H_2O_2\ (l)$

d) $2\ AgNO_3\ (aq)\ +\ Na_2S\ (aq) \leftrightarrow\ 2\ NaNO_3\ (aq)\ +\ Ag_2S\ (s)$

e) $C_2H_4\ (g)\ +\ 2\ O_2\ (g) \leftrightarrow\ 2\ CO_2\ (g)\ +\ 2\ H_2O\ (g)$

Reaction "b" shows the greatest increase in entropy. The reactants are all liquids and there are 5 particles of gas in the products.

5. For the following reaction at 25°C: **N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)**

ΔH = -91.8 kJ and ΔS = - 197 J/K. Calculate ΔG for this reaction. Which direction is favoured at this temperature? (ΔG=-33.1 kJ, forward rxn favoured)

6. Use Le Chatelier's principle to predict the effect of the following stresses on the reaction:

$$2\ N_2O_2\ (g)\ +\ H_2\ (g) \leftrightarrow\ 2\ N_2O\ (g)\ +\ H_2O\ (g)\ +\ \text{heat}$$

a) increasing concentration of H_2 (g): ⟶

b) increasing the total pressure: **no change**

c) adding N_2O (g): ⟵

d) decreasing the amount of H_2O (g): ⟶

e) adding helium to the rxn vessel: **no change**

f) removing N_2O_2 (g): ⟵

g) adding a catalyst: **no change**

h) increasing temperature: ⟵

i) increasing the volume of the rxn vessel: **no change**

j) removing N_2O (g) as it forms: ⟶

7. Write the K_{eq} expressions for the following equilibrium reactions (careful of heterogeneous systems):

a) $S\ (s)\ +\ O_2\ (g) \leftrightarrow\ SO_2\ (g)$ $\quad K_{eq} = \dfrac{[SO_2]}{[O_2]}$

b) $2\ NO\ (g)\ +\ O_2\ (g) \leftrightarrow\ 2\ NO_2\ (g)$ $\quad K_{eq} = \dfrac{[NO_2]^2}{[NO]^2\,[O_2]}$

c) $Pb(NO_3)_2\ (aq)\ +\ Zn\ (s) \leftrightarrow\ Zn(NO_3)_2\ (aq)\ +\ Pb\ (s)$ $\quad K_{eq} = \dfrac{[Zn(NO_3)_2]}{[Pb(NO_3)_2]}$

d) $N_2H_4\ (l)\ +\ H_2O_2\ (l) \leftrightarrow\ N_2\ (g)\ +\ 4\ H_2O\ (g)$ $\quad K_{eq} = [N_2]\,[H_2O]^4$

e) $Ba(OH)_2\ (s) \leftrightarrow\ Ba^{2+}\ (aq)\ +\ 2\ OH^{1-}\ (aq)$ $\quad K_{eq} = [Ba^{2+}]\,[OH^{1-}]^2$

f) $Na_2CO_3\ (s)\ +\ H_2O\ (g)\ +\ CO_2\ (g) \leftrightarrow\ 2\ NaHCO_3\ (s)$ $\quad K_{eq} = \dfrac{1}{[H_2O]\,[CO_2]}$

g) 8. For the equilibrium reaction: $2\ N_2O_2\ (g) + H_2\ (g) \leftrightarrow 2\ N_2O\ (g) + H_2O\ (g) +$ heat

At equilibrium, the concentrations of each species are measured. $[N_2O_2] = 0.073$ mol/L, $[H_2] = 0.012$ mol/L, $[N_2O] = 0.634$ mol/L , $[H_2O] = 0.484$ mol/L.

a) Calculate the value of K_{eq} for the reaction at this temperature (3.0×10^3)

b) Does the equilibrium favour the reactants or products at this temperature? (products)

c) What is the value of K_{eq} for the reverse reaction at this temperature? (3.3×10^{-4})

9. For the reaction: $2\ HI\ (g) \leftrightarrow H_2\ (g) + I_2\ (g)$ $K_{eq} = 62.5$ at 520°C

a) Does this reaction favour the reactants or products at this temperature?

- Keq is greater than 1, so the products are favoured at this temp

b) If the reaction is endothermic and the temperature is increased, what happens to the value of K_{eq}?

- if the reaction is endothermic, as temperature is increased, the equilibrium will shift to the right and more product will form
- because there will be less reactant and more product, the value of Keq will increase as temperature increases

c) If 2.22 moles of HI are placed in a 5.00 L reaction vessel and allowed to come to equilibrium at 520°C,

i) calculate the concentration of each species at equilibrium ($[H_2]=[I_2]= 0.209$ M, $[HI]= 0.026$M)

ii) at equilibrium, how many **moles** of H_2 are present? (1.05 mol)

d) If the volume of the vessel is decreased, which way will the equilibrium shift? Why?

- if the volume of the vessel is decreased, there will be no effect on the position of the equilibrium because there are the same number of particles of gas on both sides of the equation

10. For the reaction: $N_2O_2\ (g) \leftrightarrow N_2\ (g) + O_2\ (g)$

1.40 moles of N_2O_2 (g) are placed in a 2.00 L reaction vessel and allowed to come to equilibrium. At equilibrium, there are 0.76 moles of O_2 present in the vessel. Calculate the K_{eq} for this reaction. (0.45)