Spring 2009 CH302 Worksheet 4 Answer Key:

Chemical Equilibria and an Introduction to Water Chemistry

Please note that all calculations below can be worked without the aid of a calculator.

1. Write a mass action quotient for the following chemical equation:
   \[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g) \]
   \[ K = [\text{CO}_2] \]

2. Write a mass action quotient for the following chemical equation:
   \[ \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \]
   \[ K = [\text{H}^+]\cdot[\text{OH}^-] \]

3. Based on your answers to numbers 1 & 2, what types of reactants and products always appear in mass action quotients? What types never appear in mass action quotients? Why?
   Gases and dissolved species [e.g. \( \text{CO}_2(g) \), \( \text{H}^+(aq) \) & \( \text{OH}^-(aq) \)] always appear and solids and liquids [e.g. \( \text{CaCO}_3(s) \), \( \text{CaO}(s) \) & \( \text{H}_2\text{O}(l) \)] never appear. This is because the former have a changeable activity/concentration and the latter have a constant activity.

4. What are the units of all equilibrium constants?
   Equilibrium constants have no units.

5. Complete the RICE diagram below. Express unknown quantities in terms of \( X \).
   \[
   \begin{array}{cccccc}
   \text{Reaction} & \text{CO(g)} & + & \text{NO}_2(g) & \rightleftharpoons & \text{CO}_2(g) & + & \text{NO(g)} \\
   \text{Initial} & 5 \text{ M} & & 5 \text{ M} & & 0 \text{ M} & & 8-X \text{ M} \\
   \text{Change} & -X \text{ M} & & -X \text{ M} & & +X \text{ M} & & +X \text{ M} \\
   \text{Equilibrium} & 5-X \text{ M} & & 5-X \text{ M} & & X \text{ M} & & 8 \text{ M}
   \end{array}
   \]

6. Assuming \( K = 0.5 \), what was the initial concentration of \( \text{NO}(g) \)?
   \[
   0.5 = \frac{X}{(5-X)^2} \\
   0.5(5-X)^2 = 8X \\
   0.5X^2 - 5X + 12.5 = 8X \\
   0 = 0.5X^2 - 13X + 12.5 \\
   X = \{13 \pm [169 - 4(0.5)(12.5)]^{0.5}\}/2(0.5) = 13 \pm 12 = 1
   \]
   The initial concentration of \( \text{NO}(g) \) was therefore 7 M.

7. How would the chemical system in numbers 5 & 6 respond to a decrease in volume? What about addition of \( \text{CO}(g) \)? What about removal of \( \text{NO}(g) \)?
   Since the number of moles of gas is the same on both sides of the equation, decreasing the volume of the system will not affect \( Q \) or \( K \), so nothing will occur. Addition of \( \text{CO}(g) \) will push the reaction to the right. Removal of \( \text{NO}(g) \) will pull the reaction to the right.

8. The Clausius-Clapeyron equation and the van't Hoff equation are very similar in appearance. What is the main difference between the two equations and why are they so similar?
   The main difference is that the Clausius-Clapeyron equation relates vapor pressures to temperatures and the van't Hoff equation relates equilibrium constants. They are so similar because vaporization is an equilibrium process and since liquids have a constant activity, the pressure of the gas phase is directly proportional to the equilibrium constant.

9. Based on the van't Hoff equation, how will an exothermic reactions equilibrium constant respond to changes in temperature? What about an endothermic reaction?
   For an exothermic reaction, \( K \) should be inversely proportional to \( T \). For an endothermic reaction, \( K \) should be directly proportional to \( T \).
10. In a 1 liter container you initially have one mole of each species below.
   \[ 4\text{Fe}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{Fe}_2\text{O}_3(s) \quad K = 10^{12} \]
   What happens as this system approaches equilibrium?
   Since \( Q \) is substantially less than \( K \) initially (\( 10^3 \) vs \( 10^{12} \)), as the system approaches equilibrium the pressure of oxygen will decrease dramatically and most of the metallic iron will become rust.

11. List the 7 strong acids from memory.
   Hydrochloric (HCl), Hydrobromic (HBr), Hydroiodic (HI), Sulfuric (H\(_2\)SO\(_4\)), Nitric (HNO\(_3\)), Chloric (HClO\(_3\)) and Perchloric (HClO\(_4\)).

12. List the 8 strong bases from memory.
   Lithium Hydroxide (LiOH), Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH), Rubidium Hydroxide (RbOH), Cesium Hydroxide (CsOH), Calcium Hydroxide [Ca(OH)\(_2\)], Strontium Hydroxide [Sr(OH)\(_2\)], Barium Hydroxide [Ba(OH)\(_2\)].

13. What would be the pH of 1 liter of a 10 M solution of nitric acid?
   \[ \text{pH} = -1 \]

14. How many grams of barium hydroxide would be needed to neutralize the solution in number 13?
   
   \[ 10 \text{ M} \times 1 \text{ L HNO}_3 = 10 \text{ mol HNO}_3, \text{ which would be } 10 \text{ mol H}^+ \]
   
   So we need 10 mol OH\(^-\), which would require 5 mol Ba(OH\(_2\))
   
   \[ 171 \text{ g mol}^{-1} \times 5 \text{ mol} = 855 \text{ g (OH)\(_2\)} \]

15. Rank the following solutions from lowest pH to highest pH: 0.5 M HI, 0.1 M Sr(OH)\(_2\), 2 M HClO\(_4\), 0.5 M H\(_2\)SO\(_4\), 0.1 M NaOH, 2 M KOH.
   
   \[ 2 \text{ M HClO}_4 < 0.5 \text{ M H}_2\text{SO}_4 < 0.5 \text{ M HI} < 0.1 \text{ M NaOH} < 0.1 \text{ M Sr(OH)\(_2\)} < 2 \text{ M KOH} \]

16. What is meant by the term "autoprotolysis of water?" What chemical equation describes this?
   Autoprotolysis of water refers to water's tendency to spontaneously split into a hydroxide ion and a proton. \( \text{H}_2\text{O(l)} \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \)

17. What is \( K_w \)? What is its value to at room temperature? How does temperature influence \( K_w \)?
   \( K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \) at room temperature. Since autoprotolysis is endothermic, \( K_w \) is directly proportional to temperature.

18. What would be the pOH of a 0.5 M solution of a weak acid with a \( K_a = 2 \times 10^{-4} \)?
   \[ [\text{H}^+] = (K_a \cdot C_a)^{0.5} = (2 \times 10^{-4} \cdot 0.5)^{0.5} = (10^{-4})^{0.5} = 10^{-2} \]
   \[ \text{pOH} = 14 - \text{pH} = 14 - 2 = 12 \]

19. Complete the RICE diagram for the reaction of a general weak base (:B) with water. Use general terms (e.g. \( C_b \) for initial concentration of base).
   \[
   \begin{array}{cccc}
   \text{Reaction} & :\text{B}(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{BH}^+(aq) + \text{OH}^-(aq) \\
   \text{Initial} & C_b & & 0 & 10^{-7} \\
   \text{Change} & -X & +X & +X \\
   \text{Equilibrium} & C_b - X & X & 10^{-7} + X \\
   \end{array}
   \]

20. Write \( K \) for the reaction in number 19 and then substitute the values from the RICE diagram.
   \[ K = [\text{BH}^+][\text{OH}^-] / [:\text{B}] = (X)(10^{-7} + X) / (C_b - X) \]