**Answer Key for Chemical Equilibria**

1. Equilibrium constant expressions are always written as showing a ratio of products over reactants. Here is a general format for a generic equilibrium:

aA + bB ⮀ cC + dD

The equilibrium constant, Kc , has the ratio expressed as molar concentrations:

The equilibrium constant, Kc , is called an analytical equilibrium constant and it is applied to an analytical equilibrium constant expression. The analytical equilibrium constant expression will only include those components in the equilibrium that are in the same phase. Solids are never included because one cannot measure the concentration of a solid.

The equilibrium constant, Kp , is applied to gas phase equilibria. The equilibrium constant expression is expressed as a ratio in terms of the partial pressures of the gaseous components. Applying this to the same equilibrium above, assuming A, B, C and D are all gases:

Use these concepts to write the equilibrium constant expressions for the equilibria in this question:

a. N2(g) + 2 H2(g) ⮀ N2H4(g)

This is a homogeneous equilibrium, meaning all the components are in the same phase, in this case, the gas phase. Thus, we can write both a Kc expression and a Kp expression:

b. PF5(g) ⮀ PF3(g) + F2(g)

This is also a homogeneous equilibrium, thus we can write both a Kc expression and Kp expression:

c. SiCl4(g) + 2 H2O(g) ⮀ SiO2(s) + 2 Cl2(g)

This is a heterogeneous equilibrium. Solids are never included in the equilibrium constant expressions, so we will only include the gases in this equilibrium. Since gases are involved, we are able to write both a Kc and Kp equilibrium constant expression:

1. d BaSO4(s) ⮀ Ba2+(aq) + SO42- (aq)

This is also a heterogeneous equilibrium. Exclude the solid barium sulfate and only include the aqueous Ba2+ ions and SO42- ions. Since there isn’t a gas phase component only a Kc expression can be written:

Kc = [Ba2+] [SO42-] Notice the absence of a denominator term!

2. a. Refer to the explanations in problem 1 to help you with writing the Kc and Kp, if needed.

b. The value of Kc = 1.7 x 10-3 is a small number (it is < 1). Mathematically this means the denominator term must be large than the numerator term. Thus, there are more reactants (found in the denominator term) than products (found in the numerator term), so the reaction must be reactant favored.

c. Using a general reaction: aA(g) + bB(g) ⮀ cC(g) + dD(g), the relationship between Kp and Kc is derived as follows:

From PV = nRT:

Since the n/V term is expressed in moles/liter, it is effectively the molarity, M, of the gas, P = MRT.

We can now write two equivalent expressions:

Regroup the expression on the right and hopefully you will recognize the equilibrium constant generated:

This shows how Kc is actually embedded in this expression, so the expression can be simplified to:

Kp = Kc (RT)Δn

where Δn = moles of gaseous products – moles of gaseous reactants. For the equilibrium

N2(g) + O2(g) ⮀ 2 NO(g)

Δn = 2 moles of gaseous NO – (1 mole of gaseous N2 + 1 mole of gaseous O2) = 0

Kp = 1.7 x 10-3[(0.08206 L∙atm/mol∙K)(2300K)]0 = 1.7 x 10-3

For this for this problem, Kp = Kc because any expression raised to the zero power = 1.

2 d. Use the reaction quotient, Qc, to determine whether the system is at equilibrium or whether the system has to shift towards reactants or products to reach equilibrium. The Qc is evaluated using the equilibrium constant expression. The actual initial amount of each component is introduced into the equilibrium constant expression. The resulting constant, Qc, is then compared to the actual equilibrium constant value, Kc. If Qc = Kc, the system is at equilibrium. If Qc > Kc, the numerator term must be too large, so the system lies too far towards products. In order to reach equilibrium, the system must shift towards reactants. If Qc < Kc, the denominator term is too large, so the system lies too far towards reactants. In order to reach equilibrium, the system must shift towards products.

In this problem, Kc = 1.7 x 10-3. Calculate Qc and compare the value of Qc to Kc:

Qc > Kc

19 > 1.7 x 10-3

As one can see, the system is not at equilibrium. The system currently lies too far towards products. In order to reach equilibrium, the system must shift to towards reactants to reduce the amount of excess products (the numerator must decrease) and increase the amount of reactants (the denominator must increase).

e. LeChatelier’s Principle states that when a stress is placed on an equilibrium, the equilibrium shifts in the direction that removes the stress. Based on this statement, it is important to first identify the stress. The stress could be too much of something or too little of something. Once the stress is identified, it will be easy to decide the direction of the shift.

(1) N2 gas is removed from the container. The stress created is not enough nitrogen gas in the container. The equilibrium will shift towards reactants to replenish the nitrogen gas removed.

(2) NO gas is removed from the container. The stress created is not enough NO gas in the container. The equilibrium will shift toward products to replenish the NO gas removed.

(3) O2 gas is added to the container. The stress created is too much O2 gas in the container. The equilibrium will shift towards the products to remove the excess O2 gas by making more product.

(4) Argon gas is added to the container. Argon gas is not a part of this equilibrium. The partial pressures of oxygen gas, nitrogen gas and nitrogen monoxide gas are unchanged. Only the total pressure increases. Since the equilibrium doesn’t involve argon gas, no stress has been placed on the equilibrium so the equilibrium doesn’t need to shift.

(5) The temperature of the system is decreased to 1000K. The reaction is endothermic; ΔH = +180.5 kJ/mol. This means heat is absorbed by the system from the surroundings. One may consider heat as a reactant:

heat + N2(g) + O2(g) ⮀ 2 NO(g)

The stress created is too little heat. The system will shift towards reactants to replenish the heat removed by the action of cooling the system.

(6) The volume of the container is increased. According to Boyle’s Law, pressure and volume are inversely proportional. Thus, increasing the volume will decrease the pressure. The stress could be too little pressure and the system would want to shift to the side of the reaction with more moles of gas to increase the particle number to bring the pressure back to equilibrium pressure. In this case, however, the moles of gas particles is the same on both sides of the reaction, so pressure does not affect the equilibrium.

2. f. The term equilibrium “constant” means exactly what is implied. The value is a constant, but only at the temperature at which it was measures. Notice that when an equilibrium constant is given, a temperature is always associated with that constant. The origin of the equilibrium constant is from the rate constants of the forward and reverse reactions. Reaction rates are temperature dependent. Thus when components of the equilibrium are introduced or removed, the equilibrium will shift, but as long as the temperature is unchanged, the value of the equilibrium constant does not change. Hence only in problem (5) above, will the constant change. If the equilibrium shifts towards reactants, as it does in this problem, the Kc, will also decrease. If the equilibrium shifts towards products, the equilibrium constant, Kc, will increase.

3. a. We need a reference point to start the problem. In this case, the assumption we make is that only the HI is present initially; none of the H2 or I2 has formed:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0.20 M 0 M 0 M

There currently is a stress on this equilibrium; there are no products. In order to reach equilibrium, the system has to shift towards products to reach equilibrium. For each 2 moles of HI that dissociates, 1 mole of H2and 1 mole of I2 will from. Since we don’t know the exact amount of dissociation, we use the mathematical amounts using “x” to represent the amount that shifts. Thus, for HI, a 2x amount is lost (hence, -2x) and an x amount of both H2 and I2 is generated:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0.20 M 0 M 0 M

Change -2x +x +x

Combining the Initial and the changed amounts, we have the amount at equilibrium:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0.20 M 0 M 0 M

Change -2x +x +x

Equilibrium 0.20 – x +x +x

The equilibrium constant expression is written as:

Substitute the algebraic expressions at equilibrium in to the equilibrium constant expression:

Sometimes one can simplify the expression by assuming that the x amount found in the denominator term is negligibly small. Compare the magnitude of the known concentration to the magnitude of the equilibrium constant. If constant is smaller by a factor of 100 or more, the x being considered can be neglected as being negligibly small. In this case, the difference between the magnitude of the concentration and the equilibrium constant is less than 100, so x cannot be neglected, an a quadratic equation must be solved. We have to covert the equilibrium constant to quadratic form. The series of steps needed to do so is as follows:

Take the denominator term and turn it into a quadratic by performing the appropriate multiplications:

Multiply both sides of the equation by the denominator:

Distribute 0.025 through on the right hand side of the expression:

Bring all terms to the same side of the equation. In this case, x2 is subtracted from both sides of the expression:

0 = 0.0010 – 0.010x – 0.975x2

This expression as quadratic form: ax2 + bx + c = 0, where a = -0.975, b = – 0.01 and c = 0.0010.

Use the quadratic formula to solve for both solutions of x:

Work the arithmetic under the radical first:

Find the two solutions to x:

Only one of these two solutions makes any physical sense (x = 0.027). The other solution for x, x = –0.038, is impossible, as it would give an impossible amount for the equilibrium concentration of HI. One can see this by applying x to the equilibrium amounts:

For x = - 0.038, [HI] = 0.20 – 2x = 0.20 – 2(-0.038) = 0.28 M (more than one started with)

[H2] = [I2] = x = -0.038M (negative concentration values are impossible)

For x = 0.027, [HI] = 0.20 – 2x = 0.20 – 2(0.027) = 0.15 M

[H2] = [I2] = 0.027 M (these values make “physical” sense)

An alternative method to solve this problem is to recognize that your algebraic expression is a perfect square:

Take the square root of both sides of the expression to simplify the expression:

The above expression is much easier to solve for x. Start by multiplying both sides by the denominator term to have it cancel on the left hand side of the expression:

Distribute the 0.16 through on the right hand side of the expression:

Add 0.16 x to both sides to collect the x terms:

x + 0.16x = 0.032 – 0.16x + 0.16x

1.16x = 0.032

Divide both sides by 1.16 to solve for x:

x = 0.028 = [H2] = [I2]

0.20 -2x = 0.20 – 2(0.028) = 0.14 = [HI]

These values agree in the last decimal place, an acceptable error.

3. b. The solution to this problem will be analogous to the solution in the previous part of this question. In this case one must use the quadratic equation to solve the problem since we do not have a perfect square.

Set up the table as we did in part a of this problem:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0M 0.40M 0.20 M

Notice that initial amount of HI is zero, and that we have initial amounts of “products” as our reference point. This helps us decide which way the equilibrium has to shift to reach equilibrium. The stress is the lack of HI, so an unknown amount of x has to be lost by H2 and I2 to form twice as much, 2x, of HI:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0M 0.40M 0.20 M

Change +2x -x -x

Thus at equilibrium:

2 HI(g) ⮀ H2(g) + I2(g)

Initial 0M 0.40M 0.20 M

Change +2x -x -x

Equilibrium 2x 0.40 – x 0.20 – x

The equilibrium constant expression is written as:

Substitute the algebraic expressions at equilibrium in to the equilibrium constant expression:

Multiply out the factors in the numerator:

Multipy through by 2x to cancel the denominator term on the left hand side of the expression:

0.080 – 0.60x + x2 = 0.050x

Subtract 0.050x from both sides of the expression to get the equation into quadratic form:

0.080 – 0.60x – 0.050x + x2 = 0.050x – 0.050x

The equation in quadratic form is 0.080 – 0.65x + x2 = 0, where a = 1, b = -0.65 and c = 0.080.

Substitute these values into the quadratic equation:

Find the solution under the radical first then:

Solve for the two possible values of x:

Of these two solutions, 0.48 is impossible because it is greater than the original concentrations of H2 or I2. Thus, the only answer that makes physical sense is 0.16 M. Use this to find the equilibrium amounts:

[H2] = 0.40 – 2x = 0.40 –0.16 = 0.24 M

[I2] = 0.20 – x = 0.20 – 0.16 = 0.04 M

[HI] = 2x = 2(0.16) = 0.32M

3. c. If the proper stress is placed on the equilibrium, the equilibrium could be made to shift towards products. The stresses that could be used are: (1) Addition of HI, (2) removal of H2, or (3) removal of I2. A change in volume would not help here, as the moles of gaseous reactants equals the moles of gaseous products, so a pressure change as a result of a change in the volume of the container would not work. Since a enthalpy value has not been given, one cannot predict how an increase or decrease in temperature would impact the equilibrium position.

4. a. The relationship between Kp and Kc is: Kp = Kc(RT)Δn (see problem 2c for the derivation). Our reaction is:

PF5(g) ⮀ PF3(g) + F2(g)

Kp = 1.4 x 10-5[(0.08206 L∙atm/mol∙K)(1500K)]1 = 1.7 x 10-3

where Δn for this reaction is:

2 moles of gaseous products – 1 mole of gaseous reactants = 1

4. b. Set up the table of initial conditions to provide a reference point:

PF5(g) ⮀ PF3(g) + F2(g)

Initial 0.30 0 0

The stress on this equilibrium at present is the lack of products; the reaction must shift towards products by an x amount:

PF5(g) ⮀ PF3(g) + F2(g)

Initial 0.30 0 0

Change -x +x +x

The equilibrium amounts are obtained by combining the initial amount and the change:

PF5(g) ⮀ PF3(g) + F2(g)

Initial 0.30 0 0

Change -x +x +x

Equilibrium 0.30 –x x x

The equilibrium constant expression is:

Substitute the algebraic expressions into the equilibrium constant expression:

To solve for x, one can take advantage of the fact the equilibrium constant is small. This means that the x amount of PF5 lost will be negligibly small and can be ignored. The expression simplifies to:

Solve for x by first multiplying through by the denominator:

Next take the square root of both sides of the equation to solve for x. The value of x represents the equilibrium amounts of PF3 and F2. The amount of PF5 is 0.30 –x, and one can see that it was negligibly small:

x = 2.0 x 10-3M = [PF3] = [F2]

[PF5] = 0.30 – 0.002 = 0.30M

4. c. Since the container is 1.0 L in size, the new initial concentration of F2 will be 0.0010M. Set up the table showing the initial conditions , change and equilibrium conditions as before:

PF5(g) ⮀ PF3(g) + F2(g)

Initial 0.30 0 0.0010

Change -x +x +x

Equilibrium 0.30 –x x 0.0010 + x

The equilibrium constant expression is:

Substitute the algebraic expressions into the equilibrium constant expression:

The x amount of additional F2 in the expression, 0.0010 + x, is not negligibly small. Although the x in the denominator is negligible, and since we have to use the quadratic equation, we might as well not neglect any of the variables. Multiply both sides by the denominator to start converting the expression to quadratic form:

Distribute terms where needed:

0.0010x + x2 = 4.2 x 10-6 – (1.4 x 10-5)x

Collect terms and bring them to same side of the equation:

x2 + 0.0010x + (1.4 x 10-5)x – 4. 2 x 10-6 = 4.2 x 10-6 – (1.4 x 10-5)x – 4.2 x 10-6 + (1.4 x 10-5)x

The above equation simplies to quadratic form:

x2  + 1.014 x 10-3x – 4.2 x 10-6 = 0

where a = 1, b = 1.014 x 10-3 and c = – 4.2 x 10-6

Substitute these values into the quadratic equation:

Find the solution under the radical first then:

Solve for the two possible values of x:

A concentration cannot be a negative value, so –0.0026 is an impossible result. Thus, the equilibrium concentrations of all species are:

[PF5] = 0.30 – x = 0.30 – 0.0016 = 0.30M

[F2] = 0.0010 + x = 0.0010 + 0.0016 = 0.0026M

[PF3] = x = 0.0016 M