ChemQuest 62

Intro. to Equilibrium II

Name: ____________________________
Date: _______________
Hour: _____

Information: Forward and Reverse Processes

When most people think of chemical reactions, they think of reactants being transformed into products. For example, take the reaction of carbon monoxide with hydrogen gas to form methane gas and water vapor:

$CO\ (g) + 3\ H_2\ (g) \rightarrow CH_4\ (g) + H_2O\ (g)$ ……..Equation 1

If you were watching the molecules of this reaction, you would see that at the very beginning, there is no methane and no water in the container. Soon methane and water would begin to form and then the reaction would appear to stop. **However**, at this point there would still be some carbon monoxide and hydrogen present.

What happens at the molecular level is this: as the products (methane and water) begin to form, they react with each other and begin forming the reactants (carbon monoxide and hydrogen) again. There is a forward reaction and a reverse reaction. The forward reaction is written above. The reverse reaction is below:

$CH_4\ (g) + H_2O\ (g) \rightarrow CO\ (g) + 3\ H_2\ (g)$ ……………Equation 2

The best way to represent the reaction, then, is as follows:

$CO\ (g) + 3\ H_2\ (g) \leftrightarrow CH_4\ (g) + H_2O\ (g)$ ……………Equation 3

The reaction *appears* to stop when the rate of the forward reaction equals the rate of the reverse reaction. At this point we say that the reaction has reached **equilibrium**. The reaction is still occurring, but the products and reactants are being formed at the same time so there is no net change in their amounts.

Critical Thinking Questions

1. Consider the reaction above involving carbon monoxide and hydrogen. At the beginning of the reaction, there are 2.50 moles of carbon monoxide and 5.10 moles of hydrogen gas placed in a 5.0 L container. Of course, at the very beginning there is no methane or water in the container. When equilibrium is reached, there are 1.02 moles of water in the container. Calculate the number of moles of methane, hydrogen and carbon monoxide in the container at equilibrium. (For now, don't worry about the fact that it takes place in a 5.0 L container—ignore volume…for now.)

Hint: Calculate the *change* in the number of moles of water; by how many moles did the water *increase*? The number of moles of methane increased by this same amount. The number of moles of carbon monoxide *decreased* by this same amount. The number of moles of hydrogen decreased by *three times* this amount

	$CO (g) +$	$3 H_2 (g)$ ⟷	$CH_4 (g)$ +	$H_2O (g)$
Initial:	2.50 mol	5.10 mol	0 mol	0 mol
Change:				
Equilibrium:				1.02 mol

2. Consider the following reaction: N_2 (g) + 3 H_2 (g) ←→ 2 NH_3 (g). Initially, 4.25 moles of nitrogen gas and 6.33 moles of hydrogen gas are placed in a 3.35 L container. At equilibrium, 2.15 moles of NH_3 (ammonia) was present. Calculate the number of moles of nitrogen and hydrogen at equilibrium. (This is similar to question 1. Drawing your own "equilibrium table" may be helpful.)

3. As mentioned already, equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction. Assume that all reactions discussed so far are *elementary* reactions. This means that the exponents in the rate law are the same as the coefficients in the balanced equation.
   a) Write the rate law for the forward reaction of carbon monoxide and hydrogen (see Equation 3 for the balanced chemical equation). Use k_f to symbolize the rate constant for the forward reaction.

   b) Verify the following rate law for the rate law for the *reverse* reaction of carbon monoxide and hydrogen. (Again, see Equation 3 for the balanced chemical equation.) Use k_r to symbolize the rate constant for the reverse reaction. Because it is for a *reverse* reaction, notice that the products are used in the rate law.

$$\text{Rate}_{\text{reverse}} = k_r\,[CH_4][H_2O]$$

4. Now divide the reverse rate law by the forward rate law and complete the following equation.

$$\frac{\text{rate}_{\text{reverse}}}{\text{rate}_{\text{forward}}} = \underline{\hspace{6cm}}$$

5. Recall that at equilibrium, the reverse rate equals the forward rate. Why does the left side of the equation ($\text{rate}_{\text{reverse}}/\text{rate}_{\text{forward}}$) equal one in question 4?

6. Taking into account your answer to question 5, rearrange the equation that you wrote in number four and get k_f and k_r on the left side of the reaction and everything else on the right side.

$$\frac{\text{rate}_{\text{reverse}}}{\text{rate}_{\text{forward}}} = \frac{k_r[CH_4][H_2O]}{k_f[CO][H_2]^3} \Rightarrow 1 = \frac{k_r[CH_4][H_2O]}{k_f[CO][H_2]^3} \Rightarrow \frac{k_f}{k_r} = \underline{\hspace{4cm}}$$

Information The Equilibrium Constant

The equilibrium constant is a constant that allows us to compare the concentrations of products and reactants in a chemical reaction. The equilibrium constant (K) is defined as k_f/k_r.

Critical Thinking Questions

7. Given your answer to question 6 and also the information in the previous information section, you should be able to verify that the expression for the equilibrium constant for the reaction of carbon monoxide with hydrogen is as follows:

$$k_f/k_r = K = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

8. Calculate the equilibrium constant for the reaction using your answers to question number 1 and the expression in question 7. You will first need to find the molarity of each reactant and product. Recall that the volume is given in question 1 so that you can calculate the molarity of each substance. You should get a value of 2.07 for the equilibrium constant.

9. Verify that the equilibrium constant expression for the reaction described in question two can be written as

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

10. Calculate the numeric value of the equilibrium constant from question 9 using your answers and the data in question 2. (Remember to use the volume to calculate molarity!)

11. Considering questions 7 and 9, what relationship exists between the coefficients in the balanced chemical equation and the expression for the equilibrium constant?

12. Again considering your answers to questions 7 and 9, are the products of the reaction written in the numerator or the denominator of the equilibrium constant expression?

13. Write the equilibrium constant expression for each of the following reactions.

a) $2\ HI \leftrightarrow H_2 + I_2$

b) $2\ CO_2 \leftrightarrow 2\ CO + O_2$

Information: Calculating Equilibrium Constants

Consider a 100 L container that holds 80 moles of hydrogen iodide. Over time, the hydrogen iodide decomposes into hydrogen and iodine. At equilibrium, there are 8.84 moles of iodine. The balanced equation for this process is: $2\ HI \leftrightarrow H_2 + I_2$

Critical Thinking Questions

A table similar to the one you used in question one may be helpful. You can use this table as you complete questions 13-20:

	$2\ HI \leftrightarrow$	H_2 +	I_2
Initial:			
Change:			
Equilibrium:			

14. Find the <u>initial</u> concentration of HI and the <u>equilibrium</u> concentration of I_2. (Given moles ÷ given volume)

[HI] = ________________ $[I_2]$ = __________________

15. Consider the balanced equation for a moment. How will the change in iodine concentration compare to the change in hydrogen iodide? (Hint: it depends on the coefficients in the balanced equation.)

16. What was the initial concentration of I_2? Note: “initial” means *before* any reaction takes place. Since I_2 is a product, the concentration *before* any reaction happened, should be *easy*. ☺

17. What was the initial concentration of H_2?

18. What was the change in concentration for I_2? (Remember that *change* in concentration is simply the final minus the initial concentration.)

19. Calculate the change in H_2 and the change in HI concentration.

Δ in $[H_2]$ = ____________________ Δ in [HI] = ____________________

20. What is the <u>equilibrium concentration</u> (i.e. concentration at equilibrium) of HI? Note the equilibrium concentration of HI is equal to the initial concentration of HI minus the change in concentration.

21. What is the equilibrium concentration of H_2? Note the equilibrium concentration of H_2 is equal to the initial concentration of H_2 plus the change in concentration of H_2.

22. In question 19, you subtracted the change in concentration, but in question 20, you added it. Why?

23. Write the equilibrium constant expression for this reaction. (This is similar to questions 7 and 9.)

24. Calculate the equilibrium constant for this reaction.

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Information: Equilibrium Constant for Gas Pressure

So far we have looked at equations involving gases in terms of the molarity of the gas. For example, if 3 moles of a gas was in a 1.5 L container we used the value 2.0 M in calculating the equilibrium constant. The equilibrium constant, K, when dealing strictly with molarity actually has the symbol K_c. It has been unnecessary to write K_c until now.

Molarity is not the only way to express the concentration of a gas in a container. Pressure, for example, may also be used. We know that for a 1.5 L container, the higher the pressure the greater the concentration. When only pressure information about a gaseous reaction we can still calculate an equilibrium constant, K_p. It is calculated in a very similar way as K_c is calculated. Consider the following reaction.

$$N_2\,(g) + 3\,H_2\,(g) \leftrightarrow 2\,NH_3\,(g)$$

The equilibrium constant expression, K_p for this reaction is:

$$K_p = \frac{p\mathrm{NH_3}^2}{p\mathrm{N_2}\,p\mathrm{H_2}^3}$$

Note: *p* stands for the partial pressure of each gaseous reactant or product.

Critical Thinking Questions

1. Consider the following reaction: $2\,NO\,(g) + Br_2\,(g) \leftrightarrow 2\,NOBr\,(g)$. Write the expression for K_p.

Information: Relating K_c and K_p

The values K_c and K_p are related by the following equation:

$$K_p = K_c(RT)^{\Delta n}$$

R = 0.0821 (L-atm)/(mol-K) or 8.31 (L-kPa)/(mol-K). It is customary to use atmospheres (atm) to measure pressure, so <u>we will use the value 0.0821 for R</u>.
T = Kelvin temperature
Δn = the change in the number of moles of gas as the reaction proceeds.

Critical Thinking Questions

2. Verify that $\Delta n = -1$ for the reaction in question 1. (Show how you can obtain -1.)

3. Verify that $\Delta n = -2$ for the reaction N_2 (g) + 3 H_2 (g) $\leftrightarrow$ 2 NH_3 (g).

4. For the reaction referred to in questions 1 and 2 K_c equals 0.45 at 650^{o}C. What is K_p at this temperature? You should get a value of about 0.00594.

5. For the reaction in question 3, it was found that K_p equals 1.25×10^{-4} at 425^{o}C. What is K_c at this temperature?

Information: Equilibrium Constants from the Sum of Chemical Equations

Consider the following two reactions for which the equilibrium constants are known:

Reaction 1: CO + 3 H_2 $\leftrightarrow$ CH_4 + H_2O; $K_1 = 3.92$
Reaction 2: CH_4 + 2 H_2S $\leftrightarrow$ CS_2 + 4 H_2; $K_2 = 3.3 \times 10^4$

Now consider the following reaction for which the equilibrium constant is unknown:

Reaction 3: CO + 2 H_2S $\leftrightarrow$ CS_2 + H_2O + H_2; K_3 = ?

It is possible to obtain the equilibrium constant K_3 from K_1 and K_2. The following questions will show you how.

Critical Thinking Questions

6. Which of the following is the relationship between reaction 3 and reactions 1 and 2?
   A) Reaction 3 = Reaction 1 + Reaction 2 B) Reaction 3 = Reaction 2 – Reaction 1

7. Write the equilibrium constant expressions for K_1 and K_2.

$K_1 =$ $K_2 =$

8. Now write the equilibrium constant expression for K_3.

9. Consider your answers to questions 6 and 7. Which of the following equations is true:

   A) $K_3 = K_2/K_1$ B) $K_3 = K_1 + K_2$ C) $K_3 = K_1K_2$ D) $K_3 = K_1/K_2$

10. Calculate the equilibrium constant K_3.