ChemQuest 45

Intro. to Equilibrium

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:

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

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:

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

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

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

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.

   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. We know this because of the coefficients in the balanced chemical equation.

Change in moles of H_2O, CO and of CH_4 = 1.02 because coefficients in balanced equation are equal.
Change in moles of H_2 = 3(1.02) = 3.06. Therefore the final moles of each are as follows…

CH_4 = 1.02 mol; H_2 = 5.10-3.06 = 2.04 mol; CO = 2.50 – 1.02 = 1.48 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.

   There were initially 0 moles of NH_3, but at equilibrium there were 2.15 moles. From this we can calculate the change in moles of N_2 and H_2 and then the amount at equilibrium

	N_2 (g) +	3 H_2 (g) ←→	2 NH_3 (g)
Initial moles:	4.25	6.33	0
Change in moles:	-1.075	-3.225	+2.15
Final moles:	**3.175**	**3.105**	2.15

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. Use k_f to symbolize the rate constant for the forward reaction.

      Rate = $k_f\,[CO][H_2]^3$

   b) Write the rate law for the reverse reaction of carbon monoxide and hydrogen. Use k_r to symbolize the rate constant for the reverse reaction.

      Rate = $k_r\,[H_2O][CH_4]$

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

$$\frac{\text{rate}_{\text{reverse}}}{\text{rate}_{\text{forward}}} = \frac{k_r\,[H_2O][CH_4]}{k_f\,[CO][H_2]^3}$$

5. At equilibrium, the reverse rate equals the forward rate. What does the left side of the equation in question 4 equal?

   Since $\text{rate}_{\text{reverse}} = \text{rate}_{\text{forward}}$, then $\text{rate}_{\text{reverse}} \div \text{rate}_{\text{forward}} = 1$

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.

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

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 above, write the expression for the equilibrium constant for the reaction of carbon monoxide with hydrogen.

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

8. Calculate the equilibrium constant for the reaction using your answers to question number 1. You will first need to find the molarity of each reactant and product. You should get a value of 2.07.

   We need to divide each of the final moles from Q 1 by 5.0L to obtain molarity.
   $[CH_4] = [H_2O] = 1.02 \div 5 = 0.204$ M; $[H_2] = 2.04 \div 5 = 0.408$ M; $[CO] = 1.48 \div 0.296$ M

$$\frac{[H_2O][CH_4]}{[CO][H_2]^3} = \frac{(0.204)(0.204)}{(0.296)(0.408)^3} = 2.07$$

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

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

   Yes, in general, equilibrium constants are written as the concentration of the products divided by the concentration of the reactants, with each substance raised to the power of its coefficient.

10. Calculate the numeric value of the equilibrium constant from question 9 using your answers and the data in question 2.

$[NH_3] = 2.15\text{mol} \div 3.35\text{L} = 0.642\text{M}$; $[N_2] = 3.175\text{mol} \div 3.35\text{L} = 0.948\text{M}$; $[H_2] = 3.105 \div 3.35\text{L} = 0.927\text{M}$

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.642)^2}{(0.948)(0.927)^3} = 0.546$$

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

    In general, equilibrium constants are written as the concentration of the products divided by the concentration of the reactants, with each substance raised to the power of its coefficient.

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

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

$$\frac{[H_2][I_2]}{[HI]^2}$$

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

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

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

13. Find the initial concentration of HI and the equilibrium concentration of I_2.

    [HI] = 80 ÷ 100 = 0.80 M $[I_2]$ = 8.84 ÷ 100 = 0.0884 M

14. 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.)

    The change in HI will be twice the change in I_2.

15. What was the initial concentration of I_2? Note: "initial" means *before* any reaction takes place.

    Zero

16. What was the initial concentration of H_2?

    Zero

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

    0.0884 M

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

    Δ in $[H_2]$ = 0.0884 M Δ in [HI] = (0.0884)(2) = 0.177 M

19. 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.

    0.80 – 0.177 = 0.623 M

20. 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.

    0 + 0.0884 = 0.0884 M

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

    Question 19 referred to a *reactant* and the concentration of a reactant is decreasing with time. Question 20 referred to a *product* and the concentration of product increases with time.

22. Write the equilibrium constant expression for this reaction.

$$\frac{[H_2][I_2]}{[HI]^2}$$

23. Calculate the equilibrium constant for this reaction.

$$\frac{(0.0884)(0.0884)}{(0.7116)^2} = 0.0154$$

24. This problem combines all of the previous eleven questions and asks you to find the equilibrium constant for a reaction. Consider the following reaction: $2\,NO + O_2 \rightarrow 2\,NO_2$. 5.25 moles of NO and 3.15 moles of O_2 are combined in a 12.0 L container. At equilibrium 3.20 moles of NO_2 are in the container. Verify that the equilibrium constant for this reaction is 18.88. Don't forget to use molarity instead of moles!

Initial concentrations:
$[NO] = 5.25 \div 12.0 = 0.4375$ M
$[O_2] = 3.15 \div 12.0 = 0.2625$ M

Equilibrium (final) concentrations:
$[NO_2] = 3.20 \div 12.0 = 0.2667$ M

Changes in concentration:
$\Delta[NO_2] = 0.2667$ M (because there was zero to start with and at equilibrium there was 0.2667 M)
$\Delta[NO] = \Delta[NO_2] = 0.2667$ M (because coefficients are same in balanced equation)
$\Delta[O_2] = ½\,(\Delta[NO_2]) = 0.1333$ M (because there is a 1:2 ratio in balanced equation.)

Equilibrium (final) concentrations:
$[NO_2] = 0.2667$ M
$[NO] = 0.4375 - 0.2667 = 0.1708$ M
$[O_2] = 0.2625 - 0.1333 = 0.1292$ M

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(0.2667)^2}{(0.1708)^2(0.1292)} = 18.87$$

Skill Practice 45

Equilibrium Practice

Name: ______________________

Date: ______________

Hour: ____

1. What is meant when we say that a reaction has reached "equilibrium"?

   The rate of formation of products equals the rate of formation of reactants.

2. Consider the following chemical equation: $2\ N_2O_5 \leftrightarrow 2\ N_2 + 5\ O_2$. At equilibrium, the concentration of O_2 is 0.45 M, the concentration of N_2O_5 is 1.20 M, and the concentration of N_2 is 0.71 M. Calculate the equilibrium constant, K.

   0.00645 M

3. In an experiment, 0.100 mol of H_2 and 0.100 mol of I_2 are mixed in a 3.00-L container according to the following equation: $H_2 + I_2 \leftrightarrow 2\ HI$. If K = 50.0 for this reaction, what is the equilibrium concentration of I_2, H_2 and HI?

   $[H_2] = 0.0073$ M $[I_2] = 0.0073$ M $[HI] = 0.0514$ M

4. How many moles of each substance is in a 1.0 L vessel if you start with 0.500 mol of H_2 and 0.500 mol of I_2 to synthesize HI. K is 49.7.

   $[H_2] = [I_2] = 0.111$ M $[HI] = 0.778$ M

5. Consider the following reaction: $PCl_5\ (g) \leftrightarrow PCl_3\ (g) + Cl_2\ (g)$. If the initial concentration of PCl_5 is 1.00 mol/L, what is the equilibrium composition (i.e. the concentration of each substance at equilibrium) of the gaseous mixture? K is 0.0211.

   $[PCl_5] = 0.865$ M $[PCl_3] = [Cl_2] = 0.135$ M