Chapter 12 Review Questions and Text Homework Solutions

Review Questions

3. $2\ \mathrm{NOCl}(g) \rightleftharpoons 2\ \mathrm{NO}(g) + \mathrm{Cl_2}(g) \quad K = 1.6 \times 10^{-5}$

The expression for K is the product concentrations divided by the reactant concentrations. When K has a value much less than one, the product concentrations are relatively small and the reactant concentrations are relatively large.

$2\ \mathrm{NO}(g) \rightleftharpoons \mathrm{N_2}(g) + \mathrm{O_2}(g) \quad K = 1 \times 10^{31}$

When K has a value much greater than one, the product concentrations are relatively large and the reactant concentrations are relatively small. In both cases, however, the rate of the forward reaction equals the rate of the reverse reaction at equilibrium (this is a definition of equilibrium).

5. When reactants and products are all in the same phase, these are homogeneous equilibria. Heterogeneous equilibria involve more than one phase. In general, for a homogeneous gas phase equilibria, all reactants and products are included in the K expression. In heterogeneous equilibria, equilibrium does not depend on the amounts of pure solids or liquids present. The amount of solids and liquids present are not included in K expressions; they just have to be present. On the other hand, gases and solutes are always included in K expressions. Solutes have (aq) written after them.

6. For the gas phase reaction $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$:

the equilibrium constant expression is: $K = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$

and the reaction quotient has the same form: $Q = \dfrac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$

The difference is that in the expression for K, we use equilibrium concentrations, i.e., [A], [B], [C], and [D] are all in equilibrium with each other. Any set of concentrations can be plugged into the reaction quotient expression. Typically, we plug initial concentrations into the Q expression and then compare the value of Q to K to see if the reaction is at equilibrium. If $Q = K$, the reaction is at equilibrium with these concentrations. If $Q \neq K$, then the reaction will have to shift either to products or to reactants to reach equilibrium. For $Q > K$, the net change in the reaction to get to equilibrium must be a conversion of products into reactants. We say the reaction shifts left to reach equilibrium. When $Q < K$, the net change in the reaction to get to equilibrium must be a conversion of reactants into products; the reaction shifts right to reach equilibrium.

Text Homework

28. $[\mathrm{N_2O}] = \dfrac{2.00 \times 10^{-2}\ \mathrm{mol}}{2.00\ \mathrm{L}}$; $[\mathrm{N_2}] = \dfrac{2.80 \times 10^{-4}\ \mathrm{mol}}{2.00\ \mathrm{L}}$; $[\mathrm{O_2}] = \dfrac{2.50 \times 10^{-5}\ \mathrm{mol}}{2.00\ \mathrm{L}}$

$$K = \frac{[N_2O]^2}{[N_2]^2[O_2]} = \frac{\left(\frac{2.00 \times 10^{-2}}{2.00}\right)^2}{\left(\frac{2.80 \times 10^{-4}}{2.00}\right)^2\left(\frac{2.50 \times 10^{-5}}{2.00}\right)} = \frac{(1.00 \times 10^{-2})^2}{(1.40 \times 10^{-4})^2(1.25 \times 10^{-5})}$$

$$= 4.08 \times 10^8$$

If the given concentrations represent equilibrium concentrations, then they should give a value of $K = 4.08 \times 10^8$.

$$\frac{(0.200)^2}{(2.00 \times 10^{-4})^2(0.00245)} = 4.08 \times 10^8$$

Because the given concentrations when plugged into the equilibrium constant expression give a value equal to K (4.08×10^8), this set of concentrations is a system at equilibrium.

30. $K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} = \frac{(3.1 \times 10^{-2})^2}{(0.85)(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$

$$\frac{(0.0167)^2}{(0.525)(0.00761)^3} = 1.21 \times 10^3$$

When the given partial pressures in atmospheres are plugged into the K_p expression, the value does not equal the K_p value of 3.8×10^4. Therefore, one can conclude that the given set of partial pressures does not represent a system at equilibrium.

33. Solids and liquids do not appear in equilibrium expressions. Only gases and dissolved solutes appear in equilibrium expressions.

a. $K = \frac{[H_2O]}{[NH_3]^2[CO_2]}$; $K_p = \frac{P_{H_2O}}{P_{NH_3}^2 \times P_{CO_2}}$

b. $K = [N_2][Br_2]^3$; $K_p = P_{N_2} \times P_{Br_2}^3$

c. $K = [O_2]^3$; $K_p = P_{O_2}^3$

d. $K = \frac{[H_2O]}{[H_2]}$; $K_p = \frac{P_{H_2O}}{P_{H_2}}$

37. Because solids do not appear in the equilibrium constant expression, $K = 1/[O_2]^3$.

$$[O_2] = \frac{1.0 \times 10^{-3}\ \text{mol}}{2.0\ \text{L}};\ K = \frac{1}{[O_2]^3} = \frac{1}{\left(\frac{1.0 \times 10^{-3}}{2.0}\right)^3} = \frac{1}{(5.0 \times 10^{-4})^3} = 8.0 \times 10^9$$

39. $H_2O(g) + Cl_2O(g) \rightarrow 2\ HOCl(g)$ $\quad K = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = 0.0900$

Use the reaction quotient Q to determine which way the reaction shifts to reach equilibrium. For the reaction quotient, initial concentrations given in a problem are used to calculate the value for Q. If Q < K, then the reaction shifts right to reach equilibrium. If Q > K, then the reaction shifts left to reach equilibrium. If Q = K, then the reaction does not shift in either direction because the reaction is already at equilibrium.

a. $$Q = \frac{[HOCl]_0^2}{[H_2O]_0[Cl_2O]_0} = \frac{\left(\frac{1.0\text{ mol}}{1.0\text{ L}}\right)^2}{\left(\frac{0.10\text{ mol}}{1.0\text{ L}}\right)\left(\frac{0.10\text{ mol}}{1.0\text{ L}}\right)} = 1.0 \times 10^2$$

Q > K, so the reaction shifts left to produce more reactants to reach equilibrium.

b. $$Q = \frac{\left(\frac{0.084\text{ mol}}{2.0\text{ L}}\right)^2}{\left(\frac{0.98\text{ mol}}{2.0\text{ L}}\right)\left(\frac{0.080\text{ mol}}{2.0\text{ L}}\right)} = 0.090 = K; \quad \text{at equilibrium}$$

c. $$Q = \frac{\left(\frac{0.25\text{ mol}}{3.0\text{ L}}\right)^2}{\left(\frac{0.56\text{ mol}}{3.0\text{ L}}\right)\left(\frac{0.0010\text{ mol}}{3.0\text{ L}}\right)} = 110$$

Q > K, so the reaction shifts to the left to reach equilibrium.

47. When solving equilibrium problems, a common method to summarize all the information in the problem is to set up a table. We commonly call this table an ICE table because it summarizes *i*nitial concentrations, *c*hanges that must occur to reach equilibrium, and *e*quilibrium concentrations (the sum of the initial and change columns). For the change column, we will generally use the variable *x,* which will be defined as the amount of reactant (or product) that must react to reach equilibrium. In this problem, the reaction must shift right to reach equilibrium because there are no products present initially. Therefore, *x* is defined as the amount of reactant SO_3 that reacts to reach equilibrium, and we use the coefficients in the balanced equation to relate the net change in SO_3 to the net change in SO_2 and O_2. The general ICE table for this problem is:

	$2\ SO_3(g)$	$\rightleftharpoons$	$2\ SO_2(g)$	+	$O_2(g)$	$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$
Initial	12.0 mol/3.0 L		0		0	
	Let *x* mol/L of SO_3 react to reach equilibrium.					
Change	$-x$	→	$+x$		$+x/2$	
Equil.	$4.0 - x$		x		$x/2$	

From the problem, we are told that the equilibrium SO_2 concentration is 3.0 mol/3.0 L = 1.0 *M* ($[SO_2]_e = 1.0\ M$). From the ICE table setup, $[SO_2]_e = x$, so $x = 1.0$. Solving for the other equilibrium concentrations: $[SO_3]_e = 4.0 - x = 4.0 - 1.0 = 3.0\ M$; $[O_2] = x/2 = 1.0/2 = 0.50\ M$.

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.0)^2\,(0.50)}{(3.0)^2} = 0.056$$

Alternate method: Fractions in the change column can be avoided (if you want) be defining *x* differently. If we were to let 2*x* mol/L of SO_3 react to reach equilibrium, then the ICE table setup is:

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g) \qquad K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

Initial $4.0\ M$ $\quad$ 0 $\quad$ 0

Let $2x$ mol/L of SO_3 react to reach equilibrium.

Change $-2x \rightarrow +2x \quad +x$

Equil. $4.0 - 2x \quad 2x \quad x$

Solving: $2x = [SO_2]_e = 1.0\ M,\ \ x = 0.50\ M$;

$[SO_3]_e = 4.0 - 2(0.50) = 3.0\ M$; $[O_2]_e = x = 0.50\ M$

These are the same equilibrium concentrations as solved for previously, thus K will be the same (as it must be). The moral of the story is to define x in a manner that is most comfortable for you. Your final answer is independent of how you define x initially.

63. a. No effect; adding more of a pure solid or pure liquid has no effect on the equilibrium position.

b. Shifts left; HF(g) will be removed by reaction with the glass. As HF(g) is removed, the reaction will shift left to produce more HF(g).

c. Shifts right; as $H_2O(g)$ is removed, the reaction will shift right to produce more $H_2O(g)$.

68. a. Shift to left

b. Shift to right; because the reaction is endothermic (heat is a reactant), an increase in temperature will shift the equilibrium to the right.

c. No effect; the reactant and product concentrations/partial pressures are unchanged.

d. Shift to right

e. Shift to right; because there are more gaseous product molecules than gaseous reactant molecules, the equilibrium will shift right with an increase in volume.