Fundamental Equilibrium Concepts

Section 88 – Equilibrium Calculations

1. A reaction is represented by this equation: $A(aq) + 2B(aq) \rightleftharpoons 2C(aq)$ $\quad K_c = 1 \times 10^3$

   (a) Write the mathematical expression for the equilibrium constant.
   (b) Using concentrations ≤ 1 *M*, identify two sets of concentrations that describe a mixture of A, B, and C at equilibrium.

Solution

$K_c = \frac{[C]^2}{[A][B]^2}$. There are many different sets of equilibrium concentrations; two are [A] = 0.1 *M*, [B] = 0.1 *M*, [C] = 1 *M*; and [A] = 0.01, [B] = 0.250, [C] = 0.791.

2. A reaction is represented by this equation: $2W(aq) \rightleftharpoons X(aq) + 2Y(aq)$ $\quad K_c = 5 \times 10^{-4}$
   (a) Write the mathematical expression for the equilibrium constant.
   (b) Using concentrations of ≤ 1 *M*, identify two sets of concentrations that describe a mixture of W, X, and Y at equilibrium.

Solution

(a) $K_c = \frac{[X][Y]^2}{[W]^2}$. (b) Two of the many possible sets of concentrations are [X] = 0.05 *M*, [Y] = 0.015 *M*, [W] = 0.15 *M*; and [X] = 0.050 *M*, [Y] = 0.01 *M*, [W] = 0.10 *M*

3. What is the value of the equilibrium constant at 500 °C for the formation of NH_3 according to the following equation?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

An equilibrium mixture of $NH_3(g)$, $H_2(g)$, and $N_2(g)$ at 500 °C was found to contain 1.35 *M* H_2, 1.15 *M* N_2, and 4.12×10^{-1} *M* NH_3.

Solution

The reaction may be written as

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The equilibrium constant for the reaction is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(4.12 \times 10^{-1})^2}{(1.15)(1.35)^3}$$

$= 0.0600 = 6.00 \times 10^{-2}$

4. Hydrogen is prepared commercially by the reaction of methane and water vapor at elevated temperatures.

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

What is the equilibrium constant for the reaction if a mixture at equilibrium contains gases with the following concentrations: CH_4, 0.126 M; H_2O, 0.242 M; CO, 0.126 M; H_2 1.15 M, at a temperature of 760 °C?

Solution

$$K_c = \frac{[H_2]^3[CO]}{[CH_4][H_2O]} = \frac{[1.15]^3[0.126]}{[0.126][0.242]} = 6.28$$

5. A 0.72-mol sample of PCl_5 is put into a 1.00-L vessel and heated. At equilibrium, the vessel contains 0.40 mol of $PCl_3(g)$ and 0.40 mol of $Cl_2(g)$. Calculate the value of the equilibrium constant for the decomposition of PCl_5 to PCl_3 and Cl_2 at this temperature.

Solution

The decomposition of PCl_5 to PCl_3 and Cl_2 is given as

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Let x = change in $[PCl_5]$.

	$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
Initial concentration (M)	0.72	0	0
Change (M)	$-x$	x	x
Equilibrium concentration (M)	$0.72 - x = 0.32$	$0 + x = 0.40$	$0 + x = 0.40$

$$K_c = \frac{(0.40)(0.40)}{(0.32)} = 0.50$$

6. At 1 atm and 25 °C, NO_2 with an initial concentration of 1.00 M is 0.0033% decomposed into NO and O_2. Calculate the value of the equilibrium constant for the reaction.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

Solution

The decomposition forms $3.3 \times 10^{-5} \times 1.00\ M = 3.3 \times 10^{-5}\ M$ NO and $1.65 \times 10^{-5}\ M$ O_2. The amount of NO_2 remaining is $1.00\ M - 3.3 \times 10^{-5}\ M \approx 1.00\ M$

$$K_c = \frac{[NO][O_2]}{[NO_2]^2} = \frac{(3.3 \times 10^{-5}\ M)^2(1.65 \times 10^{-5}\ M)}{(1.00\ M)^2} = 1.8 \times 10^{-14}$$

7. Calculate the value of the equilibrium constant K_P for the reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ from these equilibrium pressures: NO, 0.050 atm; Cl_2, 0.30 atm; NOCl, 1.2 atm.

Solution

$$K_P = \frac{[\mathrm{NOCl}]^2}{[\mathrm{NO}]^2[\mathrm{Cl_2}]} = \frac{(1.2)^2}{(0.050)^2(0.30)} = \frac{1.44}{(2.5 \times 10^{-3})(0.30)} = 1.9 \times 10^3$$

8. When heated, iodine vapor dissociates according to this equation:

$$I_2(g) \rightleftharpoons 2\mathrm{I}(g)$$

At 1274 K, a sample exhibits a partial pressure of I_2 of 0.1122 atm and a partial pressure due to I atoms of 0.1378 atm. Determine the value of the equilibrium constant, K_P, for the decomposition at 1274 K.

Solution

$$K_P = \frac{(P_{\mathrm{I}})^2}{P_{\mathrm{I_2}}} = \frac{(0.1378)^2}{0.1122} = 0.1692$$

9. A sample of ammonium chloride was heated in a closed container.

$$\mathrm{NH_4Cl}(s) \rightleftharpoons \mathrm{NH_3}(g) + \mathrm{HCl}(g)$$

At equilibrium, the pressure of $NH_3(g)$ was found to be 1.75 atm. What is the value of the equilibrium constant K_P for the decomposition at this temperature?

Solution

Because the decomposition must generate the same pressure of HCl as NH_3, 1.75 atm of HCl must be present. $K_\mathrm{p} = P_{\mathrm{NH_3}} P_{\mathrm{HCl}} = (1.75\ \mathrm{atm})(1.75\ \mathrm{atm}) = 3.06$

10. At a temperature of 60 °C, the vapor pressure of water is 0.196 atm. What is the value of the equilibrium constant K_P for the vaporization equilibrium at 60 °C?

$$H_2O(l) \rightleftharpoons \mathrm{H_2}O(g)$$

Solution

In heterogeneous equilibrium systems such as this one, the concentration of the condensed phase is constant at a given temperature. Thus, the equilibrium expression for the transformation $H_2O(l) \rightleftharpoons \mathrm{H_2}O(g)$ is written as $K_P = P_{\mathrm{H_2O}}$. At 60 ºC, the pressure of water vapor at equilibrium with liquid water is 0.196 atm; therefore, the equilibrium constant is $K_P = 0.196$.

11. A 1.00-L vessel at 400 °C contains the following equilibrium concentrations: N_2, 1.00 *M*; H_2, 0.50 *M*; and NH_3, 0.25 *M*. How many moles of hydrogen must be removed from the vessel to increase the concentration of nitrogen to 1.1 *M*? The equilibrium reaction is

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Solution

The reaction is

$$N_2(g) + 3\mathrm{H_2}(g) \rightleftharpoons 2\mathrm{NH_3}(g)$$

The equilibrium constant is calculated from the equilibrium data.

$$K_c = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3} = \frac{(0.25)^2}{(1.00)(0.50)^3} = 0.50$$

Now the concentration of H_2 must be changed to increase the concentration of nitrogen to 1.1 *M*. The increase in nitrogen from 1.00 *M* to 1.1 *M* (an increase by 0.1 mol in the 1.00-L vessel) requires a corresponding decrease in NH_3 of 0.2 mol (i.e., the stoichiometry is $2NH_3$ for every $1N_2$). The decrease in 0.2 mol of NH_3 leaves 0.25 – 0.20 = 0.05 mol of NH_3 at the new position of equilibrium. Solve for the $[H_2]$ at equilibrium:

$$K_c = \frac{(0.05)^2}{(1.1)[H_2]^3} = 0.50$$

$$0.50[H_2]^3 = \frac{0.0025}{1.1} = 0.002273$$

$[H_2]^3 = 0.004545$

$[H_2] = 0.17$ mol/L

This is the new equilibrium amount of H_2. The amount of H_2 that would have to be removed to reach this level is

$$\begin{aligned} &\text{from original hydrogen: } 0.50 \text{ mol} - 0.17 \text{ mol} &&= 0.33 \text{ mol} \\ &\text{from decomposition of } NH_3 &&= \underline{0.30 \text{ mol}} \\ &\text{total moles of } H_2 \text{ that must be removed:} &&= 0.63 \text{ mol} \end{aligned}$$

12. Analysis of the gases in a sealed reaction vessel containing NH_3, N_2, and H_2 at equilibrium at 400°C established the concentration of N_2 to be 1.2 *M* and the concentration of H_2 to be 0.24 *M*.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.50 \text{ at } 400\ °C$$

Calculate the equilibrium molar concentration of NH_3.

Solution

Write the equilibrium constant expression and solve for $[NH_3]$.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[NH_3]^2}{[1.2][0.24]^3} = 0.50$$

$[NH_3]^2 = 1.2 \times (0.24)^3 \times 0.50 = 0.0083$

$[NH_3] = 9.1 \times 10^{-2}\ M$

13. Calculate the number of moles of HI that are at equilibrium with 1.25 mol of H_2 and 1.25 mol of I_2 in a 5.00–L flask at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ °C$$

Solution

Write the equilibrium constant expression, and then solve for [HI]. From [HI], determine the moles of HI present.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[HI]^2}{\left[\frac{1.25}{5.00}\right]\left[\frac{1.25}{5.00}\right]} = 50.2$$

$[HI]^2 = (0.250)^2 \times 50.2 = 3.14$

$[HI] = 1.77\ M$

5 L × 1.77 *M* = 8.85 mol HI

14. What is the pressure of BrCl in an equilibrium mixture of Cl_2, Br_2, and BrCl if the pressure of Cl_2 in the mixture is 0.115 atm and the pressure of Br_2 in the mixture is 0.450 atm?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g) \qquad K_P = 4.7 \times 10^{-2}$$

Solution

Write the equilibrium constant expression and solve for P_{BrCl}.

$$K_P = \frac{(P_{\mathrm{BrCl}})^2}{P_{\mathrm{Cl_2}}P_{\mathrm{Br_2}}} = \frac{(P_{\mathrm{BrCl}})^2}{(0.115)(0.450)} = 4.7 \times 10^{-2}$$

$$(P_{\mathrm{BrCl}})^2 = 0.115 \times 0.450 \times 4.7 \times 10^{-2} = 2.43 \times 10^{-3} \text{ atm}$$

$P_{\mathrm{BrCl}} = 4.9 \times 10^{-2}$atm

15. What is the pressure of CO_2 in a mixture at equilibrium that contains 0.50 atm H_2, 2.0 atm of H_2O, and 1.0 atm of CO at 990 °C?

$$H_2(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2}O(g) + \mathrm{CO}(g) \qquad K_P = 1.6 \text{ at } 990\ °\mathrm{C}$$

Solution

Write the equilibrium constant expression and solve for $P_{\mathrm{CO_2}}$.

$$K_P = \frac{P_{\mathrm{H_2O}}P_{\mathrm{CO}}}{P_{\mathrm{H_2}}P_{\mathrm{CO_2}}} = \frac{(2.0)(1.0)}{(0.50)P_{\mathrm{CO_2}}} = 1.6$$

$$P_{\mathrm{CO_2}} = \frac{2.0 \times 1.0}{0.50 \times 1.6} = 2.5 \text{ atm}$$

16. Cobalt metal can be prepared by reducing cobalt(II) oxide with carbon monoxide.

$$\mathrm{CoO}(s) + \mathrm{CO}(g) \rightleftharpoons \mathrm{Co}(s) + \mathrm{CO_2}(g) \qquad K_c = 4.90 \times 10^2 \text{at } 550\ °C$$

What concentration of CO remains in an equilibrium mixture with $[CO_2] = 0.100\ M$?

Solution

Write the equilibrium constant expression and solve for [CO].

$$K_c = \frac{[\mathrm{CO_2}]}{[\mathrm{CO}]} = \frac{0.100}{[\mathrm{CO}]} = 4.90 \times 10^2$$

$$[\mathrm{CO}] = \frac{0.100}{4.90 \times 10^2} = 2.04 \times 10^{-4}\ M$$

17. Carbon reacts with water vapor at elevated temperatures.

$$C(s) + \mathrm{H_2}O(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{H_2}(g) \qquad K_c = 0.2 \text{ at } 1000\ °C$$

Assuming a reaction mixture initially contains only reactants, what is the concentration of CO in an equilibrium mixture with $[H_2O] = 0.500\ M$ at 1000 °C?

Solution

From the equilibrium constant expression, $K_c = \frac{[\mathrm{CO}][\mathrm{H_2}]}{[\mathrm{H_2O}]} = \frac{[\mathrm{CO}][\mathrm{H_2}]}{0.500} = 0.2$. Since [CO] must equal $[H_2]$, let the concentrations of both CO and H_2 be *x*. $x^2 = 0.500 \times 0.2 = 0.01$; $x = [CO] = [H_2] = 0.3\ M$.

18. Sodium sulfate 10–hydrate, $Na_2SO_4•10H_2O$, dehydrates according to the equation

$$\mathrm{Na_2SO_4} \bullet 10H_2O(s) \rightleftharpoons \mathrm{Na_2SO_4}(s) + 10H_2O(g) \qquad K_P = 4.08 \times 10^{-25} \text{at } 25\ °C$$

What is the pressure of water vapor at equilibrium with a mixture of $Na_2SO_4•10H_2O$ and $NaSO_4$?

Solution

Because two of the substances involved in the equilibrium are solids, their activities are 1, and their pressures are constant and do not appear in the equilibrium expression.

$$K_P = 4.08 \times 10^{-25} = (P_{\text{H}_2\text{O}})^{10}$$

$$P_{\text{H}_2\text{O}} = \sqrt[10]{4.08 \times 10^{-25}} = 3.64 \times 10^{-3} \text{ atm}$$

19. Calcium chloride 6–hydrate, $CaCl_2 \cdot 6H_2O$, dehydrates according to the equation

$$\text{CaCl}_2 \bullet 6\text{H}_2O(s) \rightleftharpoons \text{CaCl}_2(s) + 6\text{H}_2O(g) \qquad K_P = 5.09 \times 10^{-44} \text{at } 25\,°C$$

What is the pressure of water vapor at equilibrium with a mixture of $CaCl_2 \cdot 6H_2O$ and $CaCl_2$ at 25 °C?

Solution

Two of the components of this system are solids and have activities of 1. Their pressures are constant and do not enter into the equilibrium expression.

$$K_P = (P_{\text{H}_2\text{O}})^6 = 5.09 \times 10^{-44}$$

$$P_{\text{H}_2\text{O}} = \sqrt[6]{5.09 \times 10^{-44}} = 6.09 \times 10^{-8} \text{ atm}$$

20. A student solved the following problem and found $[N_2O_4] = 0.16$ *M* at equilibrium. How could this student recognize that the answer was wrong without reworking the problem? The problem was: What is the equilibrium concentration of N_2O_4 in a mixture formed from a sample of NO_2 with a concentration of 0.10 *M*?

$$2\text{NO}_2(g) \rightleftharpoons \text{N}_2O_4(g) \qquad K_c = 160$$

Solution

The stoichiometry of the reaction between $2NO_2$ and N_2O_4 forces the concentration of N_2O_4 to be no larger than one-half of that of NO_2. Therefore, no concentration value for $N_2O_4 > 0.05$ *M* is possible.

21. Assume that the change in concentration of N_2O_4 is small enough to be neglected in the following problem.

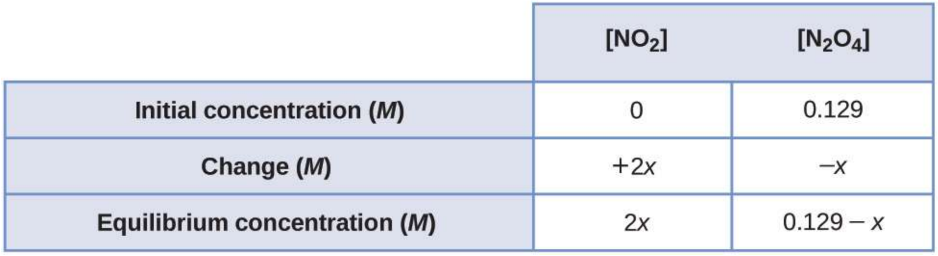
(a) Calculate the equilibrium concentration of both species in 1.00 L of a solution prepared from 0.129 mol of N_2O_4 with chloroform as the solvent.

$N_2O_4(g) \rightleftharpoons 2\text{NO}_2(g) \qquad K_c = 1.07 \times 10^{-5}$ in chloroform

(b) Confirm that the change is small enough to be neglected.

Solution

(a) Write the starting conditions, change, and equilibrium constant in tabular form.



	$[NO_2]$	$[N_2O_4]$
Initial concentration (*M*)	0	0.129
Change (*M*)	$+2x$	$-x$
Equilibrium concentration (*M*)	$2x$	$0.129 - x$

Since *K* is very small, ignore *x* in comparison with 0.129 *M*. The equilibrium expression is

$$K_c = 1.07 \times 10^{-5} = \frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]} = \frac{(2x)^2}{(0.129 - x)} = \frac{(2x)^2}{0.129}$$

$$x^2 = \frac{0.129 \times 1.07 \times 10^{-5}}{4} = 3.45 \times 10^{-7}$$

$x = 5.87 \times 10^{-4}$
The concentrations are:
$[\mathrm{NO_2}] = 2x = (5.87 \times 10^{-4})(2) = 1.17 \times 10^{-3}\ M$
$[\mathrm{N_2O_4}] = 0.129 - x = 0.129 - 5.87 \times 10^{-4} = 0.128\ M$:
(b) The assumption that x is negligibly small compared to 0.129 is confirmed by comparing the initial concentration of the N_2O_4 to its concentration at equilibrium (they differ by just 1 in the least significant digit's place).

22. Assume that the change in concentration of $COCl_2$ is small enough to be neglected in the following problem.
    (a) Calculate the equilibrium concentration of all species in an equilibrium mixture that results from the decomposition of $COCl_2$ with an initial concentration of 0.3166 M.

    $$\mathrm{COCl_2}(g) \rightleftharpoons \mathrm{CO}(g) + \mathrm{Cl_2}(g) \qquad K_c = 2.2 \times 10^{-10}$$

    (b) Confirm that the change is small enough to be neglected.

Solution
(a) Write the starting conditions, change, and equilibrium conditions in tabular form.

	[CO]	[Cl$_2$]	[COCl$_2$]
Initial concentration (M)	0	0	0.3166
Change (M)	$+x$	$+x$	$-x$
Equilibrium concentration (M)	x	x	$0.3166 - x$

Since K_c is very small, ignore x in comparison with 0.3166 M. The equilibrium constant expression is

$$K_c = \frac{[\mathrm{CO}][\mathrm{Cl_2}]}{[\mathrm{COCl_2}]} = \frac{x^2}{0.3166} = 2.2 \times 10^{-10}$$

$x^2 = 6.965 \times 10^{-11}$
$x = 8.3 \times 10^{-6} = [\mathrm{CO}] = [\mathrm{Cl_2}]$
$[\mathrm{COCl_2}] = 0.3166 - 8.3 \times 10^{-6} = 0.3166$
(b) The assumption that x is negligibly small compared to 0.3166 is confirmed by comparing the initial concentration of the $COCl_2$ to its concentration at equilibrium (they are identical when recorded to the proper number of significant digits).

23. Assume that the change in pressure of H_2S is small enough to be neglected in the following problem.
    (a) Calculate the equilibrium pressures of all species in an equilibrium mixture that results from the decomposition of H_2S with an initial pressure of 0.824 atm.

    $$2\mathrm{H_2}S(g) \rightleftharpoons 2\mathrm{H_2}(g) + \mathrm{S_2}(g) \qquad K_P = 2.2 \times 10^{-6}$$

    (b) Confirm that the change is small enough to be neglected.

Solution

(a) Write the balanced equation, and then set up a table with initial pressures and the changed pressures using *x* as the change in pressure. The simplest way to find the coefficients for the *x* values is to use the coefficient in the balanced equation.

	$2H_2S(g) \rightleftharpoons$	$2H_2(g)$ +	$S_2(g)$
Initial pressure (atm)	0.824	0	0
Change (atm)	$-2x$	$+2x$	$+x$
Equilibrium pressure (atm)	$0.824 - 2x$	$2x$	x

$$K_P = 2.2 \times 10^{-6} = \frac{(P_{S_2})(P_{H_2})^2}{(P_{H_2S})^2} = \frac{[x][2x]^2}{[0.824 - 2x]^2}$$

Neglecting the change in reactant concentration (2*x*), as instructed, yields:

$$2.2 \times 10^{-6} = \frac{[x][2x]^2}{[0.824]^2}$$

$$2.2 \times 10^{-6} = \frac{4x^3}{[0.679]}$$

$1.494 \times 10^{-6} = 4x^3$

$3.73 \times 10^{-7} = x^3$

$7.20 \times 10^{-3} = x$

Final equilibrium pressures:

$[H_2S] = 0.824 - 2x = 0.824 - 2(7.20 \times 10^{-3}) = 0.824 - 0.0144 = 0.810$ atm

$[H_2] = 2x = 2(7.2 \times 10^{-3}) = 0.014$ atm

$[S_2] = [x] = 0.0072$ atm

(b) The assumption that 2*x* is negligibly small compared to 0.824 is confirmed by comparing the initial concentration of the H_2S to its concentration at equilibrium (0.824 atm versus 0.810 atm, a difference of less than 2%).

24. What are all concentrations after a mixture that contains $[H_2O] = 1.00$ *M* and $[Cl_2O] = 1.00$ *M* comes to equilibrium at 25 °C?

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g) \qquad K_c = 0.0900$$

Solution

As all species are given in molar concentration, a simple K_c equilibrium can be solved using the balanced equation.

	$H_2O(g)$ +	$Cl_2O(g) \rightleftharpoons$	$2HOC(g)$
Initial pressure (*M*)	1.00	1.00	0
Change (*M*)	$-x$	$-x$	$+2x$
Equilibrium pressure (*M*)	$1.00 - x$	$1.00 - x$	$2x$

$$K_c = 0.0900 = \frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{[2x]^2}{[1.00 - 2x][1.00 - x]}$$

$$0.0900 = \frac{4x^2}{1.00 - 2.00x + x^2}$$

$0.0900 – 0.180x + 0.0900x^2 = 4x^2$
Arrange the terms in the form of the quadratic equation:
$ax^2 + bx + c = 0$
$3.91x^2 + 0.180x – 0.0900 = 0$
Then solve using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.180 \pm \sqrt{(0.180)^2 - 4(3.91)(-0.0900)}}{2(3.91)}$$

$$= \frac{-0.180 \pm \sqrt{(0.0324) + 1.4076}}{7.82} = \frac{-0.182 \pm 1.200}{7.82}$$

$$= 0.130\ M \text{ or } -0.176\ M$$

Since concentrations must be positive, only the positive root (0.130) is physically significant.
Final equilibrium concentrations:
$[H_2O] = [Cl_2O] = 1.00 – x = 1.00 – 0.130 = 0.870\ M$
$[HOCl] = 2x = 2(0.130\ M) = 0.260\ M$

25. What are the concentrations of PCl_5, PCl_3, and Cl_2 in an equilibrium mixture produced by the decomposition of a sample of pure PCl_5 with $[PCl_5] = 2.00\ M$?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K_c = 0.0211$$

Solution
As all species are gases and are in *M* concentration units, a simple K_c equilibrium can be solved using the balanced equation:

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g)$ +	$Cl_2(g)$
Initial concentration (*M*)	2.00	0	0
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$2.00 - x$	x	x

$$K_c = 0.0211 = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{[x][x]}{[2.00 - x]}$$

$$0.0211 = \frac{x^2}{[2.00 - x]} = 0.0422 - 0.0211x = x^2$$

Begin by arranging the terms in the form of the quadratic equation:
$ax^2 + bx + c = 0$
$x^2 + 0.0211x – 0.0422 = 0$
Next, solve for x using the quadratic formula.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0211 \pm \sqrt{(0.0211)^2 - 4(1)(-0.0422)}}{2(1)}$$

$$= \frac{-0.0211 \pm \sqrt{0.0004452 + 0.1688}}{2} = \frac{-0.0211 \pm 0.4114}{2}$$

$= 0.195\ M$ or $-0.216\ M$

Since concentrations must be positive, only the positive root (0.195) is physically significant. The final equilibrium concentrations are: $[PCl_5] = 2.00 - x = 2.00 - 0.195 = 1.80\ M$; $[PCl_3] = [Cl_2] = x = 0.195\ M$.

26. Calculate the number of grams of HI that are at equilibrium with 1.25 mol of H_2 and 63.5 g of iodine at 448 °C.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = 50.2 \text{ at } 448\ °C$$

Solution

The number of moles of I_2 is

$$\text{mol} = \frac{63.5\ \text{g}}{253.809\ \text{g mol}^{-1}} = 0.250\ \text{mol } I_2$$

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

The unit for each concentration term is moles per liter. If the volume were known for this exercise, the number of moles in each term should be divided by this volume. However, there are two terms in the numerator and two terms in the denominator, so these volumes cancel one another. Consequently, for any expression with the same number of numerator terms as denominator terms, the number for moles can be used in place of moles per liter. In this exercise, the volume is not needed even though it is given.

$(\text{mol HI})^2 = K \times \text{mol } H_2 \times \text{mol } I_2$

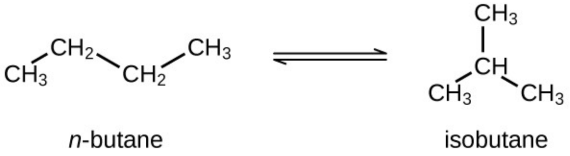
$= 50.2 \times 1.25\ \text{mol} \times 0.250\ \text{mol}$

$= 15.7\ \text{mol}^2$

$\text{mol HI} = \sqrt{15.7\ \text{mol}^2} = 3.96\ \text{mol}$

Mass(HI) = 3.96 mol × 127.9124 g/mol = 507 g

27. Butane exists as two isomers, *n*–butane and isobutane.



$K_P = 2.5$ at 25 °C

What is the pressure of isobutane in a container of the two isomers at equilibrium with a total pressure of 1.22 atm?

Solution

$$K_P = \frac{P_{\text{isobutane}}}{P_{n\text{-butane}}} = 2.5$$

Let x be the partial pressure of *n*-butane.

$$\frac{1.22\ \text{atm} - x}{x} = 2.5$$

$2.5x + x = 1.22$

$3.5x = 1.22$
$x = 0.35$ atm $= P_{\text{n-butane}}$
$P_{\text{isobutane}} = 1.22 - x = 0.87$ atm

28. What is the minimum mass of $CaCO_3$ required to establish equilibrium at a certain temperature in a 6.50-L container if the equilibrium constant (K_c) is 0.50 for the decomposition reaction of $CaCO_3$ at that temperature?

$$\mathrm{CaCO_3}(s) \rightleftharpoons \mathrm{CaO}(s) + \mathrm{CO_2}(g)$$

Solution

At equilibrium the concentration of $CO_2 = K_c = 0.50$ *M*. The number of moles CO_2 in the system is then mol $CO_2 = 6.5$ L × 0.50 mol/L = 3.3 mol. The minimum amount of $CaCO_2$ must then exceed:

$$3.3 \text{ mol CO}_2 \times \frac{1 \text{ mol CaCO}_3}{1 \text{ mol CO}_2} = 3.3 \text{ mol CaCO}_3$$

$$3.3 \text{ mol CO}_2 \times \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_{-3}} = 330 \text{ g}$$

29. The equilibrium constant (K_c) for this reaction is 1.60 at 990 °C:

$$\mathrm{H_2}(g) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{H_2O}(g) + \mathrm{CO}(g)$$

Calculate the number of moles of each component in the final equilibrium mixture obtained from adding 1.00 mol of H_2, 2.00 mol of CO_2, 0.750 mol of H_2O, and 1.00 mol of CO to a 5.00-L container at 990 °C.

Solution

For the reaction the equilibrium expression is

$$K_c = \frac{[\mathrm{H_2O}][\mathrm{CO}]}{[\mathrm{H_2}][\mathrm{CO_2}]} = 1.60$$

Initially, the concentrations of the components are

$$[\mathrm{H_2}] = \frac{1.00 \text{ mol}}{5.00 \text{ L}} = 0.200\ M$$

$$[\mathrm{CO_2}] = \frac{2.00 \text{ mol}}{5.00 \text{ L}} = 0.400\ M$$

$$[\mathrm{H_2O}] = \frac{0.75 \text{ mol}}{5.00 \text{ L}} = 0.150\ M$$

$$[\mathrm{CO}] = \frac{1.0 \text{ mol}}{5.00 \text{ L}} = 0.200\ M$$

To discern the direction in which the reaction will proceed, compute *Qc*:

$$Q_c = \frac{(0.150)(0.200)}{(0.200)(0.400)} = 0.375$$

Since *Qc* < *Kc* (1.60), the reaction will proceed in the forward direction to establish equilibrium. An ICE table may now be developed:

	$[H_2]$	$[CO_2]$	$[H_2O]$	$[CO]$
Initial concentration (*M*)	0.200	0.400	0.150	0.200
Change (*M*)	$-x$	$-x$	$+x$	$+x$
Equilibrium concentration (*M*)	$0.200 - x$	$0.400 - x$	$0.150 + x$	$0.200 + x$

$$K_c = 1.6 = \frac{(0.150 + x)(0.200 + x)}{(0.200 - x)(0.400 - x)} = \frac{(0.300 + 0.350x + x^2)}{(0.080 - 0.600x + x^2)}$$

Rearranging the expression gives
$0.60x^2 - 1.31x + 0.098 = 0$
Using the quadratic formula to solve for x,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{+1.31 \pm \sqrt{(-1.31)^2 - (4)(0.60)(0.098)}}{(2)(0.60)}$$

$$= \frac{-1.31 \pm (1.2169)}{1.2} = 0.0776 \text{ or } 2.11$$

The $x = 2.11$ value does not make physical sense because the maximum value that x could achieve is 0.200 (e.g., if all the 0.200 *M* H_2 reacted). Therefore, use $x = 0.0776$ *M*. The concentrations present are
$[H_2] = 0.200 - 0.0776 = 0.122\ M$
$[CO_2] = 0.400 - 0.0776 = 0.322\ M$
$[H_2O] = 0.150 + 0.0776 = 0.228M$
$[CO] = 0.200 + 0.0776 = 0.278M$
The total number of moles of each component present is
$[H_2] = 0.122\ M \times 5.00\ L = 0.610$ mol
$[CO_2] = 0.322\ M \times 5.00\ L = 1.61$ mol
$[H_2O] = 0.228M \times 5.00\ L = 1.14$ mol
$[CO] = 0.278M \times 5.00\ L = 1.39$ mol

30. In a 3.0-L vessel, the following equilibrium partial pressures are measured: N_2, 190 torr; H_2, 317 torr; NH_3, 1.00×10^3 torr.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(a) How will the partial pressures of H_2, N_2, and NH_3 change if H_2 is removed from the system? Will they increase, decrease, or remain the same?
(b) Hydrogen is removed from the vessel until the partial pressure of nitrogen, at equilibrium, is 250 torr. Calculate the partial pressures of the other substances under the new conditions.

Solution
(a) According to Le Châtelier’s principle, if some of a reactant is removed, the system will shift left. Removing some of a gas lowers its pressure. The removal of H_2 results in decrease in the partial pressure of H_2, an increase in the partial pressure of N_2, and a decrease in the partial pressure of NH_3.
(b) The reaction is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Converting to atm (760 torr = 1 atm)

$$P_{\text{NH}_3} = 1.00 \times 10^3 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ atm}} = 1.32 \text{ atm}$$

$$P_{\text{H}_2} = 317 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.417 \text{ atm}$$

$$P_{\text{N}_2} = 190 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.250 \text{ atm}$$

$$250 \text{ torr} \times \frac{1}{760 \text{ torr}} = 0.329 \text{ atm}$$

so the equilibrium constant is

$$K_P = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(1.32)^2}{(0.250)(0.417)^3} = 96.1$$

From the balanced equation, 1 mol N_2 produces 2 mol NH_3. The pressure change, which is equivalent to the increased pressure of N_2, increase 0.329 atm – 0.250 atm = 0.079 atm. Therefore, the pressure of NH_3 must decrease by 2(0.079); its pressure is 1.32 – 0.158 = 1.16 atm. To maintain equilibrium, hydrogen must be removed from the reaction mixture. Let x = pressure of H_2 in the final mixture. Then,

$$K_P = \frac{(1.16)^2}{(0.329)x^3} = 96.1$$

$$x^3 = \frac{(1.16)^2}{(0.329)(96.1)}$$

$x = 0.349$ atm

$P_{\text{H}_2} = x = 0.349 \text{ atm} = 265 \text{ torr}$

31. The equilibrium constant (K_c) for this reaction is 5.0 at a given temperature.

$$\text{CO}(g) + \text{H}_2O(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$$

(a) On analysis, an equilibrium mixture of the substances present at the given temperature was found to contain 0.20 mol of CO, 0.30 mol of water vapor, and 0.90 mol of H_2 in a liter. How many moles of CO_2 were there in the equilibrium mixture?

(b) Maintaining the same temperature, additional H_2 was added to the system, and some water vapor was removed by drying. A new equilibrium mixture was thereby established containing 0.40 mol of CO, 0.30 mol of water vapor, and 1.2 mol of H_2 in a liter. How many moles of CO_2 were in the new equilibrium mixture? Compare this with the quantity in part (a), and discuss whether the second value is reasonable. Explain how it is possible for the water vapor concentration to be the same in the two equilibrium solutions even though some vapor was removed before the second equilibrium was established.

Solution

(a) For this reaction, $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.0$. The concentrations at equilibrium are 0.20*M* CO, 0.30 *M* H_2O, and 0.90 *M* H_2. Substitution gives $K = 5.0 = \frac{[CO_2][0.90]}{[0.20][0.30]}$;

$[CO_2] = \frac{5.0(0.20)(0.30)}{0.90} = 0.33\ M$; Amount of CO_2 = 0.33 mol × 1 = 0.33 mol.

(b) At the particular temperature of reaction, K_c remains constant at 5.0. The new concentrations are 0.40 *M* CO, 0.30 *M* H_2O, and 1.2 *M* H_2.

$$\frac{[CO_2](1.2)}{(0.40)(0.30)} = 5.0$$

$$[CO_2] = 0.50\ M$$

Amount of CO_2 = 0.50 mol × 1 = 0.50 mol. Added H_2 forms some water as a result of a shift to the left after H_2 is added.

32. Antimony pentachloride decomposes according to this equation:

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

An equilibrium mixture in a 5.00-L flask at 448 °C contains 3.85 g of $SbCl_5$, 9.14 g of $SbCl_3$, and 2.84 g of Cl_2.How many grams of each will be found if the mixture is transferred into a 2.00-L flask at the same temperature?

Solution

The equilibrium expression $K_c = \frac{[SbCl_3][Cl_2]}{[SbCl_5]}$ shows us that if the volume of the reaction vessel is changed, the system's equilibrium is disrupted and shifts the reaction in such a way as to reestablish the equilibrium position. To calculate the equilibrium constant, first calculate the equilibrium concentrations in molar terms for the components present.

$$M(SbCl_5) = (3.85\ g)\left(\frac{1\ mol\ SbCl_5}{299.0135\ g}\right)\left(\frac{1}{5\ L}\right) = 0.00258\ M$$

$$M(SbCl_3) = (9.14\ g)\left(\frac{1\ mol\ SbCl_3}{228.1081\ g}\right)\left(\frac{1}{5\ L}\right) = 0.00801\ M$$

$$M(Cl_2) = (2.84\ g)\left(\frac{1\ mol\ Cl_2}{70.90542\ g}\right)\left(\frac{1}{5\ L}\right) = 0.00801\ M$$

From these equilibrium concentrations, calculate the equilibrium constant for this reaction.

$$K_c = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} = \frac{(0.00801)(0.00801)}{0.00258} = 0.0249$$

Changing the mixture to a 2.00-L flask would change the concentrations as follows:

$$M(\mathrm{SbCl_5}) = (3.85\ \mathrm{g})\left(\frac{1\ \mathrm{mol\ SbCl_5}}{299.0135\ \mathrm{g}}\right)\left(\frac{1}{2\ \mathrm{L}}\right) = 0.00644\ M$$

$$M(\mathrm{SbCl_3}) = (9.14\ \mathrm{g})\left(\frac{1\ \mathrm{mol\ SbCl_3}}{228.1081\ \mathrm{g}}\right)\left(\frac{1}{2\ \mathrm{L}}\right) = 0.0200\ M$$

$$M(\mathrm{Cl_2}) = (2.84\ \mathrm{g})\left(\frac{1\ \mathrm{mol\ Cl_2}}{70.90542\ \mathrm{g}}\right)\left(\frac{1}{2\ \mathrm{L}}\right) = 0.0200\ M$$

The reaction quotient becomes

$$Q = \frac{[\mathrm{SbCl_3}][\mathrm{Cl_2}]}{[\mathrm{SbCl_5}]} = \frac{(0.0200)(0.0200)}{0.00644} = 0.0621$$

The reduction in volume of the reaction vessel from 5 L to 2 L has disrupted the equilibrium of the system. Because Q_c (0.0621) > K_c(0.02493), the reaction is going to shift to the left (i.e., toward the reactants) to restore equilibrium. Calculate the new concentrations to which the system will shift to reestablish equilibrium as a result of the change of volume from 5 L to 2 L.

$$\mathrm{SbCl_5}(g) \rightleftharpoons \mathrm{SbCl_3}(g) + \mathrm{Cl_2}(g)$$

	[$SbCl_5$]	**[$SbCl_3$]**	**[Cl_2]**
Initial concentration (*M*)	0.00644	0.0200	0.0200
Change (*M*)	$+x$	$-x$	$-x$
Equilibrium concentration (*M*)	$0.00644 + x$	$0.0200 - x$	$0.0200 - x$

Putting the new equilibrium concentrations into the equilibrium expression gives

$$K_c = 0.0249 = \frac{(0.0200 - x)(0.0200 - x)}{(0.00644 + x)} = \frac{(0.0200 - x)^2}{(0.00644 + x)}$$

Rearrangement gives

$x^2 - 0.0649x + 0.00024 = 0$

Using the quadratic formula and solving for x gives

$x = 0.00394$

Calculate the new equilibrium concentrations as

$SbCl_5$ = 0.00644 + 0.00394 = 0.0104 *M*

$SbCl_3$ = 0.0200 – 0.00394 = 0.0161 *M*

Cl_2 = 0.0200 – 0.00395 = 0.0161 *M*

The component masses after equilibrium is re-established are

Mass $SbCl_5$ = (2.00 L)(0.0104 mol/L)(299.0135 g/mol) = 6.22 g

Mass $SbCl_3$ = (2.00 L)(0.0161 mol/L)(228.1081 g/mol) = 7.35 g

Mass Cl_2 = (2.00 L)(0.0161 mol/L)(70.90542 g/mol) = 2.28 g

33. Consider the equilibrium

$$4\mathrm{NO_2}(g) + 6\mathrm{H_2O}(g) \rightleftharpoons 4\mathrm{NH_3}(g) + 7\mathrm{O_2}(g)$$

(a) What is the expression for the equilibrium constant (K_c) of the reaction?

(b) How must the concentration of NH_3 change to reach equilibrium if the reaction quotient is less than the equilibrium constant?
(c) If the reaction were at equilibrium, how would an increase in the volume of the reaction vessel affect the pressure of NO_2?
(d) If the change in the pressure of NO_2 is 28 torr as a mixture of the four gases reaches equilibrium, how much will the pressure of O_2 change?

Solution

(a) $K_c = \dfrac{[NH_3]^4[O_2]^7}{[NO_2]^4[H_2O]^6}$.

(b) Because $[NH_3]$ is in the numerator of K_c, $[NH_3]$ must increase for Q_c to reach K_c.

(c) The increase in system volume would lower the partial pressures of all reactants (including NO_2).

(d) The relative changes in pressures are related by the stoichiometry of the reaction.

$$P_{O_2} = \frac{7}{4}P_{NO_2} = \frac{7}{4}(28\text{ torr}) = 49\text{ torr}$$

34. The binding of oxygen by hemoglobin (Hb), giving oxyhemoglobin (HbO_2), is partially regulated by the concentration of H_3O^+ and dissolved CO_2 in the blood. Although the equilibrium is complicated, it can be summarized as

$$\mathrm{HbO_2}(aq) + \mathrm{H_3}O^+(aq) + \mathrm{CO_2}(g) \rightleftharpoons \mathrm{CO_2} - \mathrm{Hb} - H^+ + \mathrm{O_2}(g) + \mathrm{H_2}O(l)$$

(a) Write the equilibrium constant expression for this reaction.
(b) Explain why the production of lactic acid and CO_2 in a muscle during exertion stimulates release of O_2 from the oxyhemoglobin in the blood passing through the muscle.

Solution

(a) $K_c = \dfrac{\left[CO_2 - Hb - H^+\right]\left[O_2\right]}{\left[HbO_2\right]\left[H_3O^+\right]\left[CO_2\right]}$.

(b) Lactic acid releases H_3O^+. This, along with the increased concentration of CO_2, shifts the equilibrium to the right, releasing O_2.

35. Liquid N_2O_3 is dark blue at low temperatures, but the color fades and becomes greenish at higher temperatures as the compound decomposes to NO and NO_2. At 25 °C, a value of $K_P = 1.91$ has been established for this decomposition. If 0.236 moles of N_2O_3 are placed in a 1.52-L vessel at 25 °C, calculate the equilibrium partial pressures of $N_2O_3(g)$, $NO_2(g)$, and $NO(g)$.

Solution

Write the balanced equilibrium expression. With all of the species as gases, it is a straightforward K_P problem to solve. However, *all* species must be converted to pressures, from other units related to concentration. For N_2O_3, with 0.236 mol in 1.52 L at 25 ºC:

$PV = nRT$

$$\begin{aligned} P &= \frac{n}{V}RT \\ &= \frac{0.236\ \cancel{\text{mol}}}{1.52\ \cancel{\text{L}}} \times \frac{(0.08206\ \cancel{\text{L}}\ \text{atm})(298.15\cancel{\text{K}})}{\cancel{\text{mol}}\ \cancel{\text{K}}} \\ &= 3.80\text{ atm} \end{aligned}$$

Write the balanced equation and the equilibrium changes:

	$N_2O_3(g) \rightleftharpoons$	$NO(g)$ +	$NO_2(g)$
Initial pressure (atm)	3.80	0	0
Change (atm)	$-x$	$+x$	$+x$
Equilibrium pressure (atm)	$3.80 - x$	x	x

$$K_P = \frac{(P_{NO})(P_{NO_2})}{(P_{N_2O_3})}$$

$$1.91 = \frac{x^2}{(3.80 - x)}$$

$7.258 - 1.91x = x^2$

$0 = x^2 + 1.91x - 7.258$

$0 = ax^2 + bx + c$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-1.91 \pm \sqrt{(1.91)^2 - 4(1)(-7.258)}}{2(1)}$$

$$= \frac{-1.91 \pm \sqrt{3.648 + 29.032}}{2}$$

$$= \frac{-1.91 \pm \sqrt{32.680}}{2}$$

$$= \frac{-1.91 \pm 5.717}{2}$$

= 1.90 atm or –3.81 atm

As negative pressure is physically relevant and so the positive root is used. The final pressures are: $P_{N_2O_3} = 3.80 - x = 3.80 - 1.90 = 1.90$ atm and $P_{NO} = P_{NO_2} = x = 1.90$ atm.