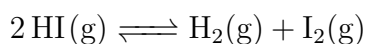


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**Problem 14.30.** Suppose 93.0 g of HI(g) is placed in a glass vessel and heated to 1107 K. At this temperature, equilibrium is quickly established between HI(g) and its decomposition products, H<sub>2</sub>(g) and I<sub>2</sub>(g):



The equilibrium constant at 1107 K is 0.0259, and the total pressure at equilibrium is observed to equal 6.45 atm. Calculate the equilibrium partial pressures of HI(g), H<sub>2</sub>(g), and I<sub>2</sub>(g).

*Solution:* Suppose the initial partial pressure of HI(g) is  $P_0$ , and the change of the partial pressure of HI(g) is  $-2\Delta P$ , then

	$2 \text{HI(g)}$	$\rightleftharpoons$	$\text{H}_2\text{(g)}$	+	$\text{I}_2\text{(g)}$
Initial, atm	$P_0$		0		0
Change, atm	$-2\Delta P$		$\Delta P$		$\Delta P$
Equilibrium, atm	$P_0 - 2\Delta P$		$\Delta P$		$\Delta P$

The total pressure of the system at equilibrium is

$$\begin{aligned} P_{total} &= (P_0 - 2\Delta P) + \Delta P + \Delta P = 6.45 \text{ atm} \\ \implies P_0 &= 6.45 \text{ atm} \end{aligned}$$

The equilibrium constant is

$$\begin{aligned} K &= \frac{P_{\text{H}_2} P_{\text{I}_2}}{P_{\text{HI}}^2} = \frac{\Delta P \cdot \Delta P}{(P_0 - 2\Delta P)^2} = \frac{\Delta P^2}{(6.45 \text{ atm} - 2\Delta P)^2} = 0.0259 \\ \implies \Delta P &= 0.785 \text{ atm} \text{ or } -0.785 \text{ atm} \text{ (unphysical!)} \end{aligned}$$

Therefore, the equilibrium partial pressure of HI(g) is

$$P_{\text{HI}} = P_0 - 2\Delta P = 6.45 \text{ atm} - 2 \times 0.785 \text{ atm} = \underline{4.88 \text{ atm}}$$

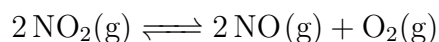
and the equilibrium partial pressure of both H<sub>2</sub>(g) and I<sub>2</sub>(g) are

$$P_{\text{H}_2} = P_{\text{I}_2} = \Delta P = \underline{0.785 \text{ atm}}$$

□

**Problem 14.34.** At 25°C, the equilibrium constant for the reaction

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is  $5.9 \times 10^{-13}$ . Suppose a container is filled with nitrogen dioxide at an initial partial pressure of 0.89 atm. Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.

*Solution:* Suppose the change of the partial pressure of  $\text{NO}_2(\text{g})$  is  $-2x$ , then

	$2\text{NO}_2(\text{g})$	$\rightleftharpoons$	$2\text{NO}(\text{g})$	+	$\text{O}_2(\text{g})$
Initial, atm	0.89		0		0
Change, atm	$-2x$		$2x$		$x$
Equilibrium, atm	$0.89 - 2x$		$2x$		$x$

The equilibrium constant for the reaction is

$$K = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2} = \frac{(2x)^2 x}{(0.89 - 2x)^2} = 5.9 \times 10^{-13}$$

Because the equilibrium constant  $K$  is very small, the change of the partial pressure of  $\text{NO}_2(\text{g})$ ,  $-2x$ , is much smaller than the initial partial pressure of  $\text{NO}_2(\text{g})$ , 0.89 atm. In this way, we have the following approximation

$$K = 5.9 \times 10^{-13} \approx \frac{4x^3}{(0.89\text{atm})^2}$$

$$\Rightarrow x = 4.9 \times 10^{-5}\text{atm}$$

Therefore, the partial pressure of  $\text{NO}_2(\text{g})$  is

$$P_{\text{NO}_2} = 0.89\text{atm} - 2x = \underline{0.889902\text{atm}}$$

the partial pressure of NO is

$$P_{\text{NO}} = 2x = \underline{9.8 \times 10^{-5}\text{atm}}$$

and the partial pressure of  $\text{O}_2$  is

$$P_{\text{O}_2} = x = \underline{4.9 \times 10^{-5}\text{atm}}$$

□

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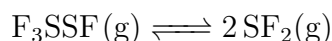
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**Problem 14.46.** Some  $\text{SF}_2$  (at a partial pressure of  $2.3 \times 10^{-4}$  atm) is placed in a closed container at 298 K with some  $\text{F}_3\text{SSF}$  (at a partial pressure of 0.0484 atm). Enough argon is added to raise the total pressure to 1.000 atm.

- (a) Calculate the initial reaction quotient for the decomposition of  $\text{F}_3\text{SSF}$  to  $\text{SF}_2$ .  
(b) As the gas mixture reaches equilibrium, will there be net formation or dissociation of  $\text{F}_3\text{SSF}$ ? (Use the data given in problem 22.)

*Solution:*

- (a) The reaction equation of decomposition of  $\text{F}_3\text{SSF}$  to  $\text{SF}_2$  is



The initial reaction quotient for this reaction is

$$Q = \frac{P_{\text{SF}_2}^2}{P_{\text{F}_3\text{SSF}}} = \frac{(2.3 \times 10^{-4})^2}{0.0484} = 1.1 \times 10^{-6}$$

- (b) From Problem 22, the equilibrium constant of this reaction is

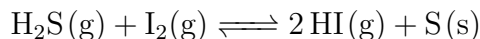
$$K = \frac{(P_{\text{SF}_2}^{eq})^2}{P_{\text{F}_3\text{SSF}}^{eq}} = \frac{(1.1 \times 10^{-4})^2}{0.0484} = 2.5 \times 10^{-7}$$

Because the initial reaction quotient for this reaction is greater than the equilibrium constant

$$Q = 1.1 \times 10^{-6} > K = 2.5 \times 10^{-7}$$

the reaction proceeds to the left and there will be net formation of  $\text{F}_3\text{SSF}$  as the gas mixture reaches equilibrium.  $\square$

**Problem 14.50.** The equilibrium constant for the reaction



at  $110^\circ\text{C}$  is equal to 0.0023. Calculate the reaction quotient  $Q$  for each of the following conditions and determine whether solid sulfur is consumed or produced as the reaction comes to equilibrium.

- (a)  $P_{\text{I}_2} = 0.461\text{atm}$ ;  $P_{\text{H}_2\text{S}} = 0.050\text{atm}$ ;  $P_{\text{HI}} = 0.0\text{atm}$   
(b)  $P_{\text{I}_2} = 0.461\text{atm}$ ;  $P_{\text{H}_2\text{S}} = 0.050\text{atm}$ ;  $P_{\text{HI}} = 9.0\text{atm}$

*Solution:*

- (a) The reaction quotient is

$$Q = \frac{P_{\text{HI}}^2}{P_{\text{H}_2\text{S}}P_{\text{I}_2}} = \frac{0.0^2}{0.050 \times 0.461} = 0.0$$

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Because the reaction quotient is smaller than the equilibrium constant

$$Q = 0.0 < K = 0.0023$$

the reaction proceeds to the right and solid sulfur is produced as the reaction comes to equilibrium.

(b) The reaction quotient is

$$Q = \frac{P_{HI}^2}{P_{H_2S}P_{I_2}} = \frac{9.0^2}{0.050 \times 0.461} = \underline{3.5 \times 10^3}$$

Because the reaction quotient is greater than the equilibrium constant

$$Q = 3.5 \times 10^3 > K = 0.0023$$

the reaction proceeds to the left and solid sulfur is consumed as the reaction comes to equilibrium. □

**Problem 15.1.** Which of the following can act as Brønsted–Lowry acids? Give the formula of the conjugate Brønsted–Lowry base for each of them.

- (a)  $\text{Cl}^-$                                       (b)  $\text{HSO}_4^-$                                       (c)  $\text{NH}_4^+$   
(d)  $\text{NH}_3$                                       (e)  $\text{H}_2\text{O}$

*Solution:* (a)  $\text{Cl}^-$  can not act as Brønsted–Lowry acids.

(b)  $\text{HSO}_4^-$  can act as Brønsted–Lowry acids and its conjugate Brønsted–Lowry base is  $\text{SO}_4^-$ .

(c)  $\text{NH}_4^+$  can act as Brønsted–Lowry acids and its conjugate Brønsted–Lowry base is  $\text{NH}_3$ .

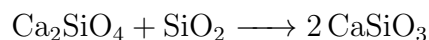
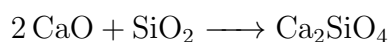
(d)  $\text{NH}_3$  can act as Brønsted–Lowry acids and its conjugate Brønsted–Lowry base is  $\text{NH}_2^-$ .

(e)  $\text{H}_2\text{O}$  can act as Brønsted–Lowry acids and its conjugate Brønsted–Lowry base is  $\text{OH}^-$ . □

**Problem 15.1.** Researchers working with glasses often think of acid–base reactions in terms of oxide donors and oxide acceptors. The oxide ion is  $\text{O}^{2-}$ .

(a) In this system, is the base the oxide donor or the oxide acceptor?

(b) Identify the acid and base in each of these reactions:



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*Solution:*

(a) The base is oxide donor.

(b) In reaction  $2\text{CaO} + \text{SiO}_2 \longrightarrow \text{Ca}_2\text{SiO}_4$ ,  $\text{SiO}_2$  is acid and  $\text{CaO}$  is base.

In reaction  $\text{Ca}_2\text{SiO}_4 + \text{SiO}_2 \longrightarrow 2\text{CaSiO}_3$ ,  $\text{SiO}_2$  is acid and  $\text{Ca}_2\text{SiO}_4$  is base.

In reaction  $\text{Ca}_2\text{SiO}_4 + \text{CaO} \longrightarrow \text{Ca}_3\text{SiO}_5$ ,  $\text{CaO}$  is acid and  $\text{Ca}_2\text{SiO}_4$  is base. □

**Problem 15.17.** The  $pK_w$  of seawater at  $25^\circ\text{C}$  is 13.776. This differs from the usual  $pK_w$  of 14.00 at this temperature because dissolved salts make seawater a nonideal solution. If the pH in seawater is 8.00, what are the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in seawater at  $25^\circ\text{C}$ ?

*Solution:* The concentration of  $\text{H}_3\text{O}^+$  in seawater is

$$[\text{H}_3\text{O}^+] = 10^{-pH} \text{mol} \cdot \text{L}^{-1} = 10^{-8.00} \text{mol} \cdot \text{L}^{-1} = \underline{1.0 \times 10^{-8} \text{mol} \cdot \text{L}^{-1}}$$

The concentration of  $\text{OH}^-$  in seawater is

$$[\text{OH}^-] = 10^{-(pK_w - pH)} \text{mol} \cdot \text{L}^{-1} = 10^{-(13.776 - 8.00)} \text{mol} \cdot \text{L}^{-1} = \underline{1.7 \times 10^{-6} \text{mol} \cdot \text{L}^{-1}}$$

□

**Problem 15.22.** Niacin ( $\text{C}_5\text{H}_4\text{NCOOH}$ ), one of the B vitamins, is an acid.

(a) Write an equation for its equilibrium reaction with water.

(b) The  $K_a$  for niacin is  $1.5 \times 10^{-5}$ . Calculate the  $K_b$  for its conjugate base.

(c) Is the conjugate base of niacin a stronger or a weaker base than pyridine,  $\text{C}_5\text{H}_5\text{N}$ ?

*Solution:*

(a)  $\text{C}_5\text{H}_4\text{NCOOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_5\text{H}_4\text{NCOO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

(b) The  $K_b$  for its conjugate base is

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-5}} = \underline{6.7 \times 10^{-10}}$$

(c) Because the  $K_b$  of the conjugate base of niacin is smaller than that of pyridine

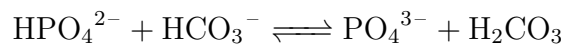
$$(K_b)_{\text{C}_5\text{H}_4\text{NCOO}^-} = 6.7 \times 10^{-10} < (K_b)_{\text{C}_5\text{H}_5\text{N}} = 1.7 \times 10^{-9}$$

the conjugate base of niacin is a weaker base than pyridine. □

**Problem 15.24.** Use the data in Table 15.2 to determine the equilibrium constant for the reaction

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Identify the stronger Brønsted–Lowry acid and the stronger Brønsted–Lowry base.

*Solution:* Because  $\text{HPO}_4^{2-}$  give out a proton and  $\text{HCO}_3^-$  accept it in the reaction,  $\text{HPO}_4^{2-}$  is Brønsted–Lowry acid and  $\text{PO}_4^{3-}$  is its conjugate base, and  $\text{HCO}_3^-$  is Brønsted–Lowry base and  $\text{H}_2\text{CO}_3$  is its conjugate acid.

Because the ionization of  $\text{H}_2\text{CO}_3$  is greater than that of  $\text{HPO}_4^{2-}$

$$K_{\text{H}_2\text{CO}_3} = 4.3 \times 10^{-7} > K_{\text{HPO}_4^{2-}} = 2.2 \times 10^{-13}$$

$\text{H}_2\text{CO}_3$  is the stronger Brønsted–Lowry acid.

Because the strength of a base is inversely related to the strength of its conjugate acid,  
 $\text{PO}_4^{3-}$  is the stronger Brønsted–Lowry base. □