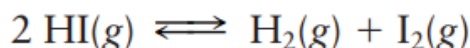


30. Suppose 93.0 g of HI(g) is placed in a glass vessel and heated to 1107 K. At this temperature, equilibrium is quickly established between HI(g) and its decomposition products, H<sub>2</sub>(g) and I<sub>2</sub>(g):



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).

The partial pressure of the hydrogen iodide is unknown at the moment that the glass vessel is filled. Let it be  $y$ . The partial pressures of the two products are both zero at the moment of filling. Attainment of equilibrium reduces the partial pressure of HI, the reactant, by some amount, say,  $2x$ , and increases the partial pressures of each product by  $x$ . This is summarized in the table:

	$2 \text{HI}(g) \rightleftharpoons$	$\text{H}_2(g) +$	$\text{I}_2(g)$
Init. pressure (atm)	$y$	0	0
Change in pressure (atm)	$-2x$	$+x$	$+x$
Equil. pressure (atm)	$y - 2x$	$x$	$x$

The total pressure at equilibrium, which is given in the problem, is the sum of the equilibrium partial pressures of the three components of the mixture:  $(y-2x)+x+x = 6.45$  atm. Clearly,  $y = 6.45$  atm. Substitute the equilibrium partial pressures into the expression for  $K$

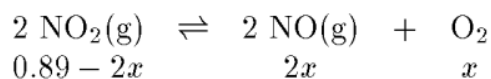
$$\frac{x^2}{(6.45 - 2x)^2} = K = 0.0259 \quad \text{so that} \quad \frac{x}{(6.45 - 2x)} = \sqrt{0.0259} = 0.1609$$

Solving this equation gives  $x = 0.785$ . Hence,  $P_{\text{H}_2} = P_{\text{I}_2} = 0.785$  atm, and  $P_{\text{HI}} = 4.88$  atm.

34. At 25°C, the equilibrium constant for the reaction



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.



$$\frac{x(2x)^2}{(0.89 - 2x)^2} = 5.9 \times 10^{-13}$$

Assume that  $2x$  is small compared to 0.89. Then

$$\begin{aligned} 4x^3 &\approx 5.9 \times 10^{-13}(0.89)^2 = 4.67 \times 10^{-13} \\ x &\approx 4.9 \times 10^{-5} \end{aligned}$$

It is clear that  $2x \ll 0.89$ . Thus at equilibrium

$$P_{\text{NO}_2} = 0.89 \text{ atm} \quad P_{\text{NO}} = 2x = 9.8 \times 10^{-5} \text{ atm} \quad P_{\text{O}_2} = x = 4.9 \times 10^{-5} \text{ atm}$$

**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.

- Calculate the initial reaction quotient for the decomposition of  $\text{F}_3\text{SSF}$  to  $\text{SF}_2$ .
- 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.)

**a)** Although the reaction quotient  $Q$  has the form of the equilibrium expression, it equals  $K$  numerically only if true equilibrium partial pressures are inserted in it. In the situation described, the system is not at equilibrium because  $Q$  differs from  $K$ :

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

The argon takes no part in the reaction and is immaterial to this computation.

**b)** The value of  $Q$  exceeds  $K$ , which from problem **14.22** equals  $2.5 \times 10^{-7}$ . The reaction tends to proceed to the left, generating  $\text{F}_3\text{SSF}$  and consuming  $\text{SF}_2$ , until  $Q$  becomes equal to  $K$ .

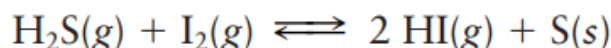
22. At 298 K,  $\text{F}_3\text{SSF}(\text{g})$  decomposes partially to  $\text{SF}_2(\text{g})$ . At equilibrium, the partial pressure of  $\text{SF}_2(\text{g})$  is  $1.1 \times 10^{-4}$  atm and the partial pressure of  $\text{F}_3\text{SSF}$  is 0.0484 atm. (a) Write a balanced equilibrium equation to represent this reaction. (b) Compute the equilibrium constant corresponding to the equation you wrote.

14.22 a) The equation is  $\text{F}_3\text{SSF}(g) \rightleftharpoons 2\text{SF}_2(g)$ .

b)

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

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)  $P_{\text{I}_2} = 0.461 \text{ atm}$ ;  $P_{\text{H}_2\text{S}} = 0.050 \text{ atm}$ ;  $P_{\text{HI}} = 9.0 \text{ atm}$

The reaction quotient has the form

$$Q = \frac{(P_{\text{HI}})^2}{P_{\text{H}_2\text{S}}P_{\text{I}_2}}$$

a) Putting the values given in the problem into the expression gives  $Q = 0$ ; only reactants are present. Some solid sulfur must be produced to reach equilibrium.

b) For this set of initial conditions  $Q = 3.5 \times 10^3$ , which exceeds  $K$ . Solid sulfur is consumed by the reaction coming to equilibrium.

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)  $\text{H}_2\text{O}$

a) The chloride ion  $\text{Cl}^-$  can never act as a Brønsted–Lowry acid because it has no hydrogen.

b) The hydrogen sulfate ion  $\text{HSO}_4^-$  can act as a Brønsted–Lowry acid; its conjugate base is  $\boxed{\text{SO}_4^{2-}}$  (the sulfate ion).

c) The ammonium ion  $\text{NH}_4^+$  can act as a Brønsted–Lowry acid; its conjugate base is  $\boxed{\text{NH}_3}$  (ammonia).

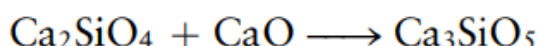
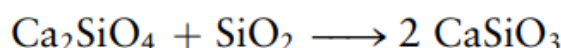
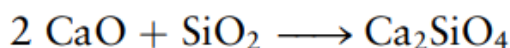
d) Ammonia  $\text{NH}_3$  can act as a Brønsted–Lowry acid; its conjugate base is  $\boxed{\text{NH}_2^-}$  (the amide ion).

e) Water  $\text{H}_2\text{O}$  can act as a Brønsted–Lowry acid; its conjugate base is  $\boxed{\text{OH}^-}$  (the hydroxide ion).

8. 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:



a) This problem follows up the extension of the acid–base concepts suggested by problems 15.6 and 15.7. In the Brønsted system, the acid is the *donor* of a *positively* charged particle (the hydrogen ion); in this system (called the Lux–Flood acid–base system) the acid is the *acceptor* of a *negatively* charged particle (the oxide ion), and the base is the donor of the oxide ion.

b) In the first reaction  $\text{CaO}$  donates  $\text{O}^{2-}$  to  $\text{SiO}_2$  so  $\text{CaO}$  is the base, and  $\text{SiO}_2$  is the acid. In the second reaction the  $\text{SiO}_2$  again accepts an  $\text{O}^{2-}$  and is again the acid. It accepts the  $\text{O}^{2-}$  from  $\text{Ca}_2\text{SiO}_4$ , which is the base. In the third reaction, the  $\text{CaO}$  donates  $\text{O}^{2-}$  to  $\text{Ca}_2\text{SiO}_4$ . The latter serves as an acid in this reaction, the opposite of its role in the second reaction.

17. The  $\text{p}K_{\text{w}}$  of seawater at  $25^\circ\text{C}$  is 13.776. This differs from the usual  $\text{p}K_{\text{w}}$  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  $25^\circ\text{C}$ ?

The pH of the seawater equals 8.00. Using the definition of pH:

$$[\text{H}_3\text{O}^+] = 10^{-8.00} = \boxed{1.0 \times 10^{-8} \text{ M}}$$

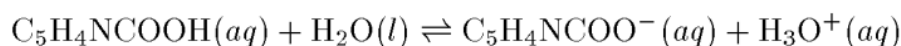
Use 13.776 instead of 14.00 as  $\text{p}K_{\text{w}}$  when calculating pOH:

$$\text{pOH} = \text{p}K_{\text{w}} - \text{pH} = 13.776 - 8.00 = 5.78 \quad [\text{OH}^-] = 10^{-5.78} = \boxed{1.7 \times 10^{-6} \text{ M}}$$

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,  $\text{C}_5\text{H}_5\text{N}$ ?

a) The ionization of niacin proceeds by the reaction

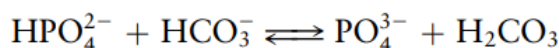


b) In aqueous solutions, the product of  $K_a$  of an acid and  $K_b$  of its conjugate base is  $K_w$ . Hence

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-5}} = 6.7 \times 10^{-10} \quad \text{at } 25^\circ\text{C}$$

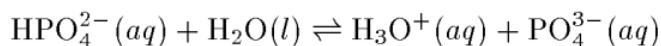
c) The  $K_a$  for the pyridinium ion appears in text Table 15.2. It is  $5.6 \times 10^{-6}$ , smaller than the  $K_a$  of niacin. Niacin is a stronger acid than pyridinium ion, which means that its conjugate base is a weaker base than pyridine.

24. Use the data in Table 15.2 to determine the equilibrium constant for the reaction

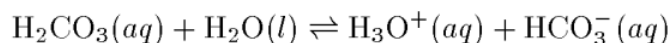


Identify the stronger Brønsted–Lowry acid and the stronger Brønsted–Lowry base.

The equation given in the problem is the sum of the chemical equation for the third acid ionization reaction of phosphoric acid



and the reverse of the equation for the first acid ionization of carbonic acid ( $\text{H}_2\text{CO}_3$ )



Hence, the desired equilibrium constant is

$$K = \frac{K_{a3, \text{H}_3\text{PO}_4}}{K_{a1, \text{H}_2\text{CO}_3}} = \frac{2.2 \times 10^{-13}}{4.3 \times 10^{-7}} = 5.1 \times 10^{-7}$$

$\text{H}_2\text{CO}_3$  is the stronger acid, and  $\text{PO}_4^{3-}$  is the stronger base.