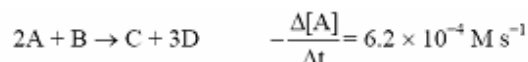


## Chapter 14 Chemical Kinetics

1. In the reaction  $2A + B \longrightarrow C + 3D$ , reactant A is found to disappear at the rate of  $6.2 \times 10^{-4} \text{ M s}^{-1}$ .  
(a) What is the rate of reaction at this point? (b) What is the rate of disappearance of B? (c) What is the rate of formation of D?

**Solution:**



- (a)  $\text{Rate} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$   
(b)  $\text{Rate of disappearance of B} = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} = 1/2(6.2 \times 10^{-4} \text{ M s}^{-1}) = 3.1 \times 10^{-4} \text{ M s}^{-1}$   
(c)  $\text{Rate of appearance of D} = -\frac{3}{2} \frac{\Delta[A]}{\Delta t} = 3(6.2 \times 10^{-4} \text{ M s}^{-1}) = 9.3 \times 10^{-4} \text{ M s}^{-1}$

7. For the reaction  $A + 2B \longrightarrow 2C$ , the rate of reaction is  $1.76 \times 10^{-5} \text{ M s}^{-1}$  at the time when  $[A] = 0.3580 \text{ M}$ .  
(a) What is the rate of formation of C?  
(b) What will  $[A]$  be 1.00 min later?  
(c) Assume the rate remains at  $1.76 \times 10^{-5} \text{ M s}^{-1}$ . How long would it take for  $[A]$  to change from 0.3580 to 0.3500 M?

**Solution:**

(a)  $\text{Rate} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[C]}{2\Delta t} = 1.76 \times 10^{-5} \text{ M s}^{-1}$

$$\frac{\Delta[C]}{\Delta t} = 2 \times 1.76 \times 10^{-5} \text{ M s}^{-1} = 3.52 \times 10^{-5} \text{ M/s}$$

(b)  $\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[C]}{2\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1}$  Assume this rate is constant.

$$[A] = 0.3580 \text{ M} + \left( -1.76 \times 10^{-5} \text{ M s}^{-1} \times 1.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \right) = 0.357 \text{ M}$$

(c)  $\frac{\Delta[A]}{\Delta t} = -1.76 \times 10^{-5} \text{ M s}^{-1}$

$$\Delta t = \frac{\Delta[A]}{-1.76 \times 10^{-5} \text{ M/s}} = \frac{0.3500 \text{ M} - 0.3580 \text{ M}}{-1.76 \times 10^{-5} \text{ M/s}} = 4.5 \times 10^2 \text{ s}$$

13. The following rates of reaction were obtained in three experiments with the reaction  $2 \text{NO}(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2 \text{NOCl}(\text{g})$ .

Expt	Initial [NO], M	Initial [Cl <sub>2</sub> ], M	Initial Rate of Reaction, M s <sup>-1</sup>
1	0.0125	0.0255	$2.27 \times 10^{-5}$
2	0.0125	0.0510	$4.55 \times 10^{-5}$
3	0.0250	0.0255	$9.08 \times 10^{-5}$

- (a) What is the rate law for this reaction?  
 (b) What is the value of the rate constant,  $k$ ?

**Solution:**

(a) From Experiment 1 to 2, [NO] remains constant while [Cl<sub>2</sub>] is doubled. At the same time the initial rate of reaction is found to double. Thus, the reaction is first-order with respect to [Cl<sub>2</sub>], since dividing reaction 2 by reaction 1 gives  $2 = 2^x$  when  $x = 1$ . From Experiment 1 to 3, [Cl<sub>2</sub>] remains constant, while [NO] is doubled, resulting in a quadrupling of the initial rate of reaction. Thus, the reaction must be second-order in [NO], since dividing reaction 3 by reaction 1 gives  $4 = 2^x$  when  $x = 2$ . Overall the reaction is third-order: Rate =  $k [\text{NO}]^2 [\text{Cl}_2]$ .

(b) The rate constant may be calculated from any one of the experiments.  
 Using data from Exp. 1,

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{2.27 \times 10^{-5} \text{ M s}^{-1}}{(0.0125 \text{ M})^2 (0.0255 \text{ M})} = 5.70 \text{ M}^{-2} \text{ s}^{-1}$$

17. The first-order reaction  $\text{A} \longrightarrow \text{products}$  has  $t_{1/2} = 180 \text{ s}$ .

- (a) What percent of a sample of A remains *unreacted* 900 s after a reaction has been started?  
 (b) What is the rate of reaction when  $[\text{A}] = 0.50 \text{ M}$ ?

**Solution:**

(a) Since the half-life is 180 s, after 900 s five half-lives have elapsed, and the original quantity of A has been cut in half five times.

$$\text{final quantity of A} = (0.5)^5 \times \text{initial quantity of A} = 0.03125 \times \text{initial quantity of A}$$

About 3.13% of the original quantity of A remains unreacted after 900 s.

or

More generally, we would calculate the value of the rate constant,  $k$ , using

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{180 \text{ s}} = 0.00385 \text{ s}^{-1} \quad \text{Now } \ln(\% \text{ unreacted}) = -kt = -0.00385 \text{ s}^{-1} \times (900\text{s}) = -$$

$$3.465$$

(% unreacted) =  $0.0313 \times 100\% = 3.13\%$  of the original quantity.

(b) Rate =  $k[\text{A}] = 0.00385 \text{ s}^{-1} \times 0.50 \text{ M} = 0.00193 \text{ M/s}$

20. In the first-order reaction  $A \longrightarrow \text{products}$ ,  $[A] = 0.816 \text{ M}$  initially and  $0.632 \text{ M}$  after  $16.0 \text{ min}$ .
- What is the value of the rate constant,  $k$ ?
  - What is the half-life of this reaction?
  - At what time will  $[A] = 0.235 \text{ M}$ ?
  - What will  $[A]$  be after  $2.5 \text{ h}$ ?

**Solution:**

(a)  $\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.632 \text{ M}}{0.816 \text{ M}} = -0.256 \quad k = -\frac{-0.256}{16.0 \text{ min}} = 0.0160 \text{ min}^{-1}$

(b)  $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0160 \text{ min}^{-1}} = 43.3 \text{ min}$

- (c) We need to solve the integrated rate equation to find the elapsed time.

$$\ln \frac{[A]_t}{[A]_0} = -kt = \ln \frac{0.235 \text{ M}}{0.816 \text{ M}} = -1.245 = -0.0160 \text{ min}^{-1} \times t \quad t = \frac{-1.245}{-0.0160 \text{ min}^{-1}} = 77.8 \text{ min}$$

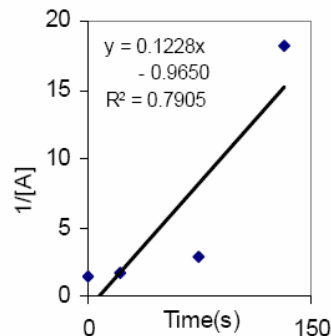
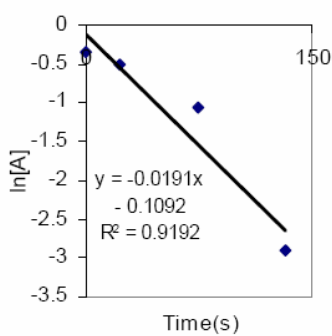
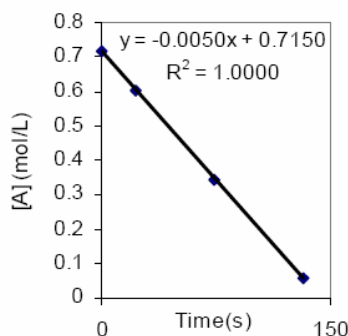
- (d)  $\ln \frac{[A]}{[A]_0} = -kt$  becomes  $\frac{[A]}{[A]_0} = e^{-kt}$  which in turn becomes

$$[A] = [A]_0 e^{-kt} = 0.816 \text{ M} \exp\left(-0.0160 \text{ min}^{-1} \times 2.5 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}}\right) = 0.816 \times 0.0907 = 0.074 \text{ M}$$

37. For the reaction  $A \longrightarrow \text{products}$ , the following data were obtained:  $t = 0 \text{ s}$ ,  $[A] = 0.715 \text{ M}$ ;  $22 \text{ s}$ ,  $0.605 \text{ M}$ ;  $74 \text{ s}$ ,  $0.345 \text{ M}$ ;  $132 \text{ s}$ ,  $0.055 \text{ M}$ . (a) What is the order of this reaction? (b) What is the half-life of the reaction?

**Solution:**

- (a) Plot  $[A]$  vs  $t$ ,  $\ln[A]$  vs  $t$ , and  $1/[A]$  vs  $t$  and see which yields a straight line.



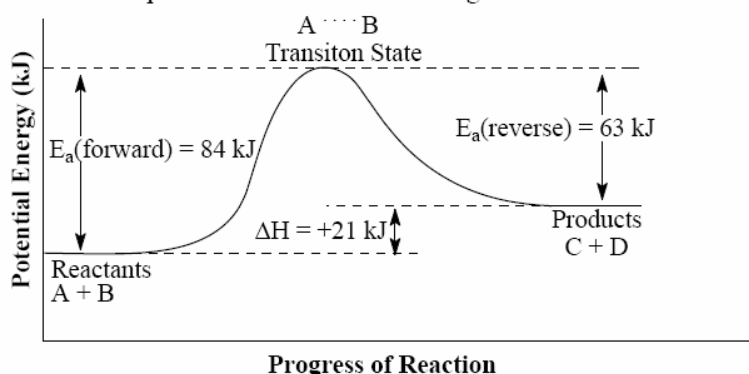
Clearly we can see that the reaction is zero-order in reactant A with a rate constant of  $5.0 \times 10^{-3}$ .

- (b) zero-order reaction  $t_{1/2} = \frac{[A]_0}{2k} = \frac{0.715 \text{ M}}{2 \times 5.0 \times 10^{-3} \text{ M/s}} = 72 \text{ s}$

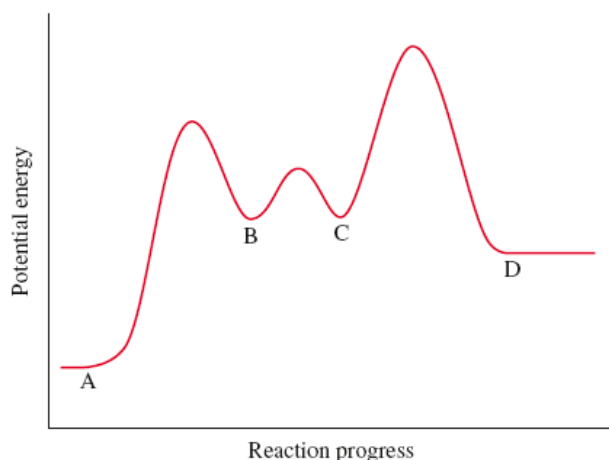
47. For the reversible reaction  $A + B \rightleftharpoons C + D$ , the enthalpy change of the forward reaction is  $+21 \text{ kJ/mol}$ . The activation energy of the forward reaction is  $84 \text{ kJ/mol}$ .
- (a) What is the activation energy of the reverse reaction?
- (b) In the manner of Figure 14-10, sketch the reaction profile of this reaction.

**Solution:**

- (a) The products are  $21 \text{ kJ/mol}$  closer in energy to the energy activated complex than are the reactants. Thus, the activation energy for the reverse reaction is  $84 \text{ kJ/mol} - 21 \text{ kJ/mol} = 63 \text{ kJ/mol}$ .
- (b) The reaction profile for the reaction in Figure 14-10 is sketched below.



50. By inspection of the reaction profile for the reaction A to D given, answer the following questions.
- (a) How many intermediates are there in the reaction?
- (b) How many transition states are there?
- (c) Which is the fastest step in the reaction?
- (d) Which step has the smallest rate constant?
- (e) Is the first step of the reaction exothermic or endothermic?
- (f) Is the overall reaction exothermic or endothermic?



**Solution:**

- (a) There are two intermediates (B and C).
- (b) There are three transition states (peaks/maxima) in the energy diagram.
- (c) The fastest step has the smallest  $E_a$ , hence, step 2 is the fastest step in the reaction.
- (d) Reactant A (step 1) has the highest  $E_a$ , and therefore the slowest smallest constant
- (e) Endothermic; energy is needed to go from A to B.
- (f) Endothermic, energy is needed to go from A to D.

**51.** The rate constant for the reaction  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$  has been determined at the following temperatures: 599 K,  $k = 5.4 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ ; 683 K,  $k = 2.8 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . Calculate the activation energy for the reaction.

**Solution:**

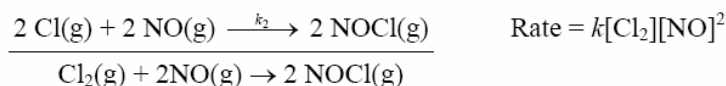
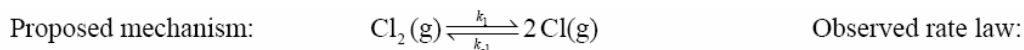
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) = \ln \frac{5.4 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}}{2.8 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}} = \frac{E_a}{R} \left( \frac{1}{683 \text{ K}} - \frac{1}{599 \text{ K}} \right)$$

$$-3.95R = -E_a \times 2.05 \times 10^{-4}$$

$$E_a = \frac{3.95 R}{2.05 \times 10^{-4}} = 1.93 \times 10^4 \text{ K}^{-1} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 1.60 \times 10^5 \text{ J / mol} = 160 \text{ kJ / mol}$$

69. The reaction  $2\text{NO} + \text{Cl}_2 \longrightarrow 2\text{NOCl}$  has the rate law: rate of reaction =  $k[\text{NO}]^2[\text{Cl}_2]$ . Propose a two-step mechanism for this reaction consisting of a fast reversible first step, followed by a slow step.

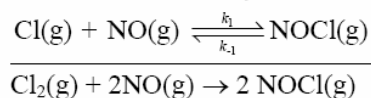
**Solution:**



The first step is a fast equilibrium reaction and step 2 is slow. Thus, the predicted rate law is  $\text{Rate} = k_2[\text{Cl}]^2[\text{NO}]^2$ . In the first step, set the rate in the forward direction for the equilibrium equal to the rate in the reverse direction. Then express  $[\text{Cl}]^2$  in terms of  $k_1, k_{-1}$  and  $[\text{Cl}_2]$ . This mechanism is almost certainly not correct because it involves a tetra molecular second step.

Rate<sub>forward</sub> = Rate<sub>reverse</sub>      Use: Rate<sub>forward</sub> =  $k_1[\text{Cl}_2]$  and Rate<sub>reverse</sub> =  $k_{-1}[\text{Cl}]^2$   
 From this we see:  $k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2$ . Rearranging (solving for  $[\text{Cl}]^2$ )  
 $[\text{Cl}]^2 = \frac{k_1[\text{Cl}_2]}{k_{-1}}$       Substitute into Rate =  $k_2[\text{Cl}]^2[\text{NO}]^2 = k_2 \frac{k_1[\text{Cl}_2]}{k_{-1}} [\text{NO}]^2 = k_{\text{obs}}[\text{Cl}_2][\text{NO}]^2$

There is another plausible mechanism.  $\text{Cl}_2(\text{g}) + \text{NO}(\text{g}) \xrightleftharpoons[k_{-1}]{k_1} \text{NOCl}(\text{g}) + \text{Cl}(\text{g})$



Rate<sub>forward</sub> = Rate<sub>reverse</sub>      Use: Rate<sub>forward</sub> =  $k_1[\text{Cl}_2][\text{NO}]$  and Rate<sub>reverse</sub> =  $k_{-1}[\text{Cl}][\text{NOCl}]$

From this we see:  $k_1[\text{Cl}_2][\text{NO}] = k_{-1}[\text{Cl}][\text{NOCl}]$ . Rearranging (solving for  $[\text{Cl}]$ )

$[\text{Cl}] = \frac{k_1[\text{Cl}_2][\text{NO}]}{k_{-1}[\text{NOCl}]}$       Substitute into Rate =  $k_2[\text{Cl}][\text{NO}] = \frac{k_2 k_1 [\text{Cl}_2][\text{NO}]^2}{k_{-1}[\text{NOCl}]}$

If  $[\text{NOCl}]$ , the product is assumed to be constant ( $\sim 0$  M using method of initial rates), then

$\frac{k_2 k_1}{k_{-1}[\text{NOCl}]} = \text{constant} = k_{\text{obs}}$  Hence, the predicted rate law is  $k_{\text{obs}}[\text{Cl}_2][\text{NO}]^2$  which agrees with

the experimental rate law. Since the predicted rate law agrees with the experimental rate law, both this and the previous mechanism are plausible, however, the first is dismissed as it has a tetramolecular elementary reaction (extremely unlikely to have four molecules simultaneously collide).

- 103.** A first order reaction  $A \longrightarrow$  products has a half-life of 13.9 min. The rate at which this reaction proceeds when  $[A] = 0.40 \text{ M}$  is (a)  $0.020 \text{ mol L}^{-1} \text{ min}^{-1}$ ; (b)  $5.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ ; (c)  $8.0 \text{ mol L}^{-1} \text{ min}^{-1}$ ; (d)  $0.125 \text{ mol L}^{-1} \text{ min}^{-1}$ .

**Solution:**

The answer is (a). Half-life  $t_{1/2} = 13.9 \text{ min}$ ,  $k = \ln 2/t_{1/2} = 0.050 \text{ min}^{-1}$ . Rate of a first-order reaction is as follows:

$$\frac{d[A]}{dt} = k[A] = (0.050 \text{ min}^{-1})(0.40 \text{ M}) = 0.020 \text{ M min}^{-1}$$

- 104.** The reaction  $A \longrightarrow$  products is second order. The initial rate of decomposition of A when  $[A]_0 = 0.50 \text{ M}$  is (a) the same as the initial rate for any other value of  $[A]_0$ ; (b) half as great as when  $[A]_0 = 1.00 \text{ M}$ ; (c) five times as great as when  $[A]_0 = 0.10 \text{ M}$ ; (d) four times as great as when  $[A]_0 = 0.25 \text{ M}$ .

**Solution:**

The answer is (d). A second-order reaction is expressed as follows:

$$\frac{d[A]}{dt} = k[A]^2$$

If the rate of the reaction when  $[A] = 0.50$  is  $k(0.50)^2 = k(0.25)$ . If  $[A] = 0.25 \text{ M}$ , then the rate is  $k(0.0625)$ , which is  $1/4$  of the rate at  $[A] = 0.50$ .

## Chapter 15 Principles of Chemical Equilibrium

9. The vapor pressure of water at 25 °C is 23.8 mmHg. Write  $K_p$  for the vaporization of water, with pressures in atmospheres. What is the value of  $K_c$  for the vaporization process?

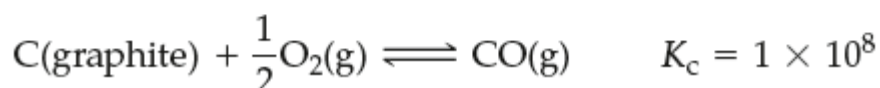
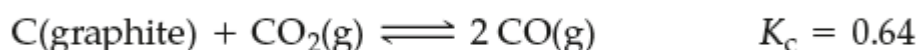
### Solution:

The equilibrium reaction is  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(g)$  with  $\Delta n_{\text{gas}} = +1$ .  $K_p = K_c (RT)^{\Delta n_g}$  gives

$$K_c = K_p (RT)^{-\Delta n_g}. \quad K_p = P\{\text{H}_2\text{O}\} = 23.8 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.0313$$

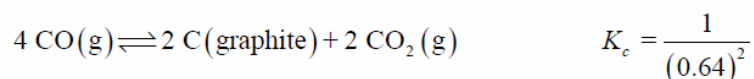
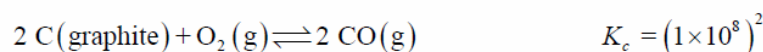
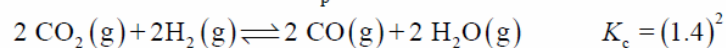
$$K_c = K_p (RT)^{-1} = \frac{K_p}{RT} = \frac{0.0313}{0.08206 \times 298} = 1.28 \times 10^{-3}$$

13. Use the following data to estimate a value of  $K_p$  at 1200 K for the reaction  $2 \text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{H}_2\text{O}(g)$



### Solution:

We combine the  $K_c$  values to obtain the value of  $K_c$  for the overall reaction, and then convert this to a value for  $K_p$ .



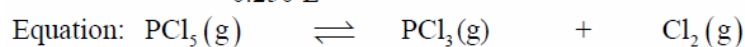


17.  $1.00 \times 10^{-3}$  mol  $\text{PCl}_5$  is introduced into a 250.0 mL flask, and equilibrium is established at  $284^\circ\text{C}$ :  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ . The quantity of  $\text{Cl}_2(\text{g})$  present at equilibrium is found to be  $9.65 \times 10^{-4}$  mol. What is the value of  $K_c$  for the dissociation reaction at  $284^\circ\text{C}$ ?

**Solution:**

First, we determine the concentration of  $\text{PCl}_5$  and of  $\text{Cl}_2$  present initially and at equilibrium, respectively. Then we use the balanced equation to help us determine the concentration of each species present at equilibrium.

$$[\text{PCl}_5]_{\text{initial}} = \frac{1.00 \times 10^{-3} \text{ mol PCl}_5}{0.250 \text{ L}} = 0.00400 \text{ M} \quad [\text{Cl}_2]_{\text{equil}} = \frac{9.65 \times 10^{-4} \text{ mol Cl}_2}{0.250 \text{ L}} = 0.00386 \text{ M}$$



Initial: 0.00400M

0 M

0 M

Changes:  $-x\text{M}$

$+x\text{M}$

$+x\text{M}$

Equil:  $0.00400\text{M}-x\text{M}$

$x\text{M}$

$x\text{M} \leftarrow 0.00386 \text{ M (from above)}$

At equilibrium,  $[\text{Cl}_2] = [\text{PCl}_3] = 0.00386 \text{ M}$  and  $[\text{PCl}_5] = 0.00400\text{M} - x\text{M} = 0.00014 \text{ M}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.00386\text{M})(0.00386\text{M})}{0.00014\text{M}} = 0.106$$

21. Write the equilibrium constant expression for the following reaction,



$$K = 9.1 \times 10^3$$

and compute the equilibrium concentration for  $[\text{Fe}^{3+}]$  at  $\text{pH} = 7$  (i.e.,  $[\text{H}^+] = 1.0 \times 10^{-7}$ ).

**Solution:**

$$K = \frac{[\text{Fe}^{3+}]}{[\text{H}^+]^3} \Rightarrow 9.1 \times 10^3 = \frac{[\text{Fe}^{3+}]}{(1.0 \times 10^{-7})^3}$$

$$[\text{Fe}^{3+}] = 9.1 \times 10^{-18} \text{ M}$$

27. An equilibrium mixture at 1000 K contains 0.276 mol  $\text{H}_2$ , 0.276 mol  $\text{CO}_2$ , 0.224 mol  $\text{CO}$ , and 0.224 mol  $\text{H}_2\text{O}$ .



- (a) Show that for this reaction,  $K_c$  is independent of the reaction volume,  $V$ .  
 (b) Determine the value of  $K_c$  and  $K_p$ .

**Solution:**

$$(a) \quad K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]} = \frac{\frac{n\{\text{CO}\}}{V} \times \frac{n\{\text{H}_2\text{O}\}}{V}}{\frac{n\{\text{CO}_2\}}{V} \times \frac{n\{\text{H}_2\}}{V}}$$

Since  $V$  is present in both the denominator and the numerator, it can be stricken from the expression. This happens here because  $\Delta n_g = 0$ . Therefore,  $K_c$  is independent of  $V$ .

- (b) Note that  $K_p = K_c$  for this reaction, since  $\Delta n_{\text{gas}} = 0$ .

$$K_c = K_p = \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol H}_2\text{O}}{0.276 \text{ mol CO}_2 \times 0.276 \text{ mol H}_2} = 0.659$$

31. In the reaction  $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$ , 0.455 mol  $\text{SO}_2$ , 0.183 mol  $\text{O}_2$ , and 0.568 mol  $\text{SO}_3$  are introduced simultaneously into a 1.90 L vessel at 1000 K.  
 (a) If  $K_c = 2.8 \times 10^2$ , is this mixture at equilibrium?  
 (b) If not, in which direction will a net change occur?

**Solution:**

- (a) We determine the concentration of each species in the gaseous mixture, use these concentrations to determine the value of the reaction quotient, and compare this value of  $Q_c$  with the value of  $K_c$ .

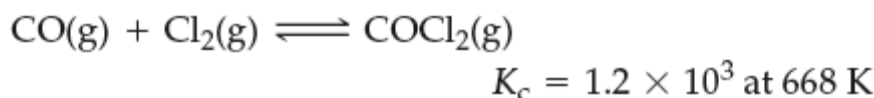
$$[\text{SO}_2] = \frac{0.455 \text{ mol SO}_2}{1.90 \text{ L}} = 0.239 \text{ M} \quad [\text{O}_2] = \frac{0.183 \text{ mol O}_2}{1.90 \text{ L}} = 0.0963 \text{ M}$$

$$[\text{SO}_3] = \frac{0.568 \text{ mol SO}_3}{1.90 \text{ L}} = 0.299 \text{ M} \quad Q_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(0.299)^2}{(0.239)^2 \cdot 0.0963} = 16.3$$

Since  $Q_c = 16.3 \neq 2.8 \times 10^2 = K_c$ , this mixture is not at equilibrium.

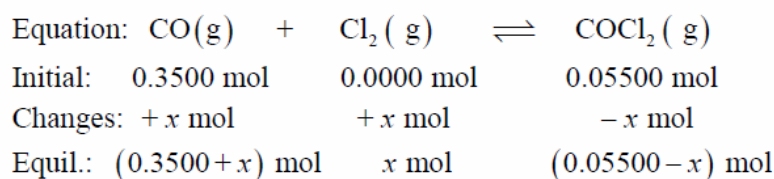
- (b) Since the value of  $Q_c$  is smaller than that of  $K_c$ , the reaction will proceed to the right, forming product and consuming reactants to reach equilibrium.

35. Starting with 0.3500 mol CO(g) and 0.05500 mol COCl<sub>2</sub>(g) in a 3.050 L flask at 668 K, how many moles of Cl<sub>2</sub>(g) will be present at equilibrium?



**Solution:**

We use the chemical equation as a basis to organize the information provided about the reaction, and then determine the final number of moles of Cl<sub>2</sub>(g) present.



$$K_c = 1.2 \times 10^3 = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{\frac{(0.0550 - x) \text{ mol}}{3.050 \text{ L}}}{\frac{(0.3500 + x) \text{ mol}}{3.050 \text{ L}} \times \frac{x \text{ mol}}{3.050 \text{ L}}}$$

$$\frac{1.2 \times 10^3}{3.050} = \frac{0.05500 - x}{(0.3500 + x)x} \quad \text{Assume } x \ll 0.0550 \text{ This produces the following expression.}$$

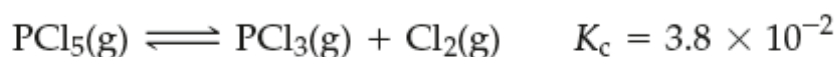
$$\frac{1.2 \times 10^3}{3.050} = \frac{0.05500}{0.3500x} \quad x = \frac{3.050 \times 0.05500}{0.3500 \times 1.2 \times 10^3} = 4.0 \times 10^{-4} \text{ mol Cl}_2$$

We use the first value we obtained,  $4.0 \times 10^{-4}$  (= 0.00040), to arrive at a second value.

$$x = \frac{3.050 \times (0.0550 - 0.00040)}{(0.3500 + 0.00040) \times 1.2 \times 10^3} = 4.0 \times 10^{-4} \text{ mol Cl}_2$$

Because the value did not change on the second iteration, we have arrived at a solution.

37. Equilibrium is established in a 2.50 L flask at 250 °C for the reaction

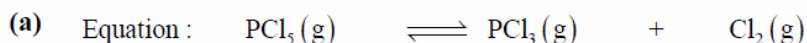


How many moles of PCl<sub>5</sub>, PCl<sub>3</sub>, and Cl<sub>2</sub> are present at equilibrium, if

- (a) 0.550 mol each of PCl<sub>5</sub> and PCl<sub>3</sub> are initially introduced into the flask?  
 (b) 0.610 mol PCl<sub>5</sub> alone is introduced into the flask?

**Solution:**

We base each of our solutions on the balanced chemical equation.



Initial :  $\frac{0.550 \text{ mol}}{2.50 \text{ L}}$        $\frac{0.550 \text{ mol}}{2.50 \text{ L}}$        $\frac{0 \text{ mol}}{2.50 \text{ L}}$

Changes :  $\frac{-x \text{ mol}}{2.50 \text{ L}}$        $\frac{+x \text{ mol}}{2.50 \text{ L}}$        $\frac{+x \text{ mol}}{2.50 \text{ L}}$

Equil :  $\frac{(0.550-x) \text{ mol}}{2.50 \text{ L}}$        $\frac{(0.550+x) \text{ mol}}{2.50 \text{ L}}$        $\frac{x \text{ mol}}{2.50 \text{ L}}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 3.8 \times 10^{-2} = \frac{\frac{(0.550+x) \text{ mol}}{2.50 \text{ L}} \times \frac{x \text{ mol}}{2.50 \text{ L}}}{\frac{(0.550-x) \text{ mol}}{2.50 \text{ L}}} = \frac{x(0.550+x)}{2.50(0.550-x)} = 3.8 \times 10^{-2}$$

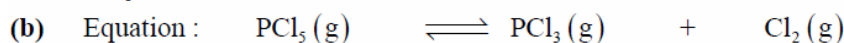
$$x^2 + 0.550x = 0.052 - 0.095x \quad x^2 + 0.645x - 0.052 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.645 \pm \sqrt{0.416 + 0.208}}{2} = 0.0725 \text{ mol}, -0.717 \text{ mol}$$

The second answer gives a negative quantity. of  $\text{Cl}_2$ , which makes no physical sense.

$$n_{\text{PCl}_5} = (0.550 - 0.0725) = 0.478 \text{ mol PCl}_5 \quad n_{\text{PCl}_3} = (0.550 + 0.0725) = 0.623 \text{ mol PCl}_3$$

$$n_{\text{Cl}_2} = x = 0.0725 \text{ mol Cl}_2$$



Initial :  $\frac{0.610 \text{ mol}}{2.50 \text{ L}}$       0 M      0 M

Changes :  $\frac{-x \text{ mol}}{2.50 \text{ L}}$        $\frac{+x \text{ mol}}{2.50 \text{ L}}$        $\frac{+x \text{ mol}}{2.50 \text{ L}}$

Equil :  $\frac{0.610-x \text{ mol}}{2.50 \text{ L}}$        $\frac{(x \text{ mol})}{2.50 \text{ L}}$        $\frac{(x \text{ mol})}{2.50 \text{ L}}$

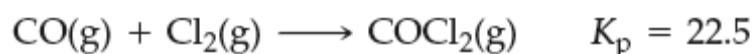
$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 3.8 \times 10^{-2} = \frac{\frac{(x \text{ mol})}{2.50 \text{ L}} \times \frac{(x \text{ mol})}{2.50 \text{ L}}}{\frac{0.610-x \text{ mol}}{2.50 \text{ L}}}$$

$$2.50 \times 3.8 \times 10^{-2} = \frac{x^2}{0.610-x} = 0.095 \quad 0.058 - 0.095x = x^2 \quad x^2 + 0.095x - 0.058 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.095 \pm \sqrt{0.0090 + 0.23}}{2} = 0.20 \text{ mol}, -0.29 \text{ mol}$$

$$\text{amount PCl}_3 = 0.20 \text{ mol} = \text{amount Cl}_2; \text{ amount PCl}_5 = 0.610 - 0.20 = 0.41 \text{ mol}$$

53. 1.00 mol *each* of CO and Cl<sub>2</sub> are introduced into an evacuated 1.75 L flask, and the following equilibrium is established at 668 K.



**Solution:**

(a) We first determine the initial pressure of each gas.

$$P\{\text{CO}\} = P\{\text{Cl}_2\} = \frac{nRT}{V} = \frac{1.00 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 668 \text{ K}}{1.75 \text{ L}} = 31.3 \text{ atm}$$

Then we calculate equilibrium partial pressures, organizing our calculation around the balanced chemical equation. We see that the equilibrium constant is not very large, meaning that we must solve the polynomial exactly (or by successive approximations).

Equation	CO(g)	+ Cl <sub>2</sub> (g)	$\rightleftharpoons$	COCl <sub>2</sub> (g)	$K_p = 22.5$
Initial:	31.3 atm	31.3 atm		0 atm	
Changes:	-x atm	-x atm		+x atm	
Equil:	31.3 - x atm	31.3 - x atm		x atm	

$$K_p = \frac{P\{\text{COCl}_2\}}{P\{\text{CO}\}P\{\text{Cl}_2\}} = 22.5 = \frac{x}{(31.3 - x)^2} = \frac{x}{(979.7 - 62.6x + x^2)}$$

$$22.5(979.7 - 62.6x + x^2) = x = 22043 - 1408.5x + 22.5x^2 = x$$

$$22043 - 1409.5x + 22.5x^2 = 0 \quad (\text{Solve by using the quadratic equation})$$

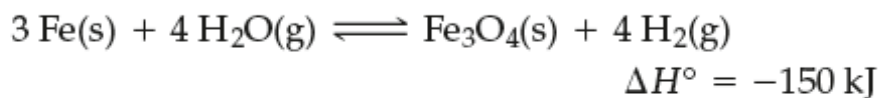
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(-1409.5) \pm \sqrt{(-1409.5)^2 - 4(22.5)(22043)}}{2(22.5)}$$

$$x = \frac{1409.5 \pm \sqrt{2818}}{45} = 30.14, 32.5 \text{ (too large)}$$

$$P\{\text{CO}\} = P\{\text{Cl}_2\} = 31.3 \text{ atm} - 30.14 \text{ atm} = 1.16 \text{ atm} \quad P\{\text{COCl}_2\} = 30.14 \text{ atm}$$

(b)  $P_{\text{total}} = P\{\text{CO}\} + P\{\text{Cl}_2\} + P\{\text{COCl}_2\} = 1.16 \text{ atm} + 1.16 \text{ atm} + 30.14 \text{ atm} = 32.46 \text{ atm}$

57. Explain how each of the following affects the amount of  $\text{H}_2$  present in an equilibrium mixture in the reaction



(a) Raising the temperature of the mixture; (b) introducing more  $\text{H}_2\text{O(g)}$ ; (c) doubling the volume of the container holding the mixture; (d) adding an appropriate catalyst.

**Solution:**

- (a) This reaction is exothermic with  $\Delta H^\circ = -150 \text{ kJ}$ . Thus, high temperatures favor the reverse reaction (endothermic reaction). The amount of  $\text{H}_2(\text{g})$  present at high temperatures will be less than that present at low temperatures.
- (b)  $\text{H}_2\text{O(g)}$  is one of the reactants involved. Introducing more will cause the equilibrium position to shift to the right, favoring products. The amount of  $\text{H}_2(\text{g})$  will increase.
- (c) Doubling the volume of the container will favor the side of the reaction with the largest sum of gaseous stoichiometric coefficients. The sum of the stoichiometric coefficients of gaseous species is the same (4) on both sides of this reaction. Therefore, increasing the volume of the container will have no effect on the amount of  $\text{H}_2(\text{g})$  present at equilibrium.
- (d) A catalyst merely speeds up the rate at which a reaction reaches the equilibrium position. The addition of a catalyst has no effect on the amount of  $\text{H}_2(\text{g})$  present at equilibrium.

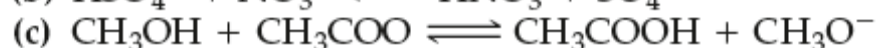
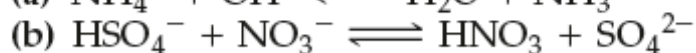
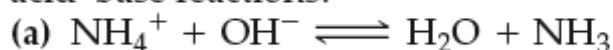
## Chapter 16 Acids and Bases

1. According to the Brønsted–Lowry theory, label each of the following as an acid or a base. (a)  $\text{HNO}_2$ ; (b)  $\text{OCl}^-$ ; (c)  $\text{NH}_2^-$ ; (d)  $\text{NH}_4^+$ ; (e)  $\text{CH}_3\text{NH}_3^+$

### Solution:

- (a)  $\text{HNO}_2$  is an acid, a proton donor. Its conjugate base is  $\text{NO}_2^-$ .  
(b)  $\text{OCl}^-$  is a base, a proton acceptor. Its conjugate acid is  $\text{HOCl}$ .  
(c)  $\text{NH}_2^-$  is a base, a proton acceptor. Its conjugate acid is  $\text{NH}_3$ .  
(d)  $\text{NH}_4^+$  is an acid, a proton donor. Its conjugate base is  $\text{NH}_3$ .  
(e)  $\text{CH}_3\text{NH}_3^+$  is an acid, a proton donor. Its conjugate base is  $\text{CH}_3\text{NH}_2$ .

7. With the aid of Table 16.1, predict the direction (forward or reverse) favored in each of the following acid–base reactions.



### Solution:

- (a) The reaction will favor the forward direction because  $\text{OH}^-$  (a strong base)  $>$   $\text{NH}_3$  (a weak base) and  $\text{NH}_4^+$  (relatively strong weak acid)  $>$   $\text{H}_2\text{O}$  (very weak acid).  
(b) The reaction will favor the reverse direction because  $\text{HNO}_3 >$   $\text{HSO}_4^-$  (a weak acid in the second ionization) (acting as acids), and  $\text{SO}_4^{2-} >$   $\text{NO}_3^-$  (acting as bases).  
(c) The reaction will favor the reverse direction because  $\text{HC}_2\text{H}_3\text{O}_2 >$   $\text{CH}_3\text{OH}$  (not usually thought of as an acid) (acting as acids), and  $\text{CH}_3\text{O}^- >$   $\text{C}_2\text{H}_3\text{O}_2^-$  (acting as bases).

15. How many milliliters of concentrated  $\text{HCl}(\text{aq})$  (36.0%  $\text{HCl}$  by mass,  $d = 1.18 \text{ g/mL}$ ) are required to produce 12.5 L of a solution with  $\text{pH} = 2.10$ ?

### Solution:

First determine the amount of  $\text{HCl}$ , and then the volume of the concentrated solution required.

$$\text{amount HCl} = 12.5 \text{ L} \times \frac{10^{-2.10} \text{ mol H}_3\text{O}^+}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol H}_3\text{O}^+} = 0.099 \text{ mol HCl}$$

$$V_{\text{solution}} = 0.099 \text{ mol HCl} \times \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} \times \frac{100.0 \text{ g soln}}{36.0 \text{ g HCl}} \times \frac{1 \text{ mL soln}}{1.18 \text{ g soln}} = 8.5 \text{ mL soln}$$

19. 50.00 mL of 0.0155 M HI(aq) is mixed with 75.00 mL of 0.0106 M KOH(aq). What is the pH of the final solution?

**Solution:**

$$50.00 \text{ mL} \times \frac{0.0155 \text{ mmol HI}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol H}_3\text{O}^+}{1 \text{ mmol HI}} = 0.775 \text{ mmol H}_3\text{O}^+$$

$$75.00 \text{ mL} \times \frac{0.0106 \text{ mmol KOH}}{1 \text{ mL soln}} \times \frac{1 \text{ mmol OH}^-}{1 \text{ mmol KOH}} = 0.795 \text{ mmol OH}^-$$

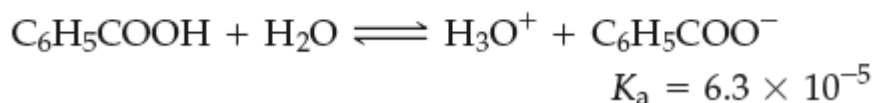
The net reaction is  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ .

There is an excess of  $\text{OH}^-$  of  $(0.795 - 0.775 =) 0.020 \text{ mmol OH}^-$ .

Thus, this is a basic solution. The total solution volume is  $(50.00 + 75.00 =) 125.00 \text{ mL}$ .

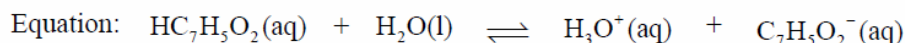
$$[\text{OH}^-] = \frac{0.020 \text{ mmol OH}^-}{125.00 \text{ mL}} = 1.6 \times 10^{-4} \text{ M}, \quad \text{pOH} = -\log(1.6 \times 10^{-4}) = 3.80, \quad \text{pH} = 10.20$$

27. What mass of benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ , would you dissolve in 350.0 mL of water to produce a solution with a pH = 2.85?



**Solution:**

Here we need to find the molarity  $S$  of the acid needed that yields  $[\text{H}_3\text{O}^+] = 10^{-2.85} = 1.4 \times 10^{-3} \text{ M}$



Initial:  $S$   $-$   $0 \text{ M}$   $0 \text{ M}$

Changes:  $-0.0014 \text{ M}$   $-$   $+0.0014 \text{ M}$   $+0.0014 \text{ M}$

Equil:  $S - 0.0014 \text{ M}$   $-$   $0.0014 \text{ M}$   $0.0014 \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_7\text{H}_5\text{O}_2^-]}{[\text{HC}_7\text{H}_5\text{O}_2]} = \frac{(0.0014)^2}{S - 0.0014} = 6.3 \times 10^{-5} \quad S - 0.0014 = \frac{(0.0014)^2}{6.3 \times 10^{-5}} = 0.031$$

$$S = 0.031 + 0.0014 = 0.032 \text{ M} = [\text{HC}_7\text{H}_5\text{O}_2]$$

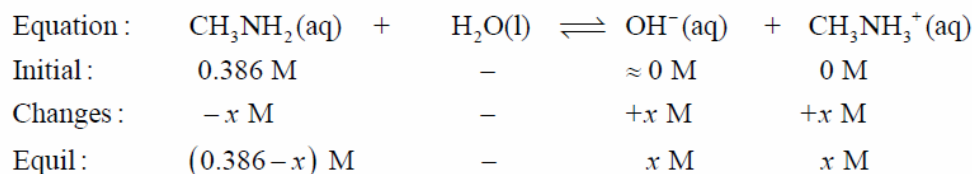
$$350.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.032 \text{ mol HC}_7\text{H}_5\text{O}_2}{1 \text{ L soln}} \times \frac{122.1 \text{ g HC}_7\text{H}_5\text{O}_2}{1 \text{ mol HC}_7\text{H}_5\text{O}_2} = 1.4 \text{ g HC}_7\text{H}_5\text{O}_2$$



30. What are  $[\text{H}_3\text{O}^+]$ ,  $[\text{OH}^-]$ , pH, and pOH of 0.386 M  $\text{CH}_3\text{NH}_2$ ?

**Solution:**

Organize the solution around the balanced chemical equation, and solve first for  $[\text{OH}^-]$ .



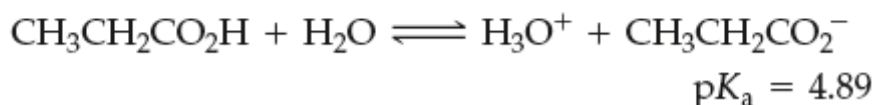
$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{NH}_3^+]}{[\text{CH}_3\text{NH}_2]} = \frac{x^2}{0.386 - x} = 4.2 \times 10^{-4} \approx \frac{x^2}{0.386} \quad \text{assuming } x \ll 0.386$$

$$x = \sqrt{0.386 \times 4.2 \times 10^{-4}} = 0.013 \text{ M} = [\text{OH}^-] \quad \text{pOH} = -\log(0.013) = 1.89$$

$$\text{pH} = 14.00 - 1.89 = 12.11 \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-12.11} = 7.8 \times 10^{-13} \text{ M}$$

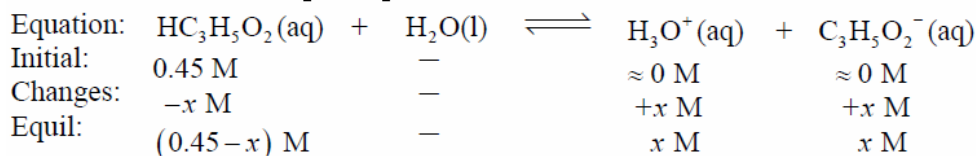
This is the same result as is determined with the quadratic equation roots formula.

39. What is the (a) degree of ionization and (b) percent ionization of propionic acid in a solution that is 0.45 M  $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ ?



**Solution:**

Let us first compute the  $[\text{H}_3\text{O}^+]$  in this solution.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{x^2}{0.45 - x} = 10^{-4.89} = 1.3 \times 10^{-5} \approx \frac{x^2}{0.45}$$

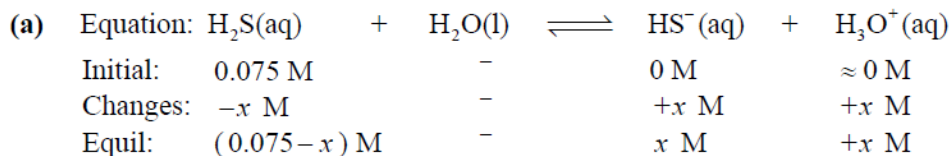
$x = 2.4 \times 10^{-3} \text{ M}$ ; We have assumed that  $x \ll 0.45 \text{ M}$ , an assumption that clearly is correct.

$$\text{(a)} \quad \alpha = \frac{[\text{H}_3\text{O}^+]_{\text{equil}}}{[\text{HC}_3\text{H}_5\text{O}_2]_{\text{initial}}} = \frac{2.4 \times 10^{-3} \text{ M}}{0.45 \text{ M}} = 0.0053 = \text{degree of ionization}$$

$$\text{(b)} \quad \% \text{ ionization} = \alpha \times 100\% = 0.0053 \times 100\% = 0.53\%$$

- 47.** Determine  $[\text{H}_3\text{O}^+]$ ,  $[\text{HS}^-]$ , and  $[\text{S}^{2-}]$  for the following  $\text{H}_2\text{S}(\text{aq})$  solutions: (a) 0.075 M  $\text{H}_2\text{S}$ ; (b) 0.0050 M  $\text{H}_2\text{S}$ ; (c)  $1.0 \times 10^{-5}$  M  $\text{H}_2\text{S}$ .

**Solution:**



$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{0.075 - x} \approx \frac{x^2}{0.075} \quad x = 8.7 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$[\text{HS}^-] = 8.7 \times 10^{-5} \text{ M} \quad \text{and} \quad [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

- (b) The set-up for this problem is the same as for part (a), with 0.0050 M replacing 0.075 M as the initial value of  $[\text{H}_2\text{S}]$ .

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{0.0050 - x} \approx \frac{x^2}{0.0050} \quad x = 2.2 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

$$[\text{HS}^-] = 2.2 \times 10^{-5} \text{ M} \quad \text{and} \quad [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

- (c) The set-up for this part is the same as for part (a), with  $1.0 \times 10^{-5}$  M replacing 0.075 M as the initial value of  $[\text{H}_2\text{S}]$ . The solution differs in that we cannot assume  $x \ll 1.0 \times 10^{-5}$ . Solve the quadratic equation to find the desired equilibrium concentrations.

$$K_{a_1} = \frac{[\text{HS}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{S}]} = 1.0 \times 10^{-7} = \frac{x^2}{1.0 \times 10^{-5} - x}$$

$$x^2 + 1.0 \times 10^{-7}x - 1.0 \times 10^{-12} = 0$$

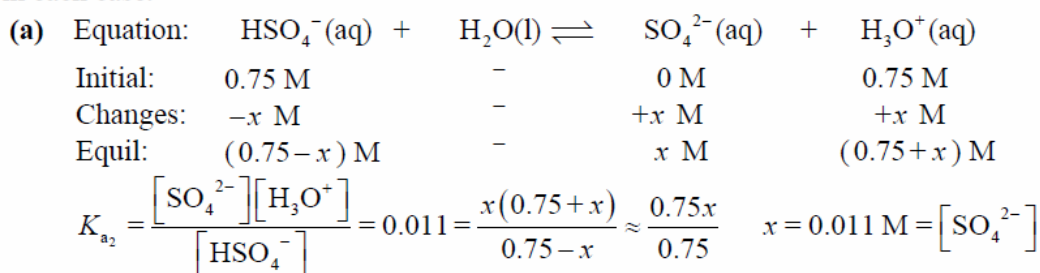
$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{1.0 \times 10^{-14} + (4 \times 1.0 \times 10^{-12})}}{2 \times (1)}$$

$$x = 9.5 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] \quad [\text{HS}^-] = 9.5 \times 10^{-7} \text{ M} \quad [\text{S}^{2-}] = K_{a_2} = 1 \times 10^{-19} \text{ M}$$

49. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{HSO}_4^-]$ , and  $[\text{SO}_4^{2-}]$  in (a) 0.75 M  $\text{H}_2\text{SO}_4$ ; (b) 0.075 M  $\text{H}_2\text{SO}_4$ ; (c)  $7.5 \times 10^{-4}$  M  $\text{H}_2\text{SO}_4$ . [Hint: Check any assumptions that you make.]

**Solution:**

In all cases, of course, the first ionization of  $\text{H}_2\text{SO}_4$  is complete, and establishes the initial values of  $[\text{H}_3\text{O}^+]$  and  $[\text{HSO}_4^-]$ . Thus, we need only deal with the second ionization in each case.



We have assumed that  $x \ll 0.75$  M, an assumption that clearly is correct.

$$[\text{HSO}_4^-] = 0.75 - 0.011 = 0.74 \text{ M} \quad [\text{H}_3\text{O}^+] = 0.75 + 0.011 = 0.76 \text{ M}$$

- (b) The set-up for this part is similar to part (a), with the exception that 0.75 M is replaced by 0.075 M.

$$K_{a_2} = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = 0.011 = \frac{x(0.075 + x)}{0.075 - x} \quad 0.011(0.075 - x) = 0.075x + x^2$$

$$x^2 + 0.086x - 8.3 \times 10^{-4} = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.086 \pm \sqrt{0.0074 + 0.0033}}{2} = 0.0087 \text{ M}$$

$$x = 0.0087 \text{ M} = [\text{SO}_4^{2-}]$$

$$[\text{HSO}_4^-] = 0.075 - 0.0087 = 0.066 \text{ M} \quad [\text{H}_3\text{O}^+] = 0.075 + 0.0088 \text{ M} = 0.084 \text{ M}$$

- (c) Again, the set-up is the same as for part (a), with the exception that 0.75 M is replaced by 0.00075 M

$$K_{a_2} = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]} = 0.011 = \frac{x(0.00075 + x)}{0.00075 - x} \quad 0.011(0.00075 - x) = 0.00075x + x^2$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.0118 \pm \sqrt{1.39 \times 10^{-4} + 3.3 \times 10^{-5}}}{2} = 6.6 \times 10^{-4}$$

$$x = 6.6 \times 10^{-4} \text{ M} = [\text{SO}_4^{2-}] \quad [\text{HSO}_4^-] = 0.00075 - 0.00066 = 9 \times 10^{-5} \text{ M}$$

$[\text{H}_3\text{O}^+] = 0.00075 + 0.00066 \text{ M} = 1.41 \times 10^{-3} \text{ M}$   $[\text{H}_3\text{O}^+]$  is almost twice the initial value of  $[\text{H}_2\text{SO}_4]$ . Thus, the second ionization of  $\text{H}_2\text{SO}_4$  is nearly complete in this dilute solution.

62. Pyridine,  $C_5H_5N$  ( $pK_b = 8.82$ ), forms a salt, pyridinium chloride, as a result of a reaction with HCl. Write an ionic equation to represent the hydrolysis of the pyridinium ion, and calculate the pH of  $0.0482\text{ M } C_5H_5NH^+Cl^-(aq)$ .

**Solution:**

Equation :	$C_5H_5NH^+(aq) + H_2O(l) \rightleftharpoons C_5H_5N(aq) + H_3O^+(aq)$
Initial :	$0.0482\text{ M} \quad \quad \quad - \quad \quad \quad 0\text{ M} \quad \quad \quad \approx 0\text{ M}$
Changes :	$-x\text{ M} \quad \quad \quad - \quad \quad \quad +x\text{ M} \quad \quad \quad +x\text{ M}$
Equil :	$(0.0482 - x)\text{ M} \quad \quad \quad - \quad \quad \quad x\text{ M} \quad \quad \quad x\text{ M}$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.5 \times 10^{-9}} = 6.7 \times 10^{-6} = \frac{[C_5H_5N][H_3O^+]}{[C_5H_5NH^+]} = \frac{x^2}{0.0482 - x} \approx \frac{x^2}{0.0482}$$

$5.7 \times 10^{-4}\text{ M} \ll 0.0482\text{ M}$ , the assumption is valid

$$x = 5.7 \times 10^{-4}\text{ M} = [H_3O^+], \quad pH = -\log(5.7 \times 10^{-4}) = 3.24$$

65. Predict which is the stronger acid: (a)  $HClO_2$  or  $HClO_3$ ; (b)  $H_2CO_3$  or  $HNO_2$ ; (c)  $H_2SiO_3$  or  $H_3PO_4$ . Explain.

**Solution:**

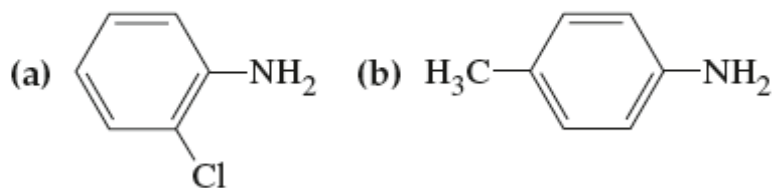
- (a)  $HClO_3$  should be a stronger acid than is  $HClO_2$ . In each acid there is an  $H-O-Cl$  grouping. The remaining oxygen atoms are bonded directly to Cl as terminal O atoms. Thus, there are two terminal O atoms in  $HClO_3$  and only one in  $HClO_2$ . For oxoacids of the same element, the one with the higher number of terminal oxygen atoms is the stronger. With more oxygen atoms, the negative charge on the conjugate base is more effectively spread out, which affords greater stability.  $HClO_3: K_{a_1} = 5 \times 10^2$  and  $HClO_2: K_a = 1.1 \times 10^{-2}$ .
- (b)  $HNO_2$  and  $H_2CO_3$  each have one terminal oxygen atom. The difference? N is more electronegative than C, which makes  $HNO_2$  ( $K_a = 7.2 \times 10^{-4}$ ), a stronger acid than  $H_2CO_3$  ( $K_{a_1} = 4.4 \times 10^{-7}$ ).
- (c)  $H_3PO_4$  and  $H_2SiO_3$  have the same number (one) of terminal oxygen atoms. They differ in P being more electronegative than Si, which makes  $H_3PO_4$  ( $K_{a_1} = 7.1 \times 10^{-3}$ ) a stronger acid than  $H_2SiO_3$  ( $K_{a_1} = 1.7 \times 10^{-10}$ ).

67. Which is the stronger acid of each of the following pairs of acids? Explain your reasoning. (a) HBr or HI; (b) HOClO or HOBr; (c) I<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>COOH or CH<sub>3</sub>CH<sub>2</sub>CCl<sub>2</sub>COOH.

**Solution:**

- (a) HI is the stronger acid because the H—I bond length is longer than the H—Br bond length and, as a result, H—I is easier to cleave.
- (b) HOClO is a stronger acid than HOBr because  
 (i) there is a terminal O in HOClO but not in HOBr  
 (ii) Cl is more electronegative than Br.
- (c) H<sub>3</sub>CCH<sub>2</sub>CCl<sub>2</sub>COOH is a stronger acid than I<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>COOH both because Cl is more electronegative than is I and because the Cl atoms are closer to the acidic hydrogen in the COOH group and thus can exert a stronger e<sup>-</sup> withdrawing effect on the O—H bond than can the more distant I atoms.

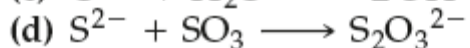
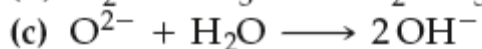
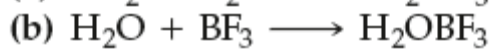
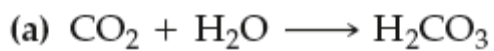
69. From the following bases, select the one with the *smallest* K<sub>b</sub> and the one with the *largest* K<sub>b</sub>, and give reasons for your choices.



**Solution:**

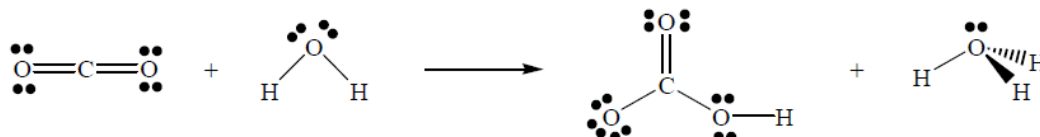
The largest K<sub>b</sub> (most basic) belongs to (c) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> (hydrocarbon chains have the lowest electronegativity). The smallest K<sub>b</sub> (least basic) is that of (a) o-chloroaniline (the nitrogen lone pair is delocalized (spread out over the ring), hence, less available to accept a proton (i.e., it is a poorer Brønsted base)).

**71.** For each reaction draw a Lewis structure for each species and indicate which is the acid and which is the base:

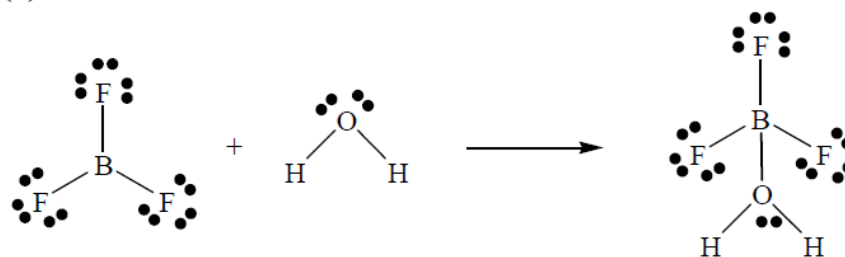


**Solution:**

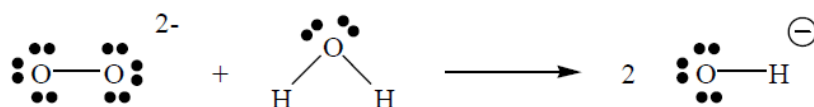
(a) acid is  $\text{CO}_2$  and base is  $\text{H}_2\text{O}$



(b) acid is  $\text{BF}_3$  and base is  $\text{H}_2\text{O}$



(c) acid is  $\text{H}_2\text{O}$  and base is  $\text{O}^{2-}$



(d) acid is  $\text{SO}_3$  and base is  $\text{S}^{2-}$

