

- 9.8 (a) When $P_{\text{N}_2\text{O}_4}$ is graphed against $P_{\text{NO}_2}^2$, they define a line that is close to straight. The slope of this line is the numerical value of K for the reaction $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$
- (b) The seven pairs of equilibrium concentrations give seven different values of K . Their mean is 28.4. The graph can also be fitted by linear least-squares.

9.12

$$(a) \frac{[\text{OH}^-]^8[\text{I}_2]^3}{[\text{I}^-]^6[\text{MnO}_4^-]^2} = K \quad (b) \frac{[\text{I}_2]}{[\text{Cu}^{2+}]^2[\text{I}^-]^4} = K \quad (c) \frac{[\text{H}_3\text{O}^+]^2}{P_{\text{O}_2}^{1/2}[\text{Sn}^{2+}]} = K$$

- 9.18 The second equation is the first equation reversed with every coefficient divided by 6. The equilibrium constant for the second equation is accordingly the reciprocal of that of the first raised to the 1/6 power:

$$K_2 = \left(\frac{1}{32.6} \right)^{\frac{1}{6}} = 0.559$$

- 9.20 The equation of interest, the third equation written in the problem, is equal to the first added to the reverse of the second. Accordingly, the equilibrium constant for the third reaction equals the equilibrium constant of the first multiplied by the reciprocal of the equilibrium constant of the second:

$$K_3 = K_1(K_2)^{-1} = \frac{K_1}{K_2} = \frac{7.0 \times 10^3}{38 \times 10^3} = 0.18$$

- 9.24 To calculate the equilibrium constant requires the partial pressures of all three gases at equilibrium. Set up a three-line table:

	$\text{SbCl}_5(g) \rightleftharpoons$	$\text{SbCl}_3(g) +$	$\text{Cl}_2(g)$
Initial partial pressure (atm)	x	0.0	0.0
Change in partial pressure(atm)	$-0.718x$	$+0.718x$	$+0.718x$
Equilibrium partial pressure (atm)	$0.282x$	$0.718x$	$0.718x$

What is different here is that the original partial pressure of SbCl_5 is not known and is represented by an x . The total pressure at equilibrium is the sum of the partial pressures of the three gases and equals 1.000 atm:

$$1.000 \text{ atm} = P_{\text{SbCl}_5} + P_{\text{SbCl}_3} + P_{\text{Cl}_2} = 0.282x + 0.718x + 0.718x$$

Solving gives $x = 0.582$ atm. The equilibrium partial pressures of the three gases are now readily computed:

$$P_{\text{SbCl}_5} = 0.164 \text{ atm}; \quad P_{\text{SbCl}_3} = P_{\text{Cl}_2} = 0.418 \text{ atm}$$

Substitution in the equilibrium expression gives

$$\frac{P_{\text{SbCl}_3} P_{\text{Cl}_2}}{P_{\text{SbCl}_5}} = \frac{(0.418)(0.418)}{(0.164)} = 1.07 = K$$

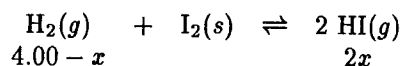
9.42 (a)

$$\frac{(P_{\text{HI}})^2}{P_{\text{H}_2}} = 0.345$$

$$P_{\text{HI}}^2 = 0.345 P_{\text{H}_2} = 0.345(1.00) = 0.345$$

$$P_{\text{HI}} = 0.587 \text{ atm}$$

(b)



$$\frac{(2x)^2}{4.00 - x} = K = 0.345$$

$$4x^2 + 0.345x - 1.38 = 0$$

$$x = \frac{-0.345 \pm \sqrt{(0.345)^2 + 4(4)(1.38)}}{8} = 0.546$$

$$P_{\text{H}_2} = 4.00 - x = 3.45 \text{ atm}$$

$$P_{\text{HI}} = 2x = 1.09 \text{ atm}$$

9.48 According to the list of partial pressures, the reaction quotient Q at the moment of mixing the four compounds equals

$$\frac{P_{\text{NO}}P_{\text{CO}_2}}{P_{\text{NO}_2}P_{\text{CO}}} = Q = \frac{(1.4)(1.4)}{(3.4)(3.4)} = 0.17$$

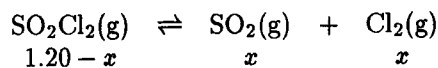
The equilibrium constant for this reaction must be greater than 0.17 because the brown NO_2 is consumed as Q tends to become equal to K . This change increases the numerator and decreases the denominator in the equilibrium expression.

9.52 (a)

$$Q = \frac{P_{\text{SO}_2}P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}} = \frac{0}{1.20} = 0$$

The reaction proceeds to the right.

(b)



$$\frac{x^2}{1.20 - x} = 2.4$$

$$x^2 + 2.4x - 2.88 = 0$$

$$x = \frac{-2.4 \pm \sqrt{(2.4)^2 + 4(2.88)}}{2} = 0.88$$

$$P_{\text{SO}_2} = P_{\text{Cl}_2} = 0.88 \text{ atm} \quad P_{\text{SO}_2\text{Cl}_2} = 1.20 - 0.88 = 0.32 \text{ atm}$$

(c) Net formation.

9.74 (a) The equilibrium constant for the dissolution of the citric acid according to the equation given in the problem is, in simple theory, just the concentration of the dissolved citric acid. For citric acid \mathcal{M} is 192.1 g mol^{-1} , so the saturated aqueous solution contains 6.77 mol L^{-1} and $K = 6.8$. This assumes that there is no ionization of the citric acid in water and also that this concentrated solution behaves ideally. Neither assumption is very defensible. The K for the dissolution in ether is, by similar reasoning, 0.11.

(b) The transfer of citric acid from water into ether equals the reverse of the dissolution of citric acid in water added to the dissolution of citric acid in ether. The partition coefficient K is therefore $0.11/6.8 = 0.017$.

9.80 (a) Let y stand for the equilibrium partial pressure of the acetic acid dimer and x stand for the equilibrium partial pressure of the monomer. According to the problem, the sum of these two partial pressures is 0.725 atm , that is, $x + y = 0.725$. Also, the two partial pressures are related by the equilibrium law

$$\frac{P_{\text{dimer}}}{P_{\text{monomer}}^2} = \frac{y}{x^2} = 3.72$$

There are thus two relationships governing two unknowns. Eliminating x and solving (by means of the quadratic formula) gives $y = 0.398 \text{ atm}$. This is the equilibrium partial pressure of the dimer.

(b) Solving for x in the previous part gives the equilibrium partial pressure of the monomeric acetic acid as 0.327 atm . If none of the acetic acid were dimerized, the partial pressure of the monomer would be $0.327 + (2 \times 0.398) = 1.123 \text{ atm}$. The pressure of monomer that is actually present is 0.327 atm . This is 29.1% of 1.123 atm ; it follows that 70.9% of the acetic acid is present as the dimer.