

SOLUTIONS

PROBLEM SET 8

CHM 3400, Dr. Chatfield

6.18 Consider the reaction

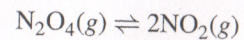


Predict what happens to the system at equilibrium if **(a)** the temperature is raised, **(b)** the pressure on the system is increased, **(c)** an inert gas is added to the system at constant pressure, **(d)** an inert gas is added to the system at constant volume, and **(e)** a catalyst is added to the system.

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- (a)** The equilibrium will shift from right to left. The equilibrium constant K_P will decrease.
- (b)** The equilibrium will shift from left to right. K_P remains unchanged.
- (c)** The volume of the system expands, and the gases are "diluted." K_P remains unchanged, but the equilibrium shifts from right to left.
- (d)** The pressure of the system will increase, but the partial pressures of NO_2 and N_2O_4 remain constant. K_P remains unchanged, and the position of equilibrium will not shift.
- (e)** The catalyst has no effect on either K_P or the position of equilibrium.
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6.20 At a certain temperature, the equilibrium pressures of NO_2 and N_2O_4 are 1.6 bar and 0.58 bar, respectively. If the volume of the container is doubled at constant temperature, what would be the partial pressures of the gases when equilibrium is re-established?

The equilibrium process is



The equilibrium constant can be calculated using the equilibrium pressures.

$$K_P = \frac{1.6^2}{0.58} = 4.41$$

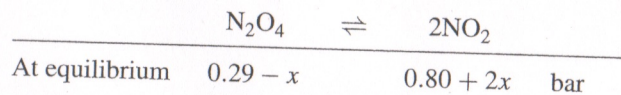
When the volume of the container is doubled at constant temperature, the partial pressures of the gases are halved. That is,

$$P_{\text{NO}_2} = 0.80 \text{ bar}$$

$$P_{\text{N}_2\text{O}_4} = 0.29 \text{ bar}$$

According to Le Chatelier's principle, when the volume is increased, the reaction will shift to produce more molecules. In the case at hand, more NO_2 will be produced.

Assume the equilibrium pressure of N_2O_4 to be $0.29 - x$ bars. The equilibrium pressure of NO_2 is obtained using the stoichiometric relationship between the two compounds.



Solve for x using the equilibrium expression and discarding the non-physical root.

$$K_P = 4.41 = \frac{(0.80 + 2x)^2}{0.29 - x}$$

$$4.41(0.29 - x) = (0.80 + 2x)^2$$

$$4x^2 + 7.61x - 0.639 = 0$$

$$x = 8.06 \times 10^{-2}$$

Therefore, when equilibrium is re-established,

$$P_{\text{N}_2\text{O}_4} = 0.29 - x = 0.21 \text{ bar}$$

$$P_{\text{NO}_2} = 0.80 + 2x = 0.96 \text{ bar}$$

6.27

The dissociation constant can be obtained by plotting $Y/[L]$ vs Y . The slope is $-1/K_d$.

L and Y are obtained using the following relations:

$$[L] = [\text{Ca}^{2+}]_{\text{total}} - [\text{Ca}^{2+}]_{\text{bound}}$$

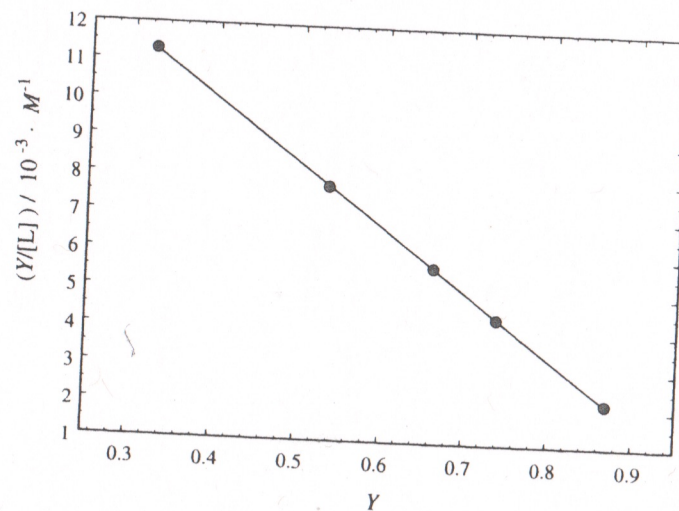
$$Y = \frac{[\text{Ca}^{2+}]_{\text{bound}}}{96 \mu\text{M}}$$

According to the data given above, the values of $[L]$, Y , and $Y/[L]$ are

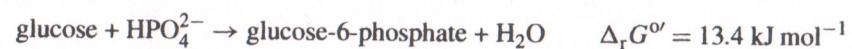
$[L]/\mu\text{M}$	28.8	68.8	116.6	169.2	396.6
Y	0.3250	0.5333	0.6604	0.7375	0.8688
$(Y/[L])/10^{-3} \cdot \text{M}^{-1}$	11.28	7.751	5.664	4.359	2.191

The slope of the plot is -16.72×10^{-3} . Therefore,

$$K_d = \frac{1}{16.72 \times 10^{-3}} = 59.8$$



6.31 Under standard-state conditions, one of the steps in glycolysis does not occur spontaneously:



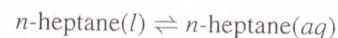
Can the reaction take place in the cytoplasm of a cell where the concentrations are $[\text{glucose}] = 4.5 \times 10^{-2} \text{ M}$, $[\text{HPO}_4^{2-}] = 2.7 \times 10^{-3} \text{ M}$, and $[\text{glucose-6-phosphate}] = 1.6 \times 10^{-4} \text{ M}$ and the temperature is 310 K?

$$\begin{aligned} \Delta_r G &= \Delta_r G^{\circ} + RT \ln Q = \Delta_r G^{\circ} + RT \ln \frac{[\text{glucose-6-phosphate}]}{[\text{glucose}] [\text{HPO}_4^{2-}]} \\ &= 13.4 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K}) \ln \frac{1.6 \times 10^{-4}}{(4.5 \times 10^{-2}) (2.7 \times 10^{-3})} \\ &= 14.1 \times 10^3 \text{ J mol}^{-1} > 0 \end{aligned}$$

Therefore, the reaction is not spontaneous.

- 6.38 The solubility of *n*-heptane in water is 0.050 g per liter of solution at 25° C. What is the Gibbs energy change for the hypothetical process of dissolving *n*-heptane in water at a concentration of 2.0 g L⁻¹ at the same temperature? (*Hint*: First calculate the value of $\Delta_r G^\circ$ from the equilibrium process and then the $\Delta_r G$ value using Equation 6.6.)

The solubility of *n*-heptane in water is $\frac{0.050 \text{ g L}^{-1}}{100.20 \text{ g mol}^{-1}} = 4.99 \times 10^{-4} \text{ M}$. The appropriate equilibrium is



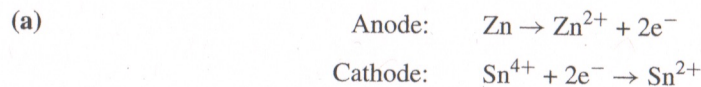
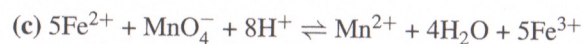
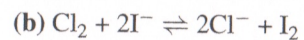
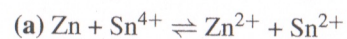
with $K_{\text{sp}}[n\text{-heptane}] = 4.99 \times 10^{-4}$. For the saturated solution, $\Delta_r G = 0$, and

$$\begin{aligned}\Delta_r G^\circ &= -RT \ln K \\ &= -\left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) (298 \text{ K}) \ln \left(4.99 \times 10^{-4}\right) \\ &= 1.88 \times 10^4 \text{ J mol}^{-1}\end{aligned}$$

For the hypothetical process, the concentration is $c = \frac{2.0 \text{ g L}^{-1}}{100.20 \text{ g mol}^{-1}} = 2.00 \times 10^{-2} \text{ M}$, and

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln c \\ &= 1.88 \times 10^4 \text{ J mol}^{-1} + \left(8.314 \text{ J K}^{-1} \text{ mol}^{-1}\right) (298 \text{ K}) \ln \left(2.00 \times 10^{-2}\right) \\ &= 9.14 \times 10^3 \text{ J mol}^{-1} \\ &= 9.1 \text{ kJ mol}^{-1}\end{aligned}$$

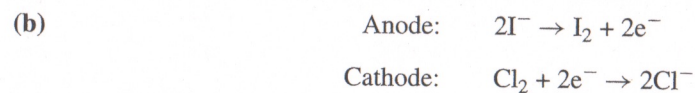
7.8 Calculate the values of E° , $\Delta_r G^\circ$, and K for the following reactions at 25°C :



$$E^\circ = 0.151\text{ V} - (-0.762\text{ V}) = 0.913\text{ V}$$

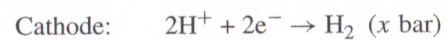
$$\Delta_r G^\circ = -\nu F E^\circ = -2 \left(96500\text{ C mol}^{-1} \right) (0.913\text{ V}) = -1.762 \times 10^5\text{ J mol}^{-1} = -1.76 \times 10^5\text{ J mol}^{-1}$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{(-1.762 \times 10^5\text{ J mol}^{-1})}{(8.314\text{ J K}^{-1}\text{ mol}^{-1})(298.2\text{ K})}\right] = 7.34 \times 10^{30}$$

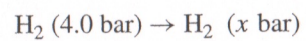


7.10 Consider a concentration cell consisting of two hydrogen electrodes. At 25° C, the cell emf is found to be 0.0267 V. If the pressure of hydrogen gas at the anode is 4.0 bar, what is the pressure of hydrogen gas at the cathode?

Let the pressure of hydrogen gas at the cathode be x bars. The half reactions are



The overall reaction is



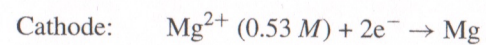
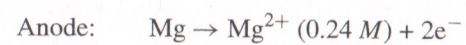
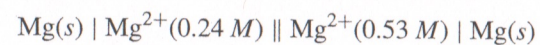
Since this is a concentration cell, $E^\circ = 0$ V. The emf for the cell is

$$E = E^\circ - \frac{0.0257 \text{ V}}{\nu} \ln \frac{x}{4.0}$$

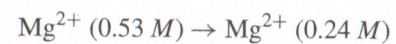
$$0.0267 \text{ V} = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{x}{4.0}$$

$$x = 0.50 \text{ bar}$$

7.14 Calculate the emf of the following concentration cell at 298 K:



The overall reaction is



The emf of the cell depends on the concentrations of Mg^{2+} at both the anode and the cathode.

$$E = E^{\circ} - \frac{0.0257 \text{ V}}{\nu} \ln \frac{0.24}{0.53} = 0 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{0.24}{0.53} = 0.010 \text{ V}$$