

# SOLUTIONS

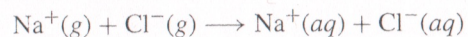
## PROBLEM SET 7

CHM 3400, Dr. Chatfield

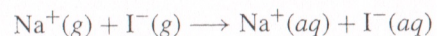
5.68 From the following data, calculate the heat of solution for KI:

	NaCl	NaI	KCl	KI
Lattice energy/ $\text{kJ}\cdot\text{mol}^{-1}$	787	700	716	643
Heat of solution/ $\text{kJ}\cdot\text{mol}^{-1}$	3.8	-5.1	17.1	?

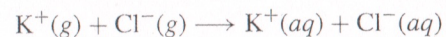
Begin by using  $\Delta_{\text{soln}}H = U_0 + \Delta_{\text{hydr}}H$ , where  $U_0$  is the lattice energy.



$$\Delta_{\text{hydr}}H = 3.8 \text{ kJ mol}^{-1} - 787 \text{ kJ mol}^{-1} = -783.2 \text{ kJ mol}^{-1} \quad (5.68.1)$$

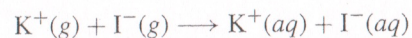


$$\Delta_{\text{hydr}}H = -5.1 \text{ kJ mol}^{-1} - 700 \text{ kJ mol}^{-1} = -705.1 \text{ kJ mol}^{-1} \quad (5.68.2)$$



$$\Delta_{\text{hydr}}H = 17.1 \text{ kJ mol}^{-1} - 716 \text{ kJ mol}^{-1} = -698.9 \text{ kJ mol}^{-1} \quad (5.68.3)$$

Taking Equations 5.68.2 plus 5.68.3 minus 5.68.1 results in



$$\Delta_{\text{hydr}}H = -705.1 \text{ kJ mol}^{-1} - 698.9 \text{ kJ mol}^{-1} + 783.2 \text{ kJ mol}^{-1} = -620.8 \text{ kJ mol}^{-1}$$

Combine this last result with the given value of the lattice energy to arrive at the desired heat of solution.

$$\begin{aligned} \Delta_{\text{soln}}H &= U_0 + \Delta_{\text{hydr}}H \\ &= 643 \text{ kJ mol}^{-1} - 620.8 \text{ kJ mol}^{-1} \\ &= 22.2 \text{ kJ mol}^{-1} \end{aligned}$$

5.69 The concentrations of  $K^+$  and  $Na^+$  ions in the intracellular fluid of a nerve cell are approximately 400 mM and 50 mM, respectively, but in the extracellular fluid the  $K^+$  and  $Na^+$  concentrations are 20 mM and 440 mM, respectively. Given that the electric potential inside the cell is  $-70$  mV relative to the outside, calculate the Gibbs energy change for the transfer of 1 mole of each type of ion against the concentration gradient at  $37^\circ C$ .

In each case the Gibbs energy change going against the concentration gradient is found using

$$\Delta G = RT \ln \frac{[K^+]_{\text{higher}}}{[K^+]_{\text{lower}}} + zF\Delta V.$$

Note that  $1 \text{ V} = 1 \text{ J C}^{-1}$ .

For  $K^+$ :

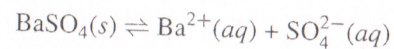
$$\begin{aligned} \Delta G &= RT \ln \frac{[K^+]_{\text{in}}}{[K^+]_{\text{out}}} + zF\Delta V \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K}) \ln \frac{400 \text{ mM}}{20 \text{ mM}} + (1) (96500 \text{ C mol}^{-1}) (-0.070 \text{ V}) \\ &= 966 \text{ J mol}^{-1} = 0.97 \text{ kJ mol}^{-1} \end{aligned}$$

For  $Na^+$ :

$$\begin{aligned} \Delta G &= RT \ln \frac{[Na^+]_{\text{out}}}{[Na^+]_{\text{in}}} + zF\Delta V \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (310 \text{ K}) \ln \frac{440 \text{ mM}}{50 \text{ mM}} + (1) (96500 \text{ C mol}^{-1}) (+0.070 \text{ V}) \\ &= 1.24 \times 10^4 \text{ J mol}^{-1} = 12 \text{ kJ mol}^{-1} \end{aligned}$$

- 5.74 Calculate the solubility of  $\text{BaSO}_4$  (in  $\text{g L}^{-1}$ ) in (a) water and (b) a  $6.5 \times 10^{-5} \text{ M}$   $\text{MgSO}_4$  solution. The solubility product of  $\text{BaSO}_4$  is  $1.1 \times 10^{-10}$ . Assume ideal behavior.

The equation for the dissolution of  $\text{BaSO}_4$  is



- (a) If the solubility of  $\text{BaSO}_4$  is  $x \text{ M}$ , then there are  $x \text{ M}$  of  $\text{Ba}^{2+}$  and  $x \text{ M}$   $\text{SO}_4^{2-}$  in the solution.

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x \cdot x$$

$$x = 1.05 \times 10^{-5}$$

Therefore,

$$\text{the solubility of } \text{BaSO}_4 = (1.05 \times 10^{-5} \text{ mol L}^{-1}) \left( \frac{233.4 \text{ g}}{1 \text{ mol}} \right) = 2.5 \times 10^{-3} \text{ g L}^{-1}$$

- (b) The  $\text{MgSO}_4$  solution contains  $6.5 \times 10^{-5} \text{ M}$  of  $\text{SO}_4^{2-}$ . If the solubility of  $\text{BaSO}_4$  is  $x \text{ M}$ , then there are  $x \text{ M}$  of  $\text{Ba}^{2+}$  and  $x + 6.5 \times 10^{-5} \text{ M}$   $\text{SO}_4^{2-}$  in the solution.

$$K_{\text{sp}} = 1.1 \times 10^{-10} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = x(x + 6.5 \times 10^{-5})$$

$$x^2 + 6.5 \times 10^{-5}x - 1.1 \times 10^{-10} = 0$$

$$x = 1.65 \times 10^{-6} \quad \text{or} \quad x = -6.67 \times 10^{-5} \text{ (nonphysical)}$$

So  $S_{\text{BaSO}_4} = (1.65 \cdot 10^{-6}) \frac{233.4 \text{ g}}{1 \text{ mol}} = 3.9 \cdot 10^{-4} \text{ g/L}$

**5.79** The osmotic pressure of blood plasma is approximately 7.5 atm at 37° C. Estimate the total concentration of dissolved species and the freezing point of blood plasma.

The total concentration of dissolved species is

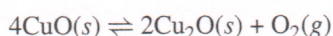
$$c = \frac{\pi}{RT} = \frac{7.5 \text{ atm}}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (310 \text{ K})} = 0.295 \text{ M} = 0.30 \text{ M}$$

Assuming that molality can be approximated by molarity, the freezing point depression caused by the dissolved species is

$$\Delta T = K_f m_2 = (1.86 \text{ K mol}^{-1} \text{ kg}) (0.295 \text{ mol kg}^{-1}) = 0.55 \text{ K}$$

Therefore, blood plasma freezes at  $-0.55^\circ \text{C}$  or 272.60 K.

**6.2** At 1024° C, the pressure of oxygen gas from the decomposition of copper (II) oxide (CuO) is 0.49 bar:



(a) What is the value of  $K_p$  for the reaction? (b) Calculate the fraction of CuO that will decompose if 0.16 mole of it is placed in a 2.0-L flask at 1024° C. (c) What would the fraction be if a 1.0-mole sample of CuO were used? (d) What is the smallest amount of CuO (in moles) that would establish the equilibrium?

(a) 
$$K_p = \frac{P_{\text{O}_2}}{P^\circ} = \frac{0.49 \text{ bar}}{1 \text{ bar}} = 0.49$$

(b) First calculate the number of moles of  $\text{O}_2$  formed by the reaction, from which the number of moles of CuO decomposed is determined. Assume  $\text{O}_2$  behaves ideally.

$$\begin{aligned} \text{Number of moles of O}_2 \text{ formed} &= \frac{PV}{RT} = \frac{(0.49 \text{ bar}) \left( \frac{1 \text{ atm}}{1.013 \text{ bar}} \right) (2.0 \text{ L})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) (1297 \text{ K})} \\ &= 9.09 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{Number of moles of CuO decomposed} = (9.09 \times 10^{-3} \text{ mol O}_2) \left( \frac{4 \text{ mol CuO}}{1 \text{ mol O}_2} \right) = 0.0364 \text{ mol}$$

Therefore,

$$\text{Fraction of CuO decomposed} = \frac{0.0364 \text{ mol}}{0.16 \text{ mol}} = 0.23$$

(c) If a 1.0-mole sample of CuO were used, the pressure of  $\text{O}_2$  would still be the same (0.49 bar) and it would be due to the same quantity of  $\text{O}_2$ . (A pure solid does not affect the equilibrium position, as long as it is in excess at equilibrium.) The number of moles of CuO lost would still be 0.0364 mol. Therefore,

$$\text{Fraction of CuO decomposed} = \frac{0.0364 \text{ mol}}{1.0 \text{ mol}} = 0.036$$

6.4

(a) Since both reactions are endothermic ( $\Delta_r H^\circ$  is positive for each), according to Le Chatelier's principle the products would be favored at high temperatures. Indeed, the steam-reforming process is carried out at very high temperatures (between  $800^\circ\text{C}$  and  $1000^\circ\text{C}$ ). It is interesting to note that in a plant that uses natural gas (methane) for both hydrogen generation and heating, about one-third of the gas is burned to maintain the high temperatures.

In each reaction there are more moles of products than reactants; therefore, products are favored at low pressures. In reality, the reactions are carried out at high pressures. The reason is that when the hydrogen gas produced is used captively (usually in the synthesis of ammonia), high pressure leads to higher yields of ammonia.

(b) (i) Using the result of Problem 6.1,

$$K_P = K_c (RT)^{\Delta n} (P^\circ)^{-\Delta n}$$

In this equation, if  $P^\circ$  is in bar,  $R$  has to be in  $\text{L bar K}^{-1} \text{mol}^{-1}$ :

$$R = (0.08206 \text{ L atm K}^{-1} \text{mol}^{-1}) \left( \frac{1.01325 \text{ bar}}{1 \text{ atm}} \right) = 0.08315 \text{ L bar K}^{-1} \text{mol}^{-1}$$

and  $\Delta n = (1 + 3) - (1 + 1) = 2$ . Therefore,

$$K_P = (18) [(0.08315) (1073)]^2 (1)^{-2} = 1.43 \times 10^5 = 1.4 \times 10^5$$

(b) (ii) The pressures need to be converted to bars in order to use the  $K_P$  expression where  $P^\circ = 1 \text{ bar}$ . The partial pressures of the reactants are

$$(15 \text{ atm}) \left( \frac{1.013 \text{ bar}}{1 \text{ atm}} \right) = 15.2 \text{ bar}$$

The initial and equilibrium pressures of all species are shown in the following.

	$\text{CH}_4$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CO}$	+	$3\text{H}_2$	
Initial	15.2		15.2		0		0	bar
At equilibrium	$15.2 - x$		$15.2 - x$		$x$		$3x$	bar

$$K_P = \frac{(P_{\text{CO}}/P^\circ) (P_{\text{H}_2}/P^\circ)^3}{(P_{\text{CH}_4}/P^\circ) (P_{\text{H}_2\text{O}}/P^\circ)}$$

$$1.43 \times 10^5 = \frac{x (3x)^3}{(15.2 - x)^2} = \frac{27x^4}{(15.2 - x)^2}$$

Take the square root of  $K_P$  and the last term in the above expression.

$$378 = \frac{5.20x^2}{15.2 - x}$$

$$5.20x^2 + 378x - 5745.6 = 0$$

$$x = 12.9 \quad \text{or} \quad -85.6 \text{ (nonphysical)}$$

Therefore, at equilibrium,

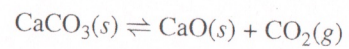
$$P_{\text{CH}_4} = (15.2 - x) \text{ bar} = 2 \text{ bar} = 2 \text{ atm}$$

$$P_{\text{H}_2\text{O}} = (15.2 - x) \text{ bar} = 2 \text{ bar} = 2 \text{ atm}$$

$$P_{\text{CO}} = x \text{ bar} = 13 \text{ bar} = 13 \text{ atm}$$

$$P_{\text{H}_2} = 3x \text{ bar} = 39 \text{ bar} = 38 \text{ atm}$$

6.8 Consider the thermal decomposition of  $\text{CaCO}_3$ :



The equilibrium vapor pressures of  $\text{CO}_2$  are 22.6 mmHg at  $700^\circ\text{C}$  and 1829 mmHg at  $950^\circ\text{C}$ . Calculate the standard enthalpy of the reaction.

The van't Hoff equation,

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right),$$

is used to solve this problem. Since

$$K_P = \frac{P_{\text{CO}_2}}{P^\circ},$$

$K_P$  is proportional to  $P_{\text{CO}_2}$ . Thus,

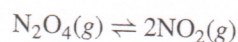
$$\ln \frac{K_2}{K_1} = \ln \frac{P_{\text{CO}_2,2}}{P_{\text{CO}_2,1}} = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{1829 \text{ mmHg}}{22.6 \text{ mmHg}} = \frac{\Delta_r H^\circ}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{973.2 \text{ K}} - \frac{1}{1223.2 \text{ K}} \right)$$

$$\Delta_r H^\circ = 1.74 \times 10^5 \text{ J mol}^{-1}$$



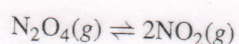
6.14 The dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  is 16.7% complete at 298 K and 1 atm:



Calculate the equilibrium constant and the standard Gibbs energy change for the reaction. [Hint: Let  $\alpha$  be the degree of dissociation and show that  $K_P = 4\alpha^2 P / (1 - \alpha^2)$ , where  $P$  is the total pressure.]

The equilibrium constant is related to the degree of dissociation,  $\alpha$ . The exact relation is derived as follows.

The dissociation reaction is



Let the initial number of moles of  $\text{N}_2\text{O}_4$  be  $n$ . At equilibrium,  $n\alpha$  moles of  $\text{N}_2\text{O}_4$  dissociates, giving  $2n\alpha$  moles of  $\text{NO}_2$ . The number of moles of  $\text{N}_2\text{O}_4$  remaining is  $n - n\alpha = n(1 - \alpha)$ . The total number of moles of gases are  $n(1 - \alpha) + 2n\alpha = n(1 + \alpha)$ .

The equilibrium constant can be calculated once the partial pressures of the gases are known. The partial pressures are calculated from the mole fractions of the gases.

$$x_{\text{N}_2\text{O}_4} = \frac{n(1 - \alpha)}{n(1 + \alpha)} = \frac{1 - \alpha}{1 + \alpha}$$

$$x_{\text{NO}_2} = \frac{2n\alpha}{n(1 + \alpha)} = \frac{2\alpha}{1 + \alpha}$$

The partial pressures are

$$P_{\text{N}_2\text{O}_4} = x_{\text{N}_2\text{O}_4} P = \frac{1 - \alpha}{1 + \alpha} P$$

$$P_{\text{NO}_2} = x_{\text{NO}_2} P = \frac{2\alpha}{1 + \alpha} P$$

The equilibrium constant can now be calculated using the partial pressures in bars. The total pressure is 1 atm, which is equivalent to 1.013 bar.

$$\begin{aligned} K_P &= \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{1 + \alpha} P\right)^2}{\frac{1 - \alpha}{1 + \alpha} P} = \frac{4\alpha^2 P}{(1 + \alpha)(1 - \alpha)} = \frac{4\alpha^2}{1 - \alpha^2} P = \frac{4(0.167)^2}{1 - 0.167^2} (1.013) \\ &= 0.1162 = 0.116 \end{aligned}$$

The standard Gibbs energy change is

$$\Delta_r G^\circ = -RT \ln K = - (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298 \text{ K}) \ln 0.1162 = 5.33 \times 10^3 \text{ J mol}^{-1}$$