Chemistry 2000 Spring 2019 Test 2 Solutions Version B



(b) The positive slope means that the solid phase is favored by higher pressures and thus, according to Le Chatelier's principle, that the solid is more dense than the liquid.

2. We start by balancing the half-reactions:

$$Se_{(s)} + 3H_2O_{(l)} \rightarrow SeO_{3(aq)}^{2-} + 6H_{(aq)}^+ + 4e^-$$
$$Cr(OH)_{3(s)} + 3H_{(aq)}^+ + 3e^- \rightarrow Cr_{(s)} + 3H_2O_{(l)}$$

An overall reaction can be obtained by multiplying the first reaction by 3 and the second by 4, and adding:

$$3Se_{(s)} + 4Cr(OH)_{3(s)} \rightarrow 3SeO_{3(aq)}^{2-} + 6H_{(aq)}^{+} + 3H_2O_{(l)} + 4Cr_{(s)}$$

To get the reaction balanced in base, add $6OH^-_{(aq)}$ to each side. Combine the hydroxide with the hydrogen ions to make water and simplify:

$$3Se_{(s)} + 4Cr(OH)_{3(s)} + 6OH^{-}_{(aq)} \rightarrow 3SeO^{2-}_{3(aq)} + 9H_2O_{(l)} + 4Cr_{(s)}$$

3. (a)

$$\Delta_r S^\circ = 2S^\circ(NO_2) - [2S^\circ(NO)S^\circ(O_2)]$$

= 2(239.9) - [2(210.65) + 205.0] J K⁻¹mol⁻¹
= -146.5 J K⁻¹mol⁻¹.

(b) The ΔS calculated above is only the ΔS for the reaction. The second law says that the entropy of the universe must increase, which includes the entropy change for the surroundings. For this reaction,

$$\Delta_r H^{\circ} = 2\Delta_f H^{\circ}(\text{NO}_2) - [2\Delta_f H^{\circ}(\text{NO})\Delta_f H^{\circ}(\text{O}_2)]$$

= 2(33.2) - [2(90.29) + 0] kJ mol⁻¹
= -114.2 kJ mol⁻¹.

Since the reaction is exothermic, the entropy of the surroundings will increase. The reaction will continue while the entropy change of the surroundings is greater than the decrease in entropy of the system.

4. (a)

$$\begin{aligned} \Delta_r G^\circ &= \Delta_f G^\circ(N_2 O_4) - 2\Delta_f G^\circ(N O_2) \\ &= 97.7 - 2(51) \,\text{kJ} \,\text{mol}^{-1} \\ &= -4 \,\text{kJ} \,\text{mol}^{-1} \\ K &= \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \\ &= \exp\left(\frac{-(-4 \times 10^3 \,\text{J} \,\text{mol}^{-1})}{(8.314 \,463 \,\text{J} \,\text{K}^{-1} \text{mol}^{-1})(298.15 \,\text{K})}\right) \\ &= 6 \end{aligned}$$

(b) There are two ways to answer this question:

i.

$$Q = \frac{a_{\rm N_2O_4}}{(a_{\rm NO_2})^2} = \frac{0.38}{(0.043)^2} = 2.1 \times 10^2.$$

Since Q > K, the reaction is not allowed. Its reverse is allowed under these conditions.

ii.

Since $\Delta_r G^{\circ} > 0$, the reaction is not allowed.

5. The equilibrium expression is

$$K = \frac{a_{\rm CO_2}}{a_{\rm CO}}$$

since the solids have activities of 1. The activity of a gas is $a = p/p^{\circ}$, and since $p^{\circ} = 1$ bar, pressures and activities are essentially interconvertible if the pressures are given in bar.

ICE table:

	CO	$\rm CO_2$
Ι	2.9	0
\mathbf{C}	-x	x
Ε	2.9 - x	x

Therefore

$$0.79 = \frac{x}{2.9 - x}$$
$$0.79(2.9 - x) = x$$
$$2.3 - 0.79x = x$$
$$2.3 = 1.79x$$
$$x = 1.3$$

The pressure of CO_2 is 1.3 bar, and the pressure of CO is 2.9 - x = 1.6 bar.

6. We need to use $p = p^{\bullet}X$.

$$\begin{split} M_{\rm cp} &= 9(12.0106) + 15(1.007\,98) + 14.0069 + 3(15.9994) + 32.068\,{\rm g\,mol}^{-1} \\ &= 217.288\,{\rm g\,mol}^{-1} \\ n_{\rm cp} &= \frac{20.5513\,{\rm g}}{217.288\,{\rm g\,mol}^{-1}} = 0.094\,5808\,{\rm mol} \\ M_{\rm cf} &= 12.0106 + 1.007\,98 + 3(35.452)\,{\rm g\,mol}^{-1} \\ &= 119.375\,{\rm g\,mol}^{-1} \\ n_{\rm cf} &= \frac{201.35\,{\rm g}}{119.375\,{\rm g\,mol}^{-1}} = 1.6867\,{\rm mol} \\ X_{\rm cf} &= \frac{n_{\rm cf}}{n_{\rm cf} + n_{\rm cp}} \\ &= \frac{1.6867\,{\rm mol}}{1.6867\,{\rm mol} + 0.094\,5808\,{\rm mol}} \\ &= 0.946\,90 \\ p_{\rm cf} &= p_{\rm cf}^{\bullet}X_{\rm cf} \\ &= (0.208\,{\rm bar})(0.946\,90) = 0.197\,{\rm bar} \end{split}$$

7. (a) For this process, $K = a(aq) = s/c^{\circ}$. Since $c^{\circ} = 1 \mod L^{-1}$, K is just s with the units removed. We're going to solve for $\Delta_r H^{\circ}$ from the formula

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

The data table already has the data laid out, so we'll just take row $1 = (T_1, K_1)$ and row $2 = (T_2, K_2)$. While there are other ways to do this, I'm going to solve for $\Delta_r H^{\circ}$ analytically, and then plug in numbers:

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

= $\frac{(8.314\,463\,\mathrm{J\,K^{-1}mol^{-1}}) \ln \left(\frac{7.92 \times 10^{-3}}{1.71 \times 10^{-3}}\right)}{\frac{1}{288.07\,\mathrm{K}} - \frac{1}{328.15\,\mathrm{K}}}$
= 30.06 kJ mol⁻¹.

(b) Now we're solving for K. We need to use one of the equilibrium constants and the enthalpy change. I'm going to use the first

equilibrium constant, but it really shouldn't make a difference. My data table is

$$T_1 = 288.07 \,\mathrm{K}, \quad K_1 = 1.71 \times 10^{-3}$$

 $T_2 = 273.15 \,\mathrm{K}, \quad K_2 = \mathrm{unknown}$

$$\ln\left(\frac{K_2}{1.71 \times 10^{-3}}\right) = \frac{30.06 \times 10^3 \,\mathrm{J \,mol^{-1}}}{8.314\,463 \,\mathrm{J \, K^{-1} mol^{-1}}} \left(\frac{1}{288.07 \,\mathrm{K}} - \frac{1}{273.15 \,\mathrm{K}}\right)$$
$$= -0.686$$
$$\therefore K_2 = (1.71 \times 10^{-3})e^{-0.686} = 8.62 \times 10^{-4}$$

Since $K = s/c^{\circ}$, $s = Kc^{\circ} = 8.62 \times 10^{-4} \operatorname{mol} L^{-1}$.

- (c) Chocolate drinks contain a number of solutes, including notably quite a bit of sugar. These solutes depress the freezing point.
- (d) The concentration of the obromine in the drink $(2.5 \times 10^{-3} \text{ mol } \text{L}^{-1})$ ends up being higher than the solubility at 0 °C $(8.62 \times 10^{-4} \text{ mol } \text{L}^{-1})$, therefore we would expect some of the theobromine to precipitate out. Since the obromine has similar neurological effects as caffeine, it turns out that chilling your chocolate drink is a literal buzz-kill.