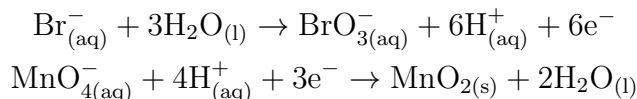


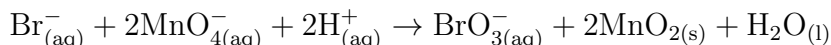
## Chemistry 2000 Spring 2019 Test 2 Solutions

### Version A

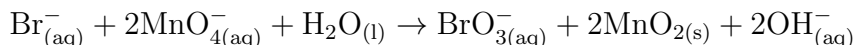
- Point a is called the **triple** point.  
Point b is called the **critical** point.
  - Going from point 1 to point 2 along path A, we would start with a sample of the liquid. When the system reaches the liquid-gas coexistence curve, a meniscus will appear separating the liquid from the gas. As the liquid evaporates, more and more of the volume would be occupied by gas, until the liquid was all gone. No further obvious changes would be observed from that time until point 2 was reached.  
Along path B, we go around the critical point, so no meniscus would ever be seen. The conversion would occur continuously, without encountering any specific point that could be identified with a phase change.
  - The triple point occurs at one very specific temperature, which makes it ideal for calibrating thermometers.
- We start by balancing the half-reactions:



An overall reaction can be obtained by multiplying the second reaction by 2 and adding:



To get the reaction balanced in base, add  $2\text{OH}^-_{(\text{aq})}$  to each side. Combine the hydroxide with the hydrogen ions to make water and simplify:



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$$\begin{aligned}\Delta_r S^\circ &= S^\circ(\text{N}_2\text{O}_4) - 2S^\circ(\text{NO}_2) \\ &= 304.3 - 2(239.9) \text{ J K}^{-1}\text{mol}^{-1} \\ &= -175.5 \text{ J K}^{-1}\text{mol}^{-1}.\end{aligned}$$

- (b) The  $\Delta S$  calculated above is only the  $\Delta S$  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,

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(\text{N}_2\text{O}_4) - 2\Delta_f H^\circ(\text{NO}_2) \\ &= 9.16 - 2(33.2) \text{ kJ mol}^{-1} \\ &= -57.2 \text{ kJ mol}^{-1}.\end{aligned}$$

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)

$$\begin{aligned}\Delta_r G^\circ &= 2\Delta_f G^\circ(\text{NO}_2) - [2\Delta_f G^\circ(\text{NO}) + \Delta_f G^\circ(\text{O}_2)] \\ &= 2(51) - [2(86.60) + 0] \text{ kJ mol}^{-1} \\ &= -71 \text{ kJ mol}^{-1} \\ K &= \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) \\ &= \exp\left(\frac{-(-71 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}\right) \\ &= 3 \times 10^{12}\end{aligned}$$

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

i.

$$Q = \frac{(a_{\text{NO}_2})^2}{(a_{\text{NO}})^2 a_{\text{O}_2}} = \frac{(25)^2}{(1.0 \times 10^{-4})^2 (2.3 \times 10^{-3})} = 2.7 \times 10^{13}.$$

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

ii.

$$\begin{aligned}
 \Delta_r G &= \Delta_r G^\circ + RT \ln Q \\
 &= \Delta_r G^\circ + RT \ln \left( \frac{(a_{\text{NO}_2})^2}{(a_{\text{NO}})^2 a_{\text{O}_2}} \right) \\
 &= -71 \text{ kJ mol}^{-1} + (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \\
 &\quad \times \ln \left( \frac{(25)^2}{(1.0 \times 10^{-4})^2 (2.3 \times 10^{-3})} \right) \\
 &= 5 \text{ kJ mol}^{-1}
 \end{aligned}$$

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

5. The equilibrium expression is

$$K = \frac{a_{\text{CO}_2}}{a_{\text{CO}}}$$

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

ICE table:

	CO	CO <sub>2</sub>
I	1.3	0
C	$-x$	$x$
E	$1.3 - x$	$x$

Therefore

$$\begin{aligned}
 0.403 &= \frac{x}{1.3 - x} \\
 0.403(1.3 - x) &= x \\
 0.52 - 0.403x &= x \\
 0.52 &= 1.403x \\
 x &= 0.37
 \end{aligned}$$

The pressure of CO<sub>2</sub> is 0.37 bar, and the pressure of CO is  $1.3 - x = 0.9 \text{ bar}$ .

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

$$\begin{aligned} M_{cz} &= 15(12.0106) + 12(1.00798) + 2(14.0069) + 15.9994 \text{ g mol}^{-1} \\ &= 236.2680 \text{ g mol}^{-1} \end{aligned}$$

$$n_{cz} = \frac{20.5513 \text{ g}}{236.2680 \text{ g mol}^{-1}} = 0.0869830 \text{ mol}$$

$$\begin{aligned} M_{ac} &= 3(12.0106) + 6(1.00798) + 15.9994 \text{ g mol}^{-1} \\ &= 58.0791 \text{ g mol}^{-1} \end{aligned}$$

$$n_{ac} = \frac{201.35 \text{ g}}{58.0791 \text{ g mol}^{-1}} = 3.4668 \text{ mol}$$

$$\begin{aligned} X_{ac} &= \frac{n_{ac}}{n_{ac} + n_{cz}} \\ &= \frac{3.4668 \text{ mol}}{3.4668 \text{ mol} + 0.0869830 \text{ mol}} \\ &= 0.97552 \end{aligned}$$

$$\begin{aligned} p_{ac} &= p_{ac}^\bullet X_{ac} \\ &= (0.246 \text{ bar})(0.97552) = 0.240 \text{ bar} \end{aligned}$$

7. (a) For this process,  $K = a(\text{aq}) = s/c^\circ$ . Since  $c^\circ = 1 \text{ mol L}^{-1}$ ,  $K$  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:

$$\begin{aligned} \Delta_r H^\circ &= \frac{R \ln \left( \frac{K_2}{K_1} \right)}{\frac{1}{T_1} - \frac{1}{T_2}} \\ &= \frac{(8.314463 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{0.218}{0.0682} \right)}{\frac{1}{288.01 \text{ K}} - \frac{1}{328.15 \text{ K}}} \\ &= 22.75 \text{ kJ mol}^{-1}. \end{aligned}$$

(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

$$\begin{aligned}T_1 &= 288.01 \text{ K}, & K_1 &= 0.0682 \\T_2 &= 273.15 \text{ K}, & K_2 &= \text{unknown}\end{aligned}$$

$$\begin{aligned}\ln\left(\frac{K_2}{0.0682}\right) &= \frac{22.75 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{288.01 \text{ K}} - \frac{1}{273.15 \text{ K}}\right) \\&= -0.517 \\ \therefore K_2 &= 0.0682e^{-0.517} = 0.0407.\end{aligned}$$

Since  $K = s/c^\circ$ ,  $s = Kc^\circ = 0.0407 \text{ mol L}^{-1}$ .

- (c) Coffee contains a number of solutes that give it its characteristic color, flavor and aroma. These solutes depress the freezing point.
- (d) The concentration of caffeine in the coffee ( $8 \times 10^{-3} \text{ mol L}^{-1}$ ) is lower than the solubility at  $0^\circ\text{C}$  ( $0.0407 \text{ mol L}^{-1}$ ), so no, caffeine won't precipitate out.