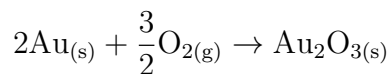


# Chemistry 2740 Spring 2018 Test 2 solutions

1. (a) Start with a balanced reaction:



For this reaction,  $\Delta_r G^\circ = \Delta_f G^\circ(\text{Au}_2\text{O}_3) = 163.2 \text{ kJ mol}^{-1}$ .

$$\begin{aligned}\Delta_r G &= \Delta_r G^\circ + RT \ln Q \\ &= \Delta_r G^\circ + RT \ln \left( \frac{1}{a_{\text{O}_2}^{3/2}} \right) \\ &= 163.2 \text{ kJ mol}^{-1} + (8.314472 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln \left( \frac{1}{300^{3/2}} \right) \\ &= 142.0 \text{ kJ mol}^{-1}\end{aligned}$$

The reaction is not thermodynamically allowed, so no, we could not make gold oxide under these conditions.

- (b) From  $\Delta_r H^\circ = \Delta_f H^\circ(\text{Au}_2\text{O}_3) = 80.75 \text{ kJ mol}^{-1}$  and the standard free energy change, we get

$$\begin{aligned}\Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T^\circ} = \frac{80.75 - 163.2 \text{ kJ mol}^{-1}}{298.15 \text{ K}} \\ &= -0.277 \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Because  $\Delta_r H^\circ$  and  $-T\Delta_r S^\circ$  are both positive,  $\Delta_r G^\circ$  will always be positive. Decreasing the temperature will decrease  $\Delta_r G^\circ$  (because the  $-T\Delta_r S^\circ$  becomes smaller), so it's possible that with a sufficiently small  $T$  and a sufficiently negative  $RT \ln Q$  term (sufficiently high pressure of  $\text{O}_2$ ), we could make  $\Delta_r G$  negative.

Let's put a few numbers in and see how this shakes out for this particular reaction. (It was not necessary to do this for full marks on this question.)

$$\begin{aligned}\Delta_r G_m &= \Delta_r G_m^\circ + RT \ln Q \\ &= \Delta_r H^\circ - T\Delta_r S^\circ + RT \ln Q \\ &= \Delta_r H^\circ + T(R \ln Q - \Delta_r S^\circ) \\ &= 80.75 \text{ kJ mol}^{-1} + T \left[ (8.314472 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{1}{300^{3/2}} \right) \right. \\ &\quad \left. - (-0.277 \text{ kJ K}^{-1} \text{ mol}^{-1}) \right] \\ &= 80.75 \text{ kJ mol}^{-1} + (0.205 \text{ kJ K}^{-1} \text{ mol}^{-1})T\end{aligned}$$

At least for  $p_{\text{O}_2} = 300 \text{ bar}$ , there is no positive temperature at which  $\Delta_r G_m < 0$ . Accordingly, we could not synthesize gold oxide without raising the pressure to absurdly large values.

As you can imagine from the outcome of this calculation, that's not how gold oxide is made.

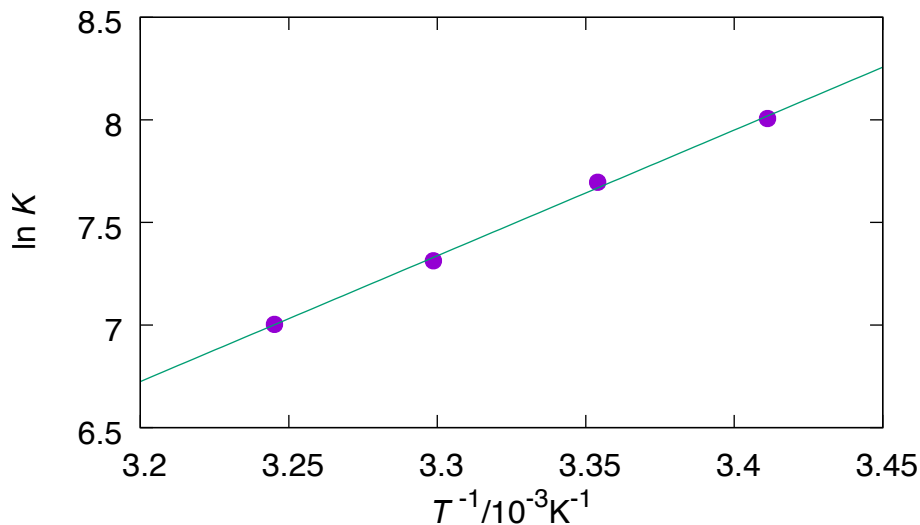
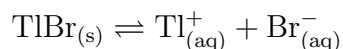


Figure 1: Graph of data from question 3

2. The reaction is



The equilibrium constant for this reaction is

$$K_{\text{sp}} = (a_{\text{Tl}^{+}})(a_{\text{Br}^{-}}) = \gamma_{\pm}^2 s^2 / (c^{\circ})^2$$

where  $s$  is the solubility in  $\text{mol L}^{-1}$ .

$$s = \frac{0.54 \text{ g L}^{-1}}{284.287 \text{ g mol}^{-1}} = 1.9 \times 10^{-3} \text{ mol L}^{-1}$$

$$I_c = \frac{1}{2} \{ (+1)^2 [\text{Tl}^{+}] + (-1)^2 [\text{Br}^{-}] \} = s = 1.9 \times 10^{-3} \text{ mol L}^{-1}$$

$$\ln \gamma_{\pm} = -A |z_+ z_-| (\epsilon T)^{-3/2} \sqrt{I_c}$$

$$= -(1.107 \times 10^{-10}) |( +1)( -1 ) | [ (6.939 \times 10^{-10})(298.15 \text{ K}) ]^{-3/2} \sqrt{1.9 \times 10^{-3} \text{ mol L}^{-1}}$$

$$= -0.051$$

$$\therefore \gamma_{\pm} = e^{-0.051} = 0.95$$

$$\therefore K_{\text{sp}} = (0.95)^2 (1.9 \times 10^{-3})^2 = 3.3 \times 10^{-6}$$

3. We're going to use the equation

$$\ln K = -\frac{\Delta_r H^{\circ}}{R} \frac{1}{T} + C$$

We want to graph  $\ln K$  vs  $T^{-1}$ . My graph is shown in Fig. 1. The slope of the graph,

obtained by linear regression, is 6129 K. Therefore

$$\begin{aligned}\Delta_r H^\circ &= -R(\text{slope}) \\ &= -(8.314\,472\text{ J K}^{-1}\text{ mol}^{-1})(6129\text{ K}) \\ &= -50.96\text{ kJ mol}^{-1}\end{aligned}$$