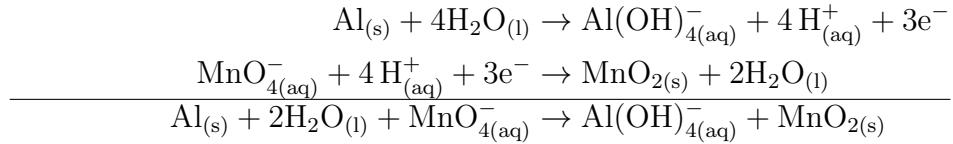


# Chemistry 2740 Spring 2022 Test 2 Solutions

1. (a)



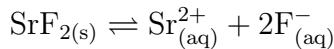
(b) From the balancing process, we have  $\nu_e = 3$ .

$$\begin{aligned}
 \Delta_r G^\circ &= \Delta_f G^\circ(\text{Al}(\text{OH})_4^-) + \Delta_f G^\circ(\text{MnO}_2) - [2\Delta_f G^\circ(\text{H}_2\text{O}) + \Delta_f G^\circ(\text{MnO}_4^-)] \\
 &= -1301 + (-465.2) - [2(-237.140) + (-425.1)] \text{ kJ mol}^{-1} \\
 &= -867 \text{ kJ mol}^{-1} \\
 E^\circ &= \frac{-\Delta_r G^\circ}{\nu_e F} \\
 &= \frac{867 \times 10^3 \text{ J mol}^{-1}}{3(96\,485.342 \text{ C mol}^{-1})} \\
 &= 2.99 \text{ V}
 \end{aligned}$$

2. This is an application of the formula

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

The reaction is



$$\begin{aligned}
 \Delta_r H^\circ &= \Delta_f H^\circ(\text{Sr}^{2+}) + 2\Delta_f H^\circ(\text{F}^-) - \Delta_f H^\circ(\text{SrF}_2) \\
 &= -545.51 + 2(-335.35) - (-1217.13) \text{ kJ mol}^{-1} \\
 &= 0.92 \text{ kJ mol}^{-1}
 \end{aligned}$$

For this problem, we have

$$\begin{aligned}
 K_1 &= 2.6 \times 10^{-9} & \text{at } T_1 = 298.15 \text{ K} \\
 K_2 \text{ is the unknown} & & \text{at } T_2 = 373.15 \text{ K}
 \end{aligned}$$

$$\begin{aligned}
 \ln\left(\frac{K_2}{2.6 \times 10^{-9}}\right) &= \frac{920 \text{ J mol}^{-1}}{8.314\,472 \text{ J K}^{-1}\text{mol}^{-1}} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{373.15 \text{ K}}\right) \\
 &= 0.075
 \end{aligned}$$

$$\begin{aligned}
 \therefore \frac{K_2}{2.6 \times 10^{-9}} &= e^{0.075} = 1.08 \\
 \therefore K_2 &= 1.08(2.6 \times 10^{-9}) = 2.8 \times 10^{-9}
 \end{aligned}$$

3. The hint says to start by solving the equilibrium problem. The relevant equilibrium is



For simplicity of notation, I will write  $\text{AH}$  for the acid, and  $\text{A}^-$  for the conjugate base. The corresponding  $K_a$  expression is

$$K_a = \frac{(a_{\text{A}^-})(a_{\text{H}^+})}{a_{\text{AH}}}$$

The activity coefficient of acid is approximately 1, so  $a_{\text{AH}} \approx [\text{AH}]/c^\circ$ . For the ions however, we have to take the activity coefficients into account. Thus,  $a_{\text{A}^-} = \gamma_{\pm}[\text{A}^-]/c^\circ$  and  $a_{\text{H}^+} = \gamma_{\pm}[\text{H}^+]/c^\circ$ . Note that I'm using  $\gamma_{\pm}$  to save a bit of algebra (although with both ions having the same charge, there isn't a real saving in this case). The concentrations of the acid, base and  $\text{H}^+$  are related, as can be determined using an ICE table:

	[AH]	[A <sup>-</sup> ]	[H <sup>+</sup> ]
I	$5.28 \times 10^{-3}$	0	0
C	$-x$	$x$	$x$
E	$5.28 \times 10^{-3} - x$	$x$	$x$

The  $K_a$  expression thus reads

$$K_a = \frac{\gamma_{\pm}^2 x^2}{5.28 \times 10^{-3} - x}$$

To calculate  $\gamma_{\pm}$ , we need the ionic strength at equilibrium:

$$\begin{aligned} I_c &= \frac{1}{2} \{ (+1)^2 [\text{H}^+] + (-1)^2 [\text{A}^-] \} \\ &= \frac{1}{2} \{ x + x \} = x \end{aligned}$$

Thus we have

$$\begin{aligned} \ln \gamma_{\pm} &= A z_+ z_- (\epsilon T)^{-3/2} \sqrt{I_c} \\ &= (1.107 \times 10^{-10}) * (1)(-1) * [(78.37)(8.854\,188 \times 10^{-12})(298.15)]^{-3/2} \sqrt{x} \\ &= -1.176 \sqrt{x} \\ \therefore \gamma_{\pm} &= e^{-1.176 \sqrt{x}} \end{aligned}$$

The final equation we have to solve is therefore

$$K_a = 1.4 \times 10^{-3} = \frac{(e^{-1.176 \sqrt{x}})^2 x^2}{5.28 \times 10^{-3} - x} = \frac{e^{-2.353 \sqrt{x}} x^2}{5.28 \times 10^{-3} - x}$$

You can solve this equation using any convenient tool. I used my TI-89 calculator with an initial guess for  $x$  of  $10^{-3}$ . The solver gave a solution of

$$x = 2.2 \times 10^{-3} \text{ mol L}^{-1}$$

We don't just want the concentration. We want the pH:

$$\begin{aligned}\text{pH} &= -\log_{10} a_{\text{H}^+} \\ a_{\text{H}^+} &= \gamma_{\pm} [\text{H}^+]/c^\circ \\ &= e^{-1.176\sqrt{x}} x/c^\circ \\ &= 2.1 \times 10^{-3} \\ \therefore \text{pH} &= -\log_{10}(2.1 \times 10^{-3}) = 2.68.\end{aligned}$$