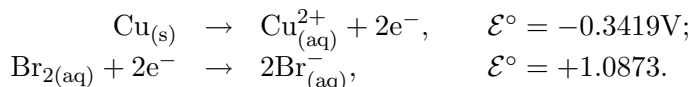
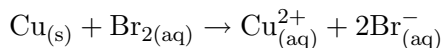


# Chemistry 2740 Spring 2008 Test 2 Solutions

1. None
2. (a) increase the temperature  
(b) use a coupled reaction that removes Q from solution
3.
  - The student used the enthalpy instead of the free energy of formation of gaseous bromine.
  - In the calculation of  $K$ ,  $\Delta_r \bar{G}^\circ$  is in kJ/mol but  $R$  is in  $\text{J K}^{-1}\text{mol}^{-1}$ . This error could probably have been avoided if the student had consistently written down his units.
  - $\Delta_r \bar{G}^\circ$  was calculated at 298.15 K. You can't mix a  $\Delta_r \bar{G}^\circ$  calculated at 298.15 K with a different temperature (283 K) in the calculation of  $K$ . You either have to correct  $\Delta_r \bar{G}^\circ$  to 283.15 K, or you calculate  $K$  at 298.15 K and then calculate  $K$  at 283.15 K.
4. The half-cell reactions are



The overall reaction is therefore



with  $\bar{n} = 2$  and  $\mathcal{E}^\circ = 0.7454\text{ V}$ . The voltage is given by the Nernst equation

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{\bar{n}\mathcal{F}} \ln Q,$$

which we can solve for  $Q$ :

$$\begin{aligned} Q &= \exp \left[ \frac{\bar{n}\mathcal{F}}{RT} (\mathcal{E}^\circ - \mathcal{E}) \right] \\ &= \exp \left[ \frac{2(96\,485.342\text{ C/mol})}{(8.314\,472\text{ J K}^{-1}\text{mol}^{-1})(298.15\text{ K})} (0.7454 - 0.7558\text{ V}) \right] \\ &= 0.4450 \end{aligned}$$

We also know that  $Q = (a_{\text{Cu}^{2+}})(a_{\text{Br}^-})^2/a_{\text{Br}_2} = \gamma_{\text{Cu}^{2+}}[\text{Cu}^{2+}]\gamma_{\text{Br}^-}^2[\text{Br}^-]^2/[\text{Br}_2]$  if we leave out the factors of  $c^\circ$  and assume the bromine behaves ideally. In the left half-cell, we have

$$\begin{aligned} I_c &= \frac{1}{2} \{ (+2)^2[\text{Cu}^{2+}] + (-2)^2[\text{SO}_4^{2-}] \} \\ &= \frac{1}{2} \{ (+2)^2(1.4 \times 10^{-3}) + (-2)^2(1.4 \times 10^{-3}\text{ mol/L}) \} \\ &= 5.6 \times 10^{-3}\text{ mol/L}. \\ \therefore \ln \gamma_{\text{Cu}^{2+}} &= -(1.107 \times 10^{-10})(2)^2 [(6.954 \times 10^{-10}\text{ C}^2\text{J}^{-1}\text{m}^{-1})(298.15\text{ K})]^{-3/2} \sqrt{5.6 \times 10^{-3}\text{ mol/L}} \\ &= -0.35. \\ \therefore \gamma_{\text{Cu}^{2+}} &= 0.70. \end{aligned}$$

In the right half-cell,

$$\begin{aligned}
I_c &= \frac{1}{2} \{ (+1)^2 [\text{Na}^+] + (-1)^2 [\text{Br}^-] \} \\
&= \frac{1}{2} \{ (+1)^2 (0.0085) + (-1)^2 (0.0085 \text{ mol/L}) \} \\
&= 0.0085 \text{ mol/L.} \\
\therefore \ln \gamma_{\text{Br}^-} &= -(1.107 \times 10^{-10})(-1)^2 [(6.954 \times 10^{-10} \text{ C}^2 \text{J}^{-1} \text{m}^{-1})(298.15 \text{ K})]^{-3/2} \sqrt{0.0085 \text{ mol/L}} \\
&= -0.11. \\
\therefore \gamma_{\text{Br}^-} &= 0.90.
\end{aligned}$$

Now going back to our expression for  $Q$ , we have

$$\begin{aligned}
[\text{Br}_2] &= \gamma_{\text{Cu}^{2+}} [\text{Cu}^{2+}] \gamma_{\text{Br}^-}^2 [\text{Br}^-]^2 / Q \\
&= (0.70)(1.4 \times 10^{-3})(0.90)^2 (0.0085)^2 / 0.4450 \\
&= 1.3 \times 10^{-7} \text{ mol/L.}
\end{aligned}$$

5. (a) In the equation

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

we see the ratio of equilibrium constants  $K_2/K_1$ . According to the Debye-Hückel theory, the activity coefficient of an ion only depends on the ionic strength and temperature. In these experiments, the ionic strength is constant, and activity coefficients depend only weakly on temperature, so the activity coefficients would roughly cancel in this ratio.

(b) We plot  $\ln K_a$  vs  $1/T$  (figure 1). The slope of the graph (obtained by linear regression) is  $-1564 \text{ K}$ .

$$\therefore \Delta_r \bar{H}^\circ = -R(\text{slope}) = -(8.314472 \text{ J K}^{-1} \text{mol}^{-1})(-1564 \text{ K}) = 13.0 \text{ kJ/mol.}$$

(c)

$$K_a = \frac{(a_{\text{HU}^-})(a_{\text{H}^+})}{a_{\text{H}_2\text{U}}} = \frac{\gamma_{\pm}^2 [\text{HU}^-][\text{H}^+]}{[\text{H}_2\text{U}]}.$$

If they ignored the activity coefficients, the authors of this study reported the apparent  $K_a$

$$K_{a,\text{app}} = \frac{[\text{HU}^-][\text{H}^+]}{[\text{H}_2\text{U}]}.$$

Thus,

$$K_a = \gamma_{\pm}^2 K_{a,\text{app}} = (0.757)^2 (5.50 \times 10^{-6}) = 3.15 \times 10^{-6}.$$

(d)

$$\begin{aligned}
\Delta_r \bar{G}^\circ &= -RT \ln K_a \\
&= -(8.314472 \text{ J K}^{-1} \text{mol}^{-1})(298.15 \text{ K}) \ln(3.15 \times 10^{-6}) \\
&= 31.4 \text{ kJ/mol.}
\end{aligned}$$

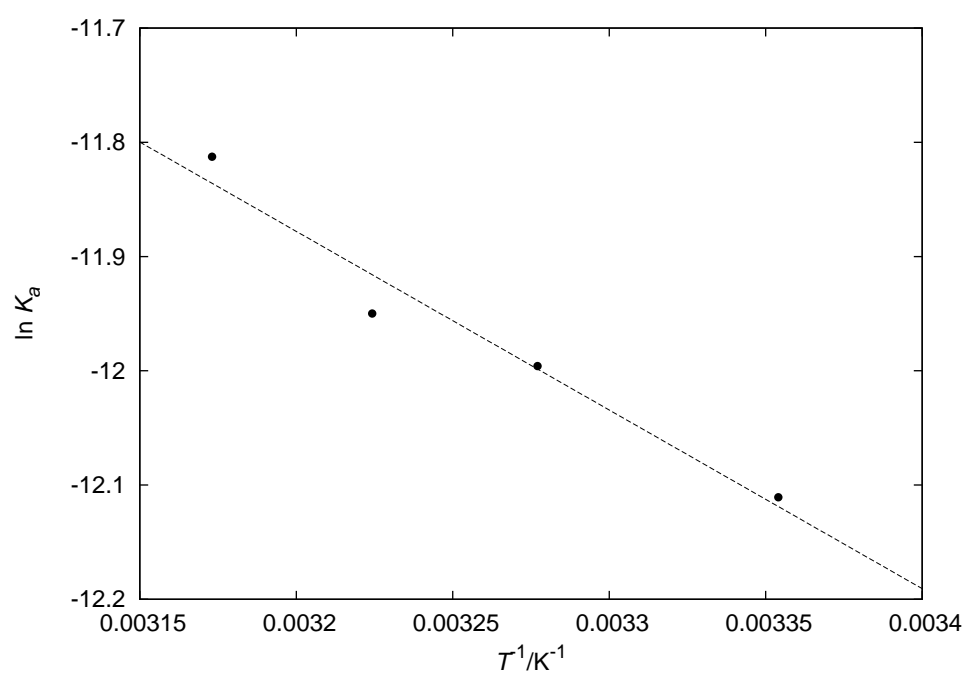


Figure 1: Plot of  $\ln K_a$  vs  $1/T$  for the first deprotonation of uric acid.