

Chemistry 2740 Spring 2008 Practice Test 2 Solutions

1. The activity of the solvent is its mole fraction. Except for very concentrated solutions, the mole fraction of the solvent is usually very close to unity.
2. A fuel cell is a voltaic cell for which the overall reaction is combustion.
3. It is impossible to create a solution that contains a single ion since ions are always accompanied by a counterion. It is therefore impossible to measure the activity coefficient of a single ion. It is however possible to measure the geometric mean of the activity coefficients of an ion-counterion pair, which is what the mean ionic activity coefficient is.
4. The vapor pressure of the solvent is associated with the equilibrium $l \rightleftharpoons g$. The equilibrium vapor pressure satisfies

$$K = \frac{a_g}{a_l} = \frac{\gamma_g p / p^\circ}{\gamma_l X}.$$

Since vapor pressures are usually small, the vapor should behave ideally, i.e. $\gamma_g \approx 1$. The vapor pressure of the pure solvent, p^\bullet , would satisfy

$$K = p^\bullet / p^\circ,$$

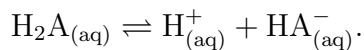
so we have

$$p^\bullet / p^\circ = \frac{p / p^\circ}{\gamma_l X},$$

or

$$\gamma_l = \frac{p}{p^\bullet X}.$$

5. The acid dissociation equilibrium is



$$\begin{aligned} \Delta_r \bar{G}^\circ &= -RT \ln K_a \\ &= -(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(5.50 \times 10^{-6}) \\ &= 30.0 \text{ kJ/mol.} \\ \Delta_r \bar{G}^\circ &= \Delta_f \bar{G}_{\text{H}_{(\text{aq})}^+}^\circ + \Delta_f \bar{G}_{\text{HA}_{(\text{aq})}^-}^\circ - \Delta_f \bar{G}_{\text{H}_2\text{A}_{(\text{aq})}}^\circ. \\ \therefore \Delta_f \bar{G}_{\text{HA}_{(\text{aq})}^-}^\circ &= \Delta_r \bar{G}^\circ - \Delta_f \bar{G}_{\text{H}_{(\text{aq})}^+}^\circ + \Delta_f \bar{G}_{\text{H}_2\text{A}_{(\text{aq})}}^\circ \\ &= 30.0 - 0 + (-356.6) \text{ kJ/mol} = -326.6 \text{ kJ/mol.} \end{aligned}$$

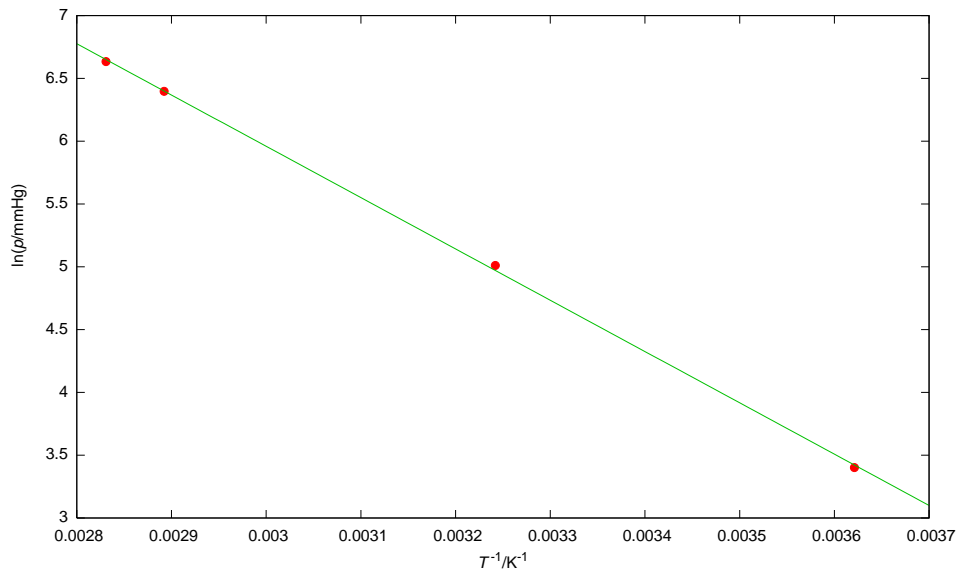


Figure 1: Plot of $\ln p$ vs $1/T$ where p is the vapor pressure of benzene.

6. The process is $l \rightarrow g$ with equilibrium constant

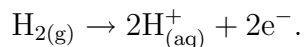
$$K = a_g/a_l = a_g = p/p^\circ.$$

A plot of $\ln K$ vs $1/T$ has a slope of $-\Delta\bar{H}/R$, in this case $-\Delta_{\text{vap}}\bar{H}/R$. Note that $\ln K = \ln(p/p^\circ) = \ln p - \ln p^\circ$, so we can just plot $\ln p$ vs $1/T$ directly since the factor involving p° only affects the intercept of the plot.

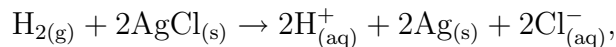
My plot is shown in figure 1. The plot is reasonably linear, with a slope of -4085 K . Therefore

$$\Delta H^\circ = -R(\text{slope}) = -(8.314472 \text{ J K}^{-1}\text{mol}^{-1})(-4085 \text{ K}) = 33.96 \text{ kJ/mol}.$$

7. The left half-cell is a standard hydrogen electrode with half-reaction



The overall reaction is therefore



for which $\bar{n} = 2$ and $\mathcal{E}^\circ = 0.22233 \text{ V}$ since $\mathcal{E}^\circ = 0$ for the standard hydrogen electrode. In the right half-cell,

$$\begin{aligned} I_c &= \frac{1}{2} [(1)^2[\text{Na}^+] + (-1)^2[\text{Cl}^-]] \\ &= \frac{1}{2} [0.004 + 0.004 \text{ mol/L}] = 0.004 \text{ mol/L}. \end{aligned}$$

$$\begin{aligned}\ln \gamma_{\text{Cl}^-} &= -(1.107 \times 10^{-10})(-1)^2 [(6.957 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2})(298.15 \text{ K})]^{-3/2} \sqrt{(0.004)} \\ &= -0.074.\end{aligned}$$

$$\therefore \gamma_{\text{Cl}^-} = 0.93.$$

$$\begin{aligned}\therefore a_{\text{Cl}^-} &= \gamma_{\text{Cl}^-} [\text{Cl}^-] / c^\circ \\ &= (0.93)(0.004) = 0.0037.\end{aligned}$$

In the left half-cell, $a_{\text{H}^+} = 10^{-p\text{H}} = 0.032$. Thus we have

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - \frac{RT}{\bar{n}\mathcal{F}} \ln \left(\frac{(a_{\text{H}^+})^2 (a_{\text{Cl}^-})^2}{a_{\text{H}_2}} \right) \\ &= 0.22233 \text{ V} - \frac{(8.314472 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(2)(96485.342 \text{ C/mol})} \ln \left(\frac{(0.032)^2 (0.0037)^2}{1} \right) \\ &= 0.45 \text{ V}.\end{aligned}$$