

Chemistry 2740 Spring 2011 Test 3 Solutions

- (a) False. A solution containing an ion always also contains a counterion.
 - (b) False. E determines whether a reaction is thermodynamically allowed or not, not E° .
 - (c) True. In order for this reaction to occur, we need to break an Fe-C bond, break up the hydroxide ion, transfer its oxygen atom to CO, and make a new bond between the iron atom and the resulting hydride ion. This seems like a lot to do in one step.

2.

$$\begin{aligned}\text{pH} &= -\log_{10} a_{\text{H}^+} = -\log_{10} (\gamma_{\text{H}^+} [\text{H}^+]/c^\circ) \\ &= -[\log_{10} \gamma_{\text{H}^+} + \log_{10} ([\text{H}^+]/c^\circ)] \\ \therefore \text{error} &= \text{pH} + \log_{10} ([\text{H}^+]/c^\circ) = -\log_{10} \gamma_{\text{H}^+} \\ &= -\log_{10} e \ln \gamma_{\text{H}^+}.\end{aligned}$$

(If you don't know this change of base trick, you can always just calculate γ_{H^+} and then plug the result back into the previous step.)

$$\begin{aligned}\ln \gamma_{\text{H}^+} &= \ln \gamma_{\pm} = -A |z_+ z_-| (\varepsilon T)^{-3/2} \sqrt{I_c} \\ \therefore \text{error} &= \log_{10} e A |z_+ z_-| (\varepsilon T)^{-3/2} \sqrt{I_c} \\ I_c &= \frac{1}{2} [0.01(+1)^2 + 0.01(-1)^2] \text{ mol/L} = 0.01 \text{ mol/L} \\ \varepsilon &= \varepsilon_r \varepsilon_0 = 78.54 (8.854 187 817 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}) = 6.954 079 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \\ \therefore \text{error} &= \log_{10} e (1.107 \times 10^{-10}) |(+1)(-1)| [(6.954 079 \times 10^{-10})(298.15)]^{-3/2} \sqrt{0.01} \\ &= 0.05.\end{aligned}$$

This is not a huge error, but it is within the significant figures of pH measurements.

- (a) $v = k[\text{Si}][\text{O}_2]$
 - (b)
 - i. Given a large excess of oxygen, the oxygen concentration will be roughly constant during the experiment. Thus, $v = (k[\text{O}_2]) [\text{Si}] = k'[\text{Si}]$ with $k' = k[\text{O}_2]$. A graph of k' vs $[\text{O}_2]$ should therefore have a slope of k and an intercept of 0.
 - ii. The graph is presented in figure 1. The slope is $k = 8.85 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$. The intercept is 5083 s^{-1} . This is smaller than any of the rate constants in the original data set, and there is some scatter in the values, so this value is in reasonable agreement with the expected intercept of zero. (To better analyze this issue, we would have to determine the standard error in the intercept,

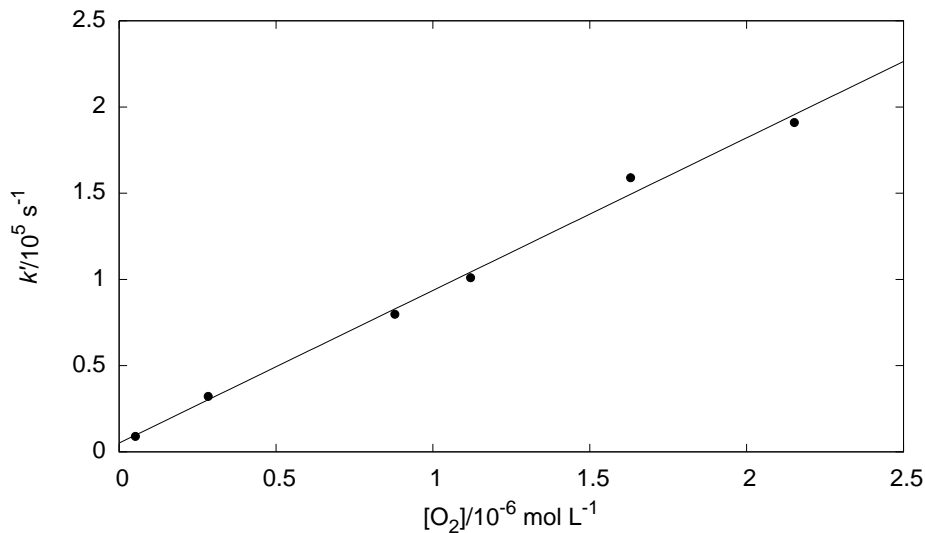


Figure 1: Plot of the pseudo-first-order rate constant k' vs $[\text{O}_2]$.

which can be done in many statistical packages, including spreadsheets like Excel. If we do this, we find that the standard error is 4134s^{-1} almost as large as the intercept itself, which is another indication that there is very little reason to believe that the intercept is significantly different from zero.)

iii. At $[\text{O}_2] = 1.12 \times 10^{-6} \text{ mol/L}$, $k' = 1.01 \times 10^5 \text{ s}^{-1}$. We use the equation

$$\ln x = \ln x_0 - k't.$$

$$\therefore t = -\frac{1}{k'} (\ln x - \ln x_0) = -\frac{1}{k'} \ln \left(\frac{x}{x_0} \right).$$

If 90% of the silicon atoms have reacted, 10% remain, so $x/x_0 = 0.1$. Thus,

$$t = -\frac{1}{1.01 \times 10^5 \text{ s}^{-1}} \ln 0.1 = 2.28 \times 10^{-5} \text{ s} \equiv 22.8 \mu\text{s}.$$