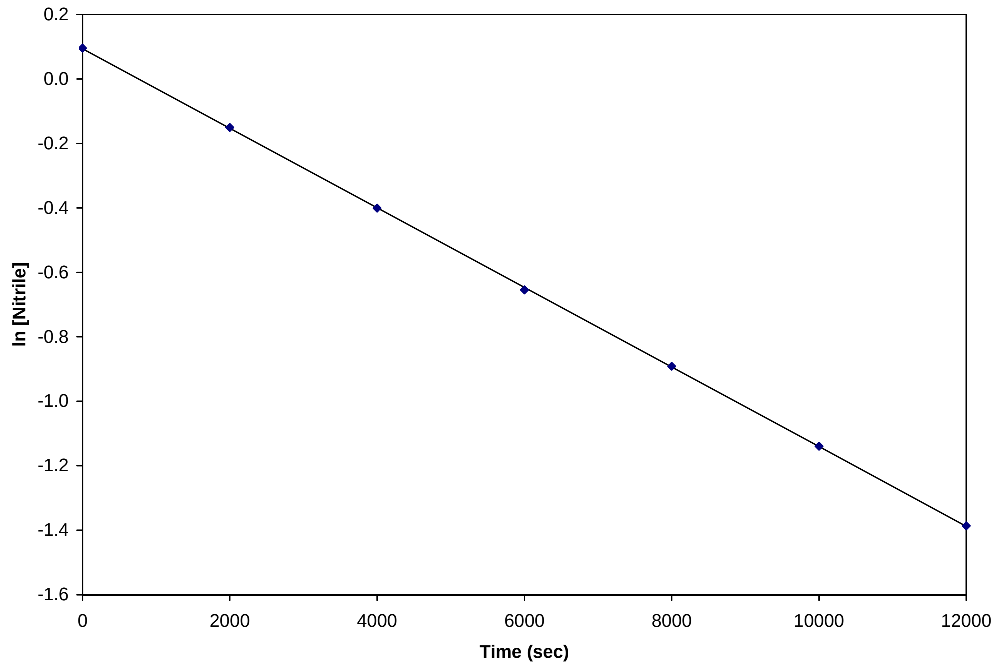
Quiz 9
CHEM 323
Fall 2008

Name: ____

1. (3 Points) The kinetics data for the thermal decomposition of a certain organic nitrile were graphed as shown below where the slope is $-1.234 \times 10^{-4}\ s^{-1}$ and the intercept is 0.094. What is the rate constant for this reaction?



A graph of the natural log of concentration as a function of time is linear for a first order reaction with the slope equal to –*k*. Therefore, the rate constant for this reaction is $1.234 \times 10^{-4}\ s^{-1}$.

2. (4 Points) Consider the cell Zn (s) | $ZnCl_2$ (aq) | Hg_2Cl_2 (s) | Hg (l). Given that E^0 for the Zn^{2+}/Zn redox couple is -0.7628 V and that E^0 for the Hg_2Cl_2/Hg couple is +0.2676 V. What is the standard redox potential for this cell?

By definition $E^0_{cell} = E^0_{cathode} - E^0_{anode}$. **When a galvanic cell is written in this shorthand notation, the anode is on the left side and the cathode on the right, by convention. Therefore,** $E^0_{cell} = (0.2676 + 0.7628)\,\text{V} = +1.0304\,\text{V}$.

For this cell E^0 is +1.0304 V.

3. (12 Points) Calculate the K_{sp} of AgI given that the emf of the cell shown below is +0.9509 V at 25.0 °C. Note that you don't need to use the Nernst equation because the reaction of interest is not a redox reaction (there is another way to relate K_{sp} to E).

$$\text{Ag (s)} \mid \text{AgI (s)} \mid \text{I}^- \text{(aq)} \parallel \text{Ag}^+ \text{(aq)} \mid \text{Ag (s)}$$

The reaction that takes place in this cell is

anode	**Ag (s) + I^- (aq) → AgI (s) + e^-**
cathode	**Ag^+ (aq) + e^- → Ag (s)**
overall	**Ag^+ (aq) + I^- (aq) → AgI (s)**

which is the reverse reaction of the one that defines the *K_{sp}* (i. e., $K_{sp} = \frac{1}{K}$, where *K* is the equilibrium constant for the reaction that takes place in this cell).

For any reaction $\Delta G = -RT\ln K$ and $\Delta G = -\nu FE$. Combining these two equations gives $\ln K = \frac{\nu FE}{RT}$ for the cell as written. Substituting in the relationship between *K* for the cell and *K_{sp}* gives $\ln K_{sp} = -\frac{\nu FE}{RT}$.

$$\ln K_{sp} = -\frac{\nu FE}{RT} = -\frac{(1)(9.64853x10^4 \text{ C}\cdot\text{mole}^{-1})(+0.9509 \text{ V})}{(8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1})(298.1_5 \text{ K})} = -37.01_0$$

$$K_{sp} = e^{-37.01_0} = 8.4x10^{-17}$$

The *K_{sp}* of AgI is 8.4x10^{-17} at 25.0 °C.

4. (7 Points) For PbI_2 (s) ⇆ Pb^{2+} (aq) + 2 I^- (aq), K = 1.4x10^{-8} at 25.0 °C. Calculate $\Delta_f G^0$ (PbI_2, aq), given that $\Delta_f G^0$ (PbI_2, s) = -173.64 kJ/mole.

For the reaction as written $\Delta_r G^0 = \Delta_f G^0(\text{PbI}_2,\text{aq}) - \Delta_f G^0(\text{PbI}_2,\text{s})$, which may be solved for $\Delta_f G^0$ (PbI_2, aq) to give $\Delta_f G^0(\text{PbI}_2,\text{aq}) = \Delta_r G^0 + \Delta_f G^0(\text{PbI}_2,\text{s})$.

For any reaction $\Delta G = -RT\ln K$, and so $\Delta_r G^0 = -RT\ln K$.

$$\Delta_r G^0 = -RT\ln K = -(8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1})(298.1_5 \text{ K})\ln(1.4x10^{-8})$$

$$\Delta_r G^0 = -(2.479_0 \text{ kJ}\cdot\text{mole}^{-1})(-18.08_4) = +44.83_0 \text{ kJ}\cdot\text{mole}^{-1}$$

$$\Delta_r G^0(\text{PbI}_2,\text{aq}) = \Delta_r G^0 + \Delta_f G^0(\text{PbI}_2,\text{s}) = (44.83_0 - 173.64)\text{ kJ}\cdot\text{mole}^{-1} = -128.81 \text{ kJ}\cdot\text{mole}^{-1}$$

Therefore, $\Delta_f G^0$ (PbI_2, aq) equals –128.81 kJ/mole.