FINAL EXAMINATION

Please answer ALL questions. Your reasoning should be clearly and concisely indicated.

Useful information:
R = 0.08206 atm.L/K.mol.
R = 8.314 J/K.mol.
F = 96485 C/mol/ of electrons
\( \Delta G = -nFE \), \( \Delta G^0 = -nF \Delta E^0 \)
E = \( E^0 - (RT/nF) \ln (a_{\text{products}}/a_{\text{reactants}}) \)
\( \Delta G = \Delta H - T \Delta S \)
\( \Delta G = \Delta G^0 + RT \ln Q \)
k = A exp(-Ea/RT)

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Emma Fink

Discussion instructor & Time

Ampan - Barney 2 pm

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1. a. Use the thermochemical equations shown below and Hess's law to determine the heat of formation (ΔH°) of NO(g):

\[ \text{O}_2 + \text{N}_2 \rightarrow 2\text{NO} \]
\[ \Delta H^o = +1398 \text{ kJ} \]

\[ 4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(l)} \]
\[ \Delta H^o = -1170 \text{ kJ} \]

\[ 4\text{NH}_3(g) + 3\text{O}_2(g) \rightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O(l)} \] (reverse)
\[ \Delta H^o = -1530 \text{ kJ} \]

\[ 4\text{NH}_3(g) + 2\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O(l)} \]
\[ \Delta H^o = -1170 \text{ kJ} \]

\[ 2\text{N}_2(g) + 3\text{O}_2(g) \rightarrow 4\text{NO}_2(g) \]
\[ \Delta H^o = 1530 \text{ kJ} \]

Thus, \( \Delta H^o (\text{NO}_2) \) for 1 moli = 90 kJ/mol
b. The addition of 20.0 J of heat to a 6.00 g sample of lead at 23.0 °C caused the temperature to rise to 48.7 °C. What is the specific heat of lead?

\[ 20J = 6g \times (x)(\Delta T) \]

\[ 20J = 6g \times (x)(48.7^\circ C - 23.0^\circ C) \]

\[ 20J = 154.2g \times (x) \]

\[ \frac{129701068.6}{51g^\circ C} \times \text{Heat of lead} \]

\[ \frac{130J}{g^\circ C} = x \times 10 \]

Let the specific heat of lead = \( \frac{130J}{g^\circ C} \times \text{Heat of lead} \)

c. In a coffee cup calorimeter (again?), 1.60 g of NH₄NO₃ is mixed with 75.0 g of water at an initial temperature of 25.00 °C. After dissolution of the salt, the final temperature of the calorimeter contents is 23.34 °C. Assuming that the solution has heat capacity of 4.18 J°C⁻¹g⁻¹ and that there is no heat loss to the calorimeter, calculate the enthalpy change for the dissolution of NH₄NO₃ in kJ/mol.

If it were not in a calorimeter, \( \Delta H = q \)

\[ 1.60g \times 76.6g \]

\[ q = 4.185 \frac{J}{g \cdot ^\circ C} \times (76.6g) (23.34^\circ C - 25^\circ C) \]

\[ q = -531.51208J \]

Since the temperature of the solution decreases, the reaction is exothermic. Thus \( q \) will be positive. From the point of view of the system, thermal energy is being converted to chemical energy. Thus \( \Delta H \) of this reaction = -531.51208 J.

But this reaction does not move another mol of NH₄NO₃.

\[ \frac{1.60g \times (NH₄NO₃)}{80g \times (NH₄NO₃)} = \frac{0.02mol}{10} \]

Thus the \( \Delta H \) we found is for 0.02 mol. Dividing by 0.02, we get a \( \Delta H \) at 26.575604 kJ/mol = 26.6 kJ/mol of NH₄NO₃.
2. An electrochemical cell is constructed at 25 °C to plate (coat) the cathode with Copper (Cu). The following setup was used:

The anode compartment contains 50.00 ml of a 0.10 M solution of ZnSO₄.
The cathode compartment contains 50.00 ml of a 0.10 M solution of CuSO₄.
The standard reduction potential for Cu²⁺ is 0.34 volts, and for Zn²⁺ is -0.76 volts

a. Calculate the standard cell potential for the above electrochemical cell

\[
\text{Standard cell potential } = 0.34 \text{V} - (-0.76 \text{V}) = 1.11 \text{V}
\]

\[\text{Zn(s)} \rightarrow 2\text{e}^- + \text{Zn}^{2+}\]

\[\text{SO}_4^{2-} \text{ is also SO}_4^{2-}\]

\[\text{Zn(s)} + \text{SO}_4^{2-} \rightarrow 2\text{e}^- + 2\text{ZnSO}_4^{2-}\]

\[\text{CuSO}_4 + 2\text{e}^- \rightarrow \text{Cu(s)} + \text{SO}_4^{2-}\]

\[\text{Zn(s)} + \text{Cu}^{2+} \rightarrow \text{Cu(s)} + \text{Zn}^{2+}\]

\[\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad 0.34 \text{V}\]

\[\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad -0.76 \text{V}\]
b. Write the balanced net reaction and calculate the equilibrium constant for that reaction

\[
\text{Zn}^+ + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}(s)
\]

\[
\alpha, \text{ neglecting SO}_4^-\]

\[
\text{Zn}(s) + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}(s)
\]

\[
\Delta G^0 = -nF\theta^0 \
\frac{n\theta^0}{RT} = \ln K
\]

\[
\frac{\Delta G^0}{RT} = \ln K
\]

\[
(2 \text{ mol}) (96485 \text{ J/mol K}) (1.11V) = \ln K
\]

\[
10.314 \text{ J/mol K} / 298 \text{ (K)}
\]

\[
85.607 \times 10^{-12} = \ln K
\]

\[
1.605 \times 10^{37} \approx \text{equilibrium constant}
\]

\[
1.605 \times 10^{37} \approx K_e
\]

\[
V = 1.11 \text{ V}
\]

\[
\text{maximum voltage is then } E^0 = 1.11 \text{ V}
\]

\[
\text{maximum voltage}
\]

\[
E = E^0 - \frac{RT}{nF} \ln Q
\]

\[
E = 1.11 - \frac{(8.3144 \times 298)}{2(96485 \text{ J/mol K})} \ln Q
\]

\[
\text{This max voltage is then } E^0 = 1.11 \text{ V}
\]

\[
E = 1.11 - \frac{8.3144 \times 298}{2 \times 96485} \ln Q
\]

\[
E = 1.11 - \frac{8.3144 \times 298}{2 \times 96485} \ln Q
\]

\[
\text{This max voltage occurs when } \frac{R}{nF} \ln Q = 0
\]

\[
0 = -\frac{RT}{nF} \ln Q = 0 \text{ when } \ln Q = 0
\]

\[
\text{thus } Q = 1, \text{ which is unrealistic.}
\]

\[
\text{reaction begins. For } -\frac{RT}{nF} \ln Q
\]

\[
\text{to be positive, } \ln Q \text{ would have to be}. \text{ This would require}
\]

\[
Q < 1, \text{ since our reaction}
\]

\[
\text{starts with } Q = 1 \text{ and cannot go}
\]

\[
\text{backwards, as this would change}
\]

\[
E^0 / Q \text{ will not be less than 1}.
\]

\[
\text{This max voltage occurs when } -\frac{RT}{nF} \ln Q = 0
\]

\[
\text{when } Q = 1.
\]
d. Suppose you want to use the above battery to run an electric motor. What is the maximum amount of work that can be obtained from this battery?

Maximum amount of work that can be obtained from this battery is $\Delta W$

$$\Delta W = nFE$$

So

$$\Delta W^0 = -nFE$$

$$\Delta W^0 = -2 \text{ mol} \times (96,485 \text{ C/mol}) \times (1.10 \text{ V})$$

$$\Delta W^0 = -212,260 \text{ J}$$

$$\Delta W^0 = -212,260 \text{ J}$$

So from the point of the system, $W$ will be negative since it is system acting on surroundings. Thus $W_{\text{max}} = -212.3 \text{ kJ}$.

$$|W_{\text{max}}| = 212.3 \text{ kJ} \quad \text{(This positive value will indicate work done by the system on the surroundings.)}$$

$\Delta W^0 = 212 \text{ kJ}$
3. Consider the following reaction taking place at 25 °C:

\[ \text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g}) \]

\( \Delta H^\circ \) for this reaction is equal to -103.8 kJ at 25 °C. In a given experiment, 1.0 atm of \( \text{H}_2 \) gas and 1.0 atm of \( \text{Br}_2 \) gas were mixed in a 1.0 L flask and allowed to reach equilibrium. At that point, the reaction mixture was analyzed. It was found that the number of moles of \( \text{H}_2 \) gas present at equilibrium is equal to \( 1.8 \times 10^{-11} \) mol. Assuming that all gases behave ideally, calculate the value of the equilibrium constant \( K \), and \( \Delta S^\circ \) for this reaction.

\[ K_{eq} = \frac{[\text{H}_2][\text{Br}_2]}{[\text{HBr}]} \]

Initial # moles:
\[ PV = nRT \]
\[ \text{Init} \quad \text{H}_2: 1 \text{ mol} \quad \text{Br}_2: 1 \text{ mol} \]

\[ \text{# moles H}_2 \text{ remaining} = \left( \frac{2}{1} \right) \left( 0.0108933061 - 1.8 \times 10^{-11} \right) \]

\[ K_{eq} = \frac{1.8 \times 10^{-11}}{1.8 \times 10^{-11}} \]

\[ K_{eq} = 2.064521583 \times 10^{19} \]

\[ \Delta G^\circ = -RT \ln K \]
\[ \Delta G^\circ = -8.314 \text{ J/kmol}(298 \text{ K}) \ln(2.064521583 \times 10^{19}) \]

\[ \Delta G^\circ = -110187.575 \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]
\[ -110187.575 = -103800 - (298) \Delta S^\circ \]

\[ \Delta S^\circ = 21.43 \text{ J/K} \times 45^\circ \]
4. A step in the formation of sulfuric acid from dissolved SO₂ in acid rain is the oxidation of hydrogen sulfite ion by hydrogen peroxide:

\[ \text{HSO}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{HSO}_4^- + \text{H}_2\text{O} \ (\text{liq}) \]

The mechanism involves peroxymonosulfurous acid SO₂OOH⁻:

\[ \begin{array}{c}
\text{HSO}_3^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{SO}_2\text{OOH}^- + \text{H}_2\text{O} \ (k_1 / k_{-1}) \\
\text{SO}_2\text{OOH}^- + \text{H}_3\text{O}^+ \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+ \ (k_2)
\end{array} \]

By making a steady state assumption for the peroxymonosulfurous acid intermediate, express the rate of formation of \( \text{HSO}_4^- \) in terms of the concentrations of \( \text{HSO}_3^- \), \( \text{H}_2\text{O}_2 \), and \( \text{H}_3\text{O}^+ \).

\[ \frac{d[\text{HSO}_4^-]}{dt} = k_2 [\text{SO}_2\text{OOH}^-][\text{H}_3\text{O}^+] \]

\[ \frac{d[\text{SO}_2\text{OOH}^-]}{dt} = k_1 [\text{HSO}_3^-][\text{H}_2\text{O}_2] - k_{-1} [\text{SO}_2\text{OOH}^-][\text{H}_3\text{O}^+] + k_2 [\text{SO}_2\text{OOH}^-][\text{H}_3\text{O}^+] = 0 \]

\[ k_1 [\text{HSO}_3^-][\text{H}_2\text{O}_2] = k_{-1} [\text{SO}_2\text{OOH}^-] + k_2 [\text{SO}_2\text{OOH}^-][\text{H}_3\text{O}^+] \]

\[ \frac{k_1 [\text{HSO}_3^-][\text{H}_2\text{O}_2]}{k_{-1} + k_2 [\text{H}_3\text{O}^+]} = [\text{SO}_2\text{OOH}^-] \]

\[ \frac{d[\text{HSO}_4^-]}{dt} = \frac{k_2 k_1 [\text{HSO}_3^-][\text{H}_2\text{O}_2]}{k_{-1} + k_2 [\text{H}_3\text{O}^+]} [\text{H}_3\text{O}^+] \]
neglect change in volume?

5. 8.23E-3 mol of InCl solid is placed in 1.00 L of 0.010 M HCl at 75°C. The InCl dissolves quickly, and then the following reaction occurs:

\[ 3 \text{In}^+ \rightarrow 2 \text{In} \text{ (solid)} + \text{In}^{3+} \]

As this disproportionation proceeds, the solution is periodically analyzed for the remaining In\(^+\) concentration.

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<th>Time, seconds</th>
<th>[In(^+)], mol/L</th>
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<tr>
<td>0</td>
<td>8.23E-3</td>
</tr>
<tr>
<td>240</td>
<td>6.41E-3</td>
</tr>
<tr>
<td>480</td>
<td>5.00E-3</td>
</tr>
<tr>
<td>720</td>
<td>3.89E-3</td>
</tr>
<tr>
<td>1000</td>
<td>3.03E-3</td>
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<tr>
<td>1200</td>
<td>3.03E-3</td>
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<tr>
<td>10000</td>
<td>3.03E-3</td>
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a) Plot ln [In\(^+\)] versus time and find the apparent rate constant for this first-order reaction. (Graph paper supplied.)

For first order rxn

\[ \ln [A] = -kt + \ln [A]_0 \]

leaving at the last 3 points since the reaction appears to have reached equilibrium by then,

\[ r^2 = .99999 \]

Thus \( k = \) 0.00104023 \( \approx 1.04 \times 10^{-3} \) sec\(^{-1} \)
b) Determine the half life of the reaction.

\[
\ln \left( \frac{[A]}{[A_0]} \right) = -kt + \ln([A_0])
\]

\[
\ln \left( \frac{[A]}{[A_0]} \right) = -kt_{1/2} + \ln([A_0])
\]

\[
\ln [A] - \ln [A_0] = -kt_{1/2} + \ln [A_0]
\]

\[
\ln \frac{[A]}{[A_0]} = -kt_{1/2}
\]

\[
\frac{\ln 2}{k} = t_{1/2}
\]

The half life of a first order reaction is \( \frac{\ln 2}{k} \)

\[
\frac{\ln 2}{k} = \frac{\ln 2}{0.001640231} \text{ sec}^{-1}
\]

\[
t_{1/2} \approx 660 \text{ sec}
\]

c) Determine the equilibrium constant for the reaction under these conditions.

\[
75^\circ C
\]

\[
K_{eq} = \frac{[\text{In}^{3+}]}{[\text{In}^+]^3}
\]

\[
K_{eq} = \frac{0.001733333}{(3.03 \times 10^{-3})^3}
\]

\[
K_{eq} = 6.23 \times 10^4
\]

\[
K_{eq} \times 6.2300 = 6.23 \times 10^4
\]

\[
\approx 6.2 \times 10^4
\]
6. The rate constant of the elementary reaction

\[ \text{BH}_4^- (aq) + \text{NH}_4^+ (aq) \rightarrow \text{BH}_3\text{NH}_3 (aq) + \text{H}_2 (g) \]

is 1.94E-4 L mol\(^{-1}\) sec\(^{-1}\) at 30.0°C, and the reaction has an activation barrier of 161 kJ mol\(^{-1}\).

\[ k = 303k \]

a) Compute the rate constant of the reaction at 40.0°C. \[ = 313k \]

\[ k(303k) \]

After equal concentrations of BH\(_4^-\) and NH\(_4^+\) are mixed at 30.0°C. 1.00E+3 sec is required for half of them to be consumed. How long will it take for half of the reactants to be consumed if an identical experiment is performed at 40.0°C?

2nd order

\[ \frac{1}{[A]} = k \tau + \frac{1}{[A]_0} \]

\[ \frac{2}{[A]_0} = k \tau + \frac{1}{[A]_0} \]

\[ \frac{2}{[A]_0} - \frac{1}{[A]_0} > k \tau/2 \]

\[ \frac{1}{[A]_0} = \frac{k \tau}{2} \]

\[ \frac{[A]_0}{k} = \tau/2 \]

\[ [A]_0 = \frac{k \tau}{2} \]

\[ \frac{1}{2} [A]_0 = \frac{\tau}{4} \]

\[ \text{Since consumed} \]

\[ \text{in} \]

\[ \text{they will be at half initial concentration at same time} \]

\[ \text{true half life} \]

\[ \frac{1}{2} \tau = 1297.85 \text{ sec} \]

\[ \tau/2 = 1.30 \times 10^{3} \text{ sec} \]