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

$\Delta G = -nFE,$

$E = E° - (RT/nF) \ln (a_{products}/a_{reactants})$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta G° + RT \ln Q$

$k = A \exp(-E_a/RT)$

(handwritten notes)

$\Delta G° = -n7E°$

$0 \qquad 1^{st} \qquad 2^{nd}$

$A \text{ vs } t \qquad \ln A \text{ vs } t \qquad \frac{1}{A} \text{ vs } t$

$\dfrac{d \ln K}{dT} = \dfrac{-\Delta H°}{RT^2} \; ?$

_____
Name

Emma Fink

_____
Discussion instructor & Time

Ampah – Barry 2pm

| 1	30	30
2	40	40
3	20	20
4	30	30
5	50	50
6	30	30
Σ	200	200

any you had me confused for aint...

1.

a. Use the thermochemical equations shown below and Hess's law to determine the heat of formation (ΔH°_f) of $NO_{(g)}$:

$O_2 + N \rightarrow NO$

$4NO_{2(g)} + 6H_2O_{(l)} \rightarrow 4NH_{3(g)} + 7O_{2(g)}$ ~~(crossed out)~~ $\Delta H^\circ = +1398$ kJ

$\left(4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(l)} \right)$ $\Delta H^\circ = -1170$ kJ

$\left(4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(l)} \right)$ reverse $\Delta H^\circ = -1530$ kJ

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l) \quad \Delta H^\circ = -1170 \text{ kJ}$$

+

$$2N_2(g) + 6H_2O(l) \rightarrow 4NH_3(g) + 3O_2(g) \quad \Delta H^\circ = 1530 \text{ kJ}$$
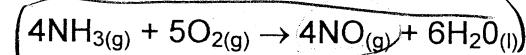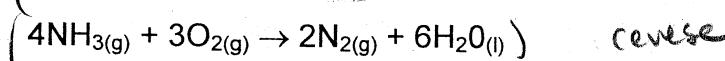
$$2N_2(g) + 2O_2(g) \rightarrow 4NO(g) \quad \Delta H^\circ = 360 \text{ kJ}$$

for formation of 4 mol $NO(g)$

Thus $\Delta H^\circ_f (NO_{(g)})$ (for 1 mol)

$= 90$ kJ/mol

$\dfrac{10}{10}$
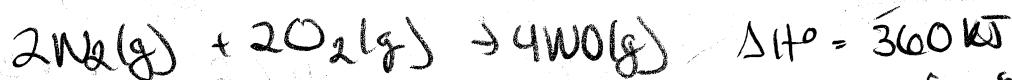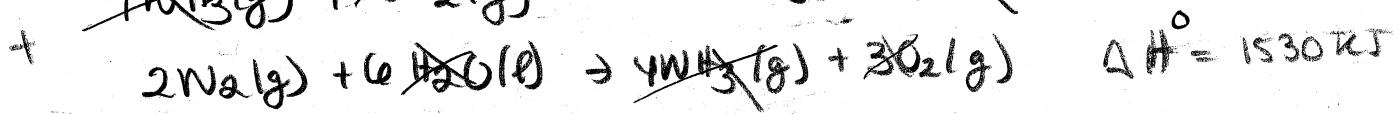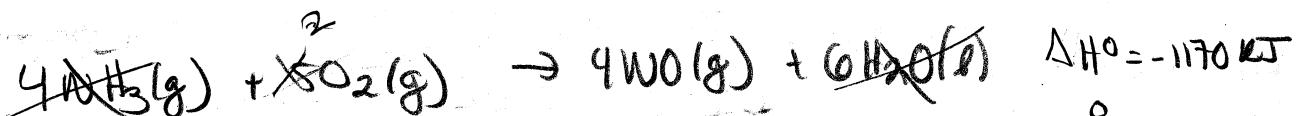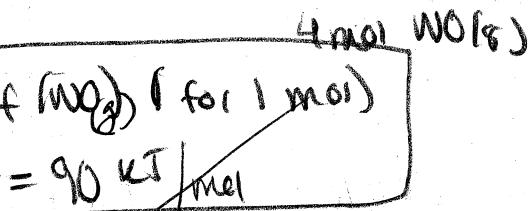
$q = C\Delta t$ ← heat capacity ← temp change
↑ heat

✓

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?

Let the
X = heat of lead specific

$$20 J = 6g (X)(\Delta T)$$

$$20 J = 6g (X)(48.7\,°C - 23.0\,°C)$$

$$20 J = 154.2 g\,°C\,(X)$$

$$.12970168661\ J/g\,°C = X \qquad 10/10$$

$$\boxed{.130\ J/g\,°C \approx \text{specific heat of lead}} \checkmark$$

✓

c. In a coffee cup calorimeter (again?), 1.60g of NH_4NO_3 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 $J°C^{-1}g^{-1}$ and that there is no heat loss to the calorimeter, calculate the enthalpy change for the dissolution of NH_4NO_3 in kJ/mol. → not in calorimeter? yes

constant atmospheric pressure, no non-pv work so $\Delta H = q$

If it were not in a calorimeter $\Delta H = q$

$q =$

$$1.6 + 75 = 76.6 g$$

$$q = 4.18 J/°Cg\ (76.6g)(23.34\,°C - 25\,°C)$$

$$q = -531.51208\ J$$

Since the temperature of the solution decreasing the reaction is endothermic. Thus q will be positive from the point of view of the system, as thermal energy is being converted to chemical energy. Thus ΔH of this reaction = 531.51208 J. But this reaction does not involve another mol of NH_4NO_3.

$$1.60g\ (NH_4NO_3)\left(\frac{1\ mol\ NH_4NO_3}{80g\ NH_4NO_3}\right) = .02\ mol \qquad 10/10$$

Thus the ΔH we found is for .02mol. Dividing by .02, we get a ΔH of 26.575604 kJ/mol $\approx$ $\boxed{26.6\ kJ/mol.}$ of NH_4NO_3

2. An electrochemical cell is constructed at 25 °C to plate (coat) the cathode with Copper (Cu). The following setup was used:

LEO

OX

The anode compartment contains 50.00 ml of a 0.10 M solution of $ZnSO_4$.

The cathode compartment contains 50.00 ml of a 0.10 M solution of $CuSO_4$.

The standard reduction potential for Cu^{2+} is 0.34 volts, and for Zn^{2+} is - 0.76 volts

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

Standard cell potential = $.34V - (-.76V) = \boxed{1.1 V}$ 10

$Zn(s) \longrightarrow 2e^- + Zn^{2+}$

there is also SO_4^{2-}

So with SO_4^{2-}
$Zn(s) + SO_4^{2-} \rightarrow 2e^- + ZnSO_4^{2-}$

$CuSO_4 + 2e^- \rightarrow Cu(s) + SO_4^{2-}$

$Zn(s) + Cu^{2+} \rightarrow Cu(s) + Zn^{2+}$

$Cu^{2+} + 2e^- \longrightarrow Cu \qquad .34V$

$Zn \rightarrow Zn^{2+} + 2e^- \qquad -.76V$
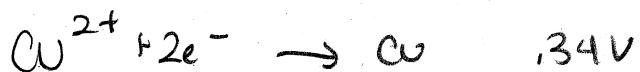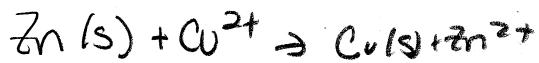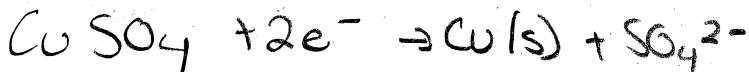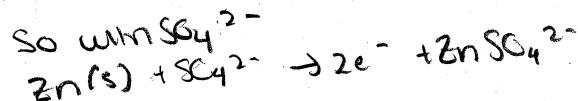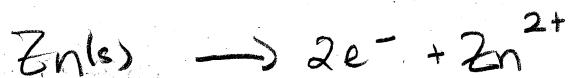
b. Write the balanced net reaction and calculate the equilibrium constant for that reaction

$$Zn_{(s)} + CuSO_4 \rightarrow ZnSO_4 + Cu(s)$$

or, neglecting SO_4,

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} + Cu(s)$$
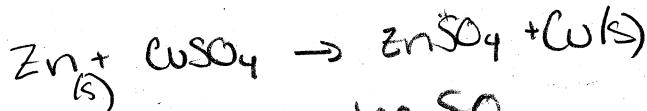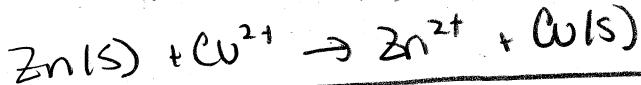
$$\Delta G^{\circ} = -n\mathcal{F}\mathcal{E}^{\circ} \qquad n\mathcal{F}\mathcal{E}^{\circ} = RT\ln K$$

$$\Delta G^{\circ} = -RT\ln K$$

$$\frac{n\mathcal{F}\mathcal{E}^{\circ}}{RT} = \ln K$$

$$\frac{(2\,mol)(96485\frac{c}{mol})(1.1V)}{(8.314\frac{J}{K\cdot mol})(298K)} = \ln K$$

$$85.676541125 = \ln K$$

$$e$$

$$\frac{Zn^{2+}}{Cu^{2+}} \qquad \checkmark$$

$$\boxed{\begin{array}{l} 1.615691129 \times 10^{37} = K \\ 1.62 \times 10^{37} \approx K_{eq} \leftarrow \text{equilibrium} \\ \text{constant} \end{array}} \quad \checkmark \text{\tiny 10} \qquad \approx 1.6 \times 10^{37}$$

c. Calculate the maximum voltage that can be obtained from the above battery

maximum voltage

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

$$\mathcal{E} = 1.1V - \frac{(8.314\frac{J}{K\cdot mol})(298K)}{2(96485\frac{c}{mol})}\ln Q$$

$$\boxed{\text{This max voltage is then } \mathcal{E}^{\circ} = 1.1V}$$

$$\mathcal{E}_{max} = 1.1V \qquad Q$$

The maximum value of $\mathcal{E}$ occurs when $-\frac{RT}{n\mathcal{F}}\ln Q$ is positive or 0. $-\frac{RT}{n\mathcal{F}}\ln Q = 0$ when $\ln Q = $ thus $Q = 1$, which is where the reaction began. For $-\frac{RT}{n\mathcal{F}}\ln Q$ to be positive, $\ln Q$ would have to be $-$. This would require $Q < 1$. Since our reaction starts with $Q = 1$ and cannot go backwards, as this would change $\mathcal{E}^{\circ}$, Q will not be less than 1. This max voltage occurs when $-\frac{RT}{n\mathcal{F}}\ln Q = 0$ 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 ΔG

$$\Delta G = -nFE \qquad \text{max voltage is at } E = E^\circ$$

so

$$\Delta G^\circ = -nFE^\circ$$

$$\Delta G^\circ = -(2 \, mol)(96485 \tfrac{C}{mol})(1.1V)$$

$$\Delta G^\circ = -212267 \, J$$
$$= -212.267 \, kJ$$

SO from the point of the system, w (work) will be negative since it is system acting on surroundings. Thus $w_{max} \approx -212.3 \, kJ$.

$$\approx -212 \, kJ$$

$$10$$

$$|w_{max}| = 212.3 \, kJ$$
$$\approx 212 \, kJ$$

(This positive value will be the work from the point of view of the surroundings ie motor etc)

$\checkmark$

3. Consider the following reaction taking place at 25 °C:

$$H_{2\,(g)} + Br_{2\,(g)} \leftrightarrows 2\,HBr_{(g)}$$
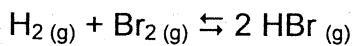
298 K

$\Delta H°$ for this reaction is equal to -103.8 kJ at 25 °C. In a given experiment, 1.0 atm of H_2 gas and 1.0 atm of 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 H_2 gas present at equilibrium is equal to 1.8×10^{-11} mol. Assuming that all gases behave ideally, calculate the value of the equilibrium constant (K), and $\Delta S°$ for this reaction.

$\boxed{[ABc]}$

$K_{eq} = \dfrac{[HBr]}{[H_2][Br_2]}$
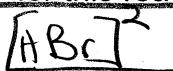
$\checkmark$ since same # [ ] on both top → bottom, volume can be excluded + mol # can be used plus its in 1 L

Initial # moles:

$PV = nRT$

$(1\,atm)(1L) = n\,(.08206\,\frac{L\cdot atm}{K\cdot mol})(298K)$

Initial .04089330061 mol = n = # mol for both H_2 & Br_2

Since H_2 and Br_2 react in 1:1 ratio had same initial # moles

moles H_2 remaining =
moles Br_2 remaining

$K_{eq} = \dfrac{\left(2\,(.04089330061 - 1.8\times10^{-11}\,mol)\right)^2}{(1.8\times10^{-11}\,mol)(1.8\times10^{-11}\,mol)}$

moles that reacted to form HBr

Change in # moles
.04089330061 - X = 1.8×10⁻¹¹ mol

.04089330061 - 1.8×10⁻¹¹ = X

2X = # moles HBr formed
since 1 mol H_2 → 2 HBr
1 mol Br_2 → 2 HBr

$K_{eq} = 2.064521583 \times 10^{19}$

$\boxed{K_{eq} \approx 2.06 \times 10^{19}}$ $\checkmark$ 10

$\Delta G° = -RT \ln K$ $\checkmark$

$\Delta G° = -(8.314\,J/K\cdot mol)(298K) \ln(2.064521583 \times 10^{19})$

-110187.575 $\Delta G° = -110187.575$

$\Delta G° = \Delta H° - T\Delta S°$ $\checkmark$

$-110187.575 = -103800\,J - (298)(\Delta S°)$

$-6387.575 = -298\,\Delta S°$

$21.43481544 = \Delta S°$ $\checkmark$

$\boxed{21.4\,J/K \approx \Delta S°}$ $\checkmark$

4.   A step in the formation of sulfuric acid from dissolved SO_2 in acid rain is the oxidation of hydrogen sulfite ion by hydrogen peroxide:

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O \ (liq)$$
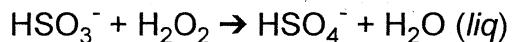
The mechanism involves peroxymonosulfurous acid SO_2OOH^-:

$$HSO_3^- + H_2O_2 \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} SO_2OOH^- + H_2O \ (k_1 / k_{-1})$$

$$SO_2OOH^- + H_3O^+ \overset{k_2}{\rightarrow} HSO_4^- + H_3O^+ \ (k_2)$$
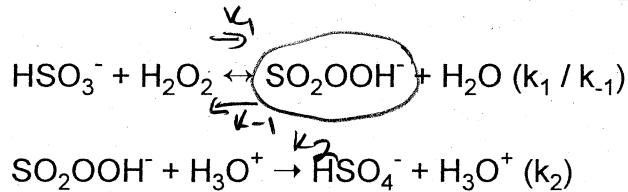
By making a steady state assumption for the peroxymonosulfurous acid intermediate, express the rate of formation of HSO$_4^-$ in terms of the concentrations of HSO_3^-, H_2O_2, and H_3O^+.

Can leave H_2O at as my do in the back because it's a solvent and it's concurred is pretty much constant throughout ✓

$$\frac{d[HSO_4^-]}{dt} = k_2[SO_2OOH^-][H_3O^+]$$

$$\frac{d[SO_2OOH^-]}{dt} = k_1[HSO_3^-][H_2O_2] - k_{-1}[SO_2OOH^-] - k_2[SO_2OOH^-][H_3O^+] = 0$$

$$k_1[HSO_3^-][H_2O_2] = k_{-1}[SO_2OOH^-] + k_2[SO_2OOH^-][H_3O^-]$$

$$k_1[HSO_3^-][H_2O_2] = [SO_2OOH^-]\left(k_{-1} + k_2[H_3O^+]\right)$$

$$\frac{k_1[HSO_3^-][H_2O_2]}{k_{-1} + k_2[H_3O^+]} = [SO_2OOH^-]$$

30

$$\frac{d[HSO_4^-]}{dt} = \frac{k_2 k_1[HSO_3^-][H_2O_2]([H_3O^+])}{k_{-1} + k_2[H_3O^+]}$$

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

$$3 \, In^+ \rightarrow 2 \, In \, (solid) + In^{3+}$$
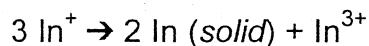
As this disproportionation proceeds, the solution is periodically analyzed for the remaining In^+ concentration.

Time, seconds	$[In^+]$, mol/L
0	8.23E-3
240	6.41E-3
480	5.00E-3
720	3.89E-3
1000	3.03E-3
1200	3.03E-3
10000	3.03E-3

a)   Plot ln $[In^+]$ versus time and find the apparent rate constant for this first-order reaction. (Graph paper supplied.)

For first order rxn

$$\ln [A] = -kt + \ln [A]_o$$

Leaving at the last 3 points since the reaction appears to have reached equilibrium by then.

we get the line

time   1320

$y = -.00104023 \, x - 4.799899401$

$r^2 = .9999$

Thus $k = .00104023 \doteq \boxed{1.04 \times 10^{-3} \quad sec^{-1}}$

-4.63

ln $[In^+]$

1200

1000

-5.969
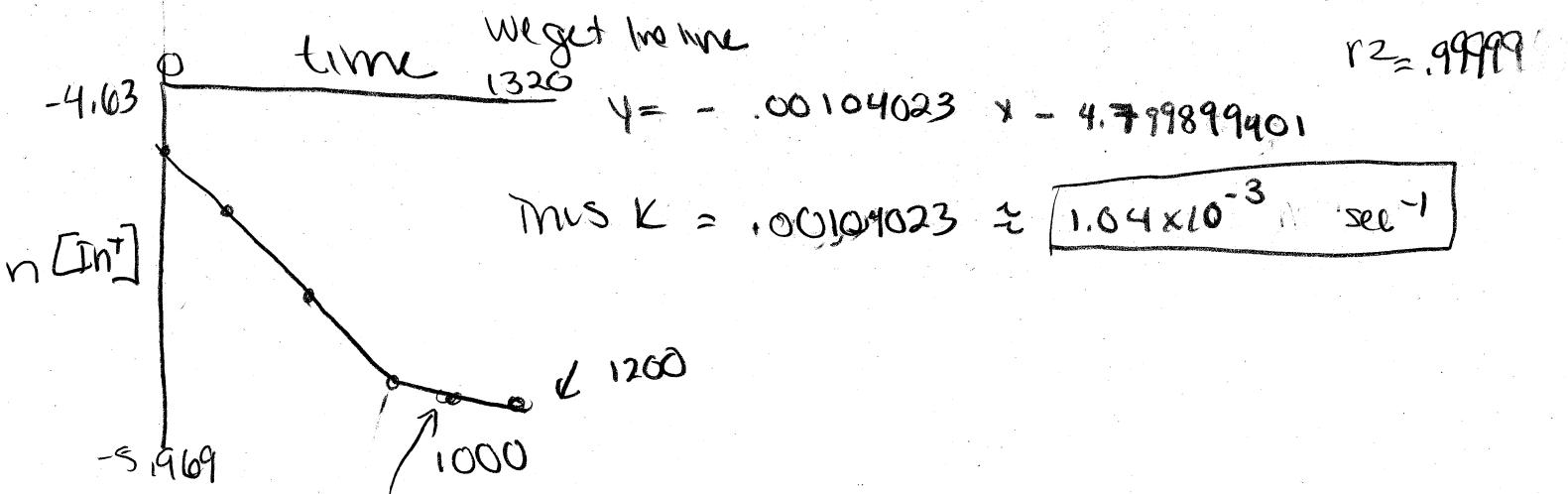
b) Determine the half life of the reaction.

$\ln [A] = -kt + \ln [A_0]$

$\ln \frac{[A_0]}{2} = -k\tau_{1/2} + \ln [A]_0$

$\ln [A_0] - \ln 2 = -k\tau_{1/2} + \ln A_0$

$-\ln 2 = -k T_{1/2}$

$\frac{\ln 2}{k} = \tau_{1/2}$

The half life of a first order rxn

is $\frac{\ln 2}{k} = \tau_{1/2}$

$\tau_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{.00104023 \, sec^{-1}} = 666.3403099 \, sec$

$\tau_{1/2} \approx \boxed{666 \, sec}$

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

condensed phases, like solid In omitted in this equation.

7SC

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

$K_{eq} = \frac{.0017333333}{(3.03 \times 10^{-3})^3}$

$K_{eq} = 62309.49098$

$\boxed{K_{eq} \approx 62300 = 6.23 \times 10^4}$

$\approx 6.2 \times 10^4$

team only page

rxn is at equilibrium when $[In^+] = 3.03 \times 10^{-3}$

Total volume = 1L so mal # can be used

$8.23 \times 10^{-3} - 3.03 \times 10^{-3} \, mol = .0052 \, mol$

has be used up making In^{3+}

Since $3 In^+$ makes $1 \, In^{3+}$

$\frac{.0052 \, mol}{3} \cdot \frac{mol}{1 \, In^{3+}}$
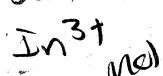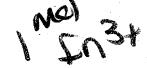
.00173 mol In^{3+} has been made

$\approx .00173 \, mol$ at equilibrium

6. The rate constant of the elementary reaction

$$BH_4^- \ (aq) + NH_4^+ \ (aq) \rightarrow BH_3NH_3 \ (aq) + H_2 \ (g)$$
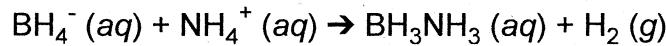
is 1.94E-4 L mol^{-1} sec^{-1} at 30.0°C, and the reaction has an activation barrier of 161 kJ mol^{-1}. "303 k

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

$k(313k)$

$\frac{\text{k evaluated}}{\text{at } 313 k}$

$$K = Ae^{-Ea/RT}$$

$$\frac{k(303 k)}{k(313k)} = \frac{e^{-Ea/R(303k)}}{e^{-Ea/R(313k)}}$$

$$\ln \frac{k(303 k)}{k(313k)} = \frac{-Ea}{R(303k)} + \frac{Ea}{R(313k)}$$

$$\ln \frac{1.94 \times 10^{-4} \ L \ mol^{-1} s^{-1}}{k(313k)} = \frac{Ea}{R} \left| \frac{1}{313k} - \frac{1}{303} \right.$$

$$\ln \frac{1.94 \times 10^{-4} \ L \ mol^{-1} s^{-1}}{k(313 k)} = \frac{(161)(1000)J}{8.314 \ J/kmol} \left| \frac{1}{313 \ k} - \frac{1}{30} \right.$$

$$\frac{1.94 \times 10^{-4} \ L \ mol^{-1} s^{-1}}{k(313k)} = .1297852953$$

$$\frac{1.94 \times 10^{-4} \ L mol^{-1} s^{-1}}{.1297852953} = k(313k)$$

$$.0014947964 \frac{Lmol^{-1}}{sec^{-1}} = k(313)$$

$$\boxed{1.49 \times 10^{-3} \ L \ mol^{-1} \ sec^{-1} = k(313k)}$$

b) After equal concentrations of BH_4^- and NH_4^+ are mixed at 30.0°C, 1.00E+4 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?   ← +4

2nd order

$3u$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A_0]}$$

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

$$\frac{\frac{1}{[A_0]}}{k} = \frac{kt_{1/2}}{k}$$

$$\frac{1}{k[A_0]} = t_{1/2}$$

K at 30°C = 1.94×10^{-4} L mol^{-1}s^{-1}

$$1 \times 10^4 \ sec = \frac{1}{(1.94 \times 10^{-4} L \ mol^{-1}s^{-1})(\text{initial conc})}$$

Since consumed in 1:1 they will be at half initial concentration at same time thus equal half lives

$$1.94 \times \ Lmol^{-1} \left(\frac{\text{initial conc}}{\text{initial conc}} \right) = 1$$
$$= .515463917\overline{5} \ M$$

$$T_{1/2} = \frac{1}{(1.4947964 \times 10^{-3} \frac{L}{molsec})(.51546)}$$
$$M$$

$$T_{1/2} = 1297.85 \ 2977 \ sec$$

$$\boxed{t_{1/2} = 1.30 \times 10^3 \ sec}$$