Exam 3 – Solution Set – Spring 2019

BCH 341 - Physical Chemistry with a Biological Focus
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DUE Tuesday, Sept. 25, 2018 by 11:59 PM (UTC-7). Turn in completed exam as a single PDF document into the assignment link on ASU Canvas. Please make sure the completed exam is organized, self-contained and legible.

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To aid in the anonymous peer review process, you do NOT need to include your full name, just your first and last initials, and an email address for contact purposes. The exam consists of 8 numerical problems. The first 4 problems are worth 10 pts each and the last 4 problems are worth 15 pts each. Hence, the exam is worth a total of 100 points. You are required to explicitly show all equations, numerical calculations and associated units. All assumptions need to be clearly and concisely stated. If thermodynamic parameters are used, the citation, reference or link to where this thermodynamics data came from must be stated.

1. Calculate the potential of the electrochemical cell (express your answer in units of Volts, V):

$$Ag(s)\ |\ AgCl\ (s)\ |\ KCl\ (aq,\ 0.025\ mol/kg)\ \|\ AgNO_3\ (aq,\ 0.01\ mol/kg)\ |\ Ag\ (s)$$

R: $Ag^+ (aq) + e^- \rightarrow Ag (s)$ $E^{\varnothing}(Ag^+/Ag) = + 0.8$ V

L: $AgCl (s) + e^- \rightarrow Ag (s) + Cl^- (aq)$ $E^{\varnothing}(AgCl/Ag,Cl^-) = + 0.22$ V

Cell: $Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$ $E^{\varnothing}(Cell) = E^{\varnothing}_R - E^{\varnothing}_L = + 0.58$ V

$\nu = 1$

$$E_{cell} = E^{\oplus}_{cell} - \frac{RT}{\nu F} ln\left(\frac{1}{a_{Ag^+}a_{Cl^-}}\right) = +0.37\ V = +0.4\ V$$

Similar to Suggested Hwk: Atkins, Chapter 5, problem 27.

2. Is the conversion of pyruvate ion to lactate ion

$$Pyruvate^- (aq) + NADH (aq) + H^+ (aq) \rightarrow Lactate^- (aq) + NAD^+ (aq)$$

A redox reaction (1 pt)? Explain or justify your answer (9 pts).

Suggested Hwk: Atkins, Chapter 5, problem 17.

Yes, $\nu=2$

This is a redox reaction. NADH is oxidized as it loses H^-, which is equivalent to the loss of electrons. Pyruvate is reduced as it has a reduction in the number of carbon-oxygen bonds during the conversion of the carbonyl group to an alcohol group. A conversion that is equivalent to the acquisition of electrons.

3. Calculate the masses of (a) $Ca(NO_3)_2$ and, separately, (b) NaCl to add to a 0.150 mol/kg solution of KNO_3 (aq) containing 500.0 g of solvent to raise its ionic strength to 0.20.

Suggested Hwk: Atkins, Chapter 5, problem 10.

$I_{KNO3} = b_{KNO3} = 0.150$

Therefore, the ionic strengths of the added salts must be 0.05 to result in a total of 0.20

(a) $Ca(NO_3)_2$ (s) + Water → Ca^{2+} (aq) + $2NO_3^-$ (aq)

Therefore, $z_+ = 2$, $z_- = -1$, $b_+ = b$, $b_- = 2b$.

$I_{Ca(NO3)2} = ½ \Sigma z_i^2 b_i/b^o = ½\{ z_+^2 b_+ + z_-^2 b_- \}/ b^o$, where $b^o = 1$ mol/kg

$0.05 = ½\{ 2^2\, 1 + 1^2\, 2 \}b / b^o$

b = 0.01667 mol/kg

$m_{Ca(NO3)2} = b\, M_{Ca(NO3)2}\, m_{solvent}$ = 0.01667 mol/kg * 164.1 g/mol * 0.50 kg = 1.37 g $Ca(NO_3)_2$ (s)

(b) NaCl (s) + Water → Na^+ (aq) + Cl^- (aq)

Therefore, $z_+ = 1$, $z_- = -1$, $b_+ = b_- = b$

$I_{NaCl} = ½ \Sigma z_i^2 b_i/b^o = ½\{ z_+^2 b_+ + z_-^2 b_- \}/ b^o$, where $b^o = 1$ mol/kg

$0.05 = ½\{ 1^2 * 1 + 1^2 * 1 \}b / b^o$

b = 0.05 mol/kg

$m_{NaCl} = b\, M_{NaCl}\, m_{solvent}$ = 0.05 mol/kg * 58.44 g/mol * 0.50 kg = 1.46 g NaCl (s)

4. Estimate the mean ionic activity coefficient and activity of a solution that is 10.0 mM $CaCl_2$ (aq) and 20 mM NaCl (aq).

Suggested Hwk: Atkins, Chapter 5, problem 12.

The concentrations $b_{CaCl2}/b^o = 0.01$ and $b_{NaCl}/b^o = 0.02$ are sufficiently dilute for the Debye-Huckel limiting law to give a reasonable estimate of the mean ionic activity coefficients.

Water is the solvent, so 1 molal is 1 molar (mol/L = mol/kg)

$I = ½ \Sigma z_i^2 b_i = I_{CaCl2} + I_{NaCl} = ½ \{(4x0.01)+(1x0.02)\} + ½ \{(1x0.02)+(1x0.02)\} = 0.050$

For $CaCl_2$ (aq):

$\log(\gamma_\pm)_{CaCl2} = -A \mid z_+ z_- \mid I^{½} = -0.509 \text{ x } |2 \text{ x } (-1)| \text{ x } (0.050)^{½} = -0.228$

$(\gamma_\pm)_{CaCl2} = 0.592$

$a_{Ca2+} = (\gamma_\pm)_{CaCl2}\ b_{Ca2+} = 0.592 \text{ x } 0.01 = 0.006$

$a_{Cl-} = (\gamma_\pm)_{CaCl2}\ b_{Cl-} = 0.592 \text{ x } 0.02 = 0.012$

For NaCl (aq):

$\log(\gamma_\pm)_{NaCl} = -A \mid z_+ z_- \mid I^{½} = -0.509 \text{ x } |1 \text{ x } (-1)| \text{ x } (0.050)^{½} = -0.114$

$(\gamma_\pm)_{NaCl} = 0.770$

$a_{Na+} = (\gamma_\pm)_{NaCl}\ b_{Na+} = 0.770 \text{ x } 0.02 = 0.015$

$a_{Cl-} = (\gamma_\pm)_{NaCl}\ b_{Cl-} = 0.770 \text{ x } 0.02 = 0.015$

5. (a) Calculate the standard potential of the cell

$$\mathrm{Pt\ (s)\ |\ cysteine\ (aq)\ ,\ cystine\ (aq)\ \|\ H^+\ (aq)\ |\ O_2\ (g)\ |\ Pt\ (s)}$$

(b) Calculate the standard Gibbs energy and enthalpy of the cell reaction at 25^{o}C.

(c) Estimate the value of the Gibbs energy of the cell reaction at 35^{o}C.

(a) Pt (s) is catalysis, on both sides of the cell and can be ignored

* Table 3 in Atkins (back of textbook) used for standard reduction electrode potentials. (or Wikipedia)

* Assume L-cys chirality.

R: $O_2\ (g) + 4\ H^+\ (aq) + 4\ e^- \rightarrow 2\ H_2O$ $E^ø_R = +\ 0.815$ V

L: L-cystine (aq) + 2 H^+ (aq) + 2 e^- $\rightarrow$ 2 L-cysteine (aq) $E^ø_L = -\ 0.355$ V

R-L: 4 L-cysteine (aq) + O_2 (g) $\rightarrow$ 2 L-cystine (aq) + 2 H_2O (l) $E^ø_{Cell} = E^ø_R - E^ø_L = \underline{+1.17\ V}$

$\underline{\nu = 4}$

(b) $\Delta_r G^ø = -\nu FE = -4\ (96.485\ kC/mol)\ (1.17\ kJ/kC) = \underline{-451.5\ kJ/mol}$

- Using Atkins Table 3 (back of the textbook) one can work out the change in entropy, S, explicitly and students that do this should get a few bonus points for rigor in their approach! However, the following assumption is also reasonable to make….
- Assuming that the *aq* phase reaction entropy changes balance to a value that is negligibly small compared to the entropy change of gas consumption, that standard reaction entropy is given by

$\Delta_r S^ø = 2\ S_m^ø(\text{cystine, aq}) + 2\ S_m^ø(H_2O, l)\ -\ 4\ S_m^ø(\text{cysteine, aq})\ )\ -\ S_m^ø(O_2, g)$

$\Delta_r S^ø \sim -\ S_m^o\ (O_2, g) = -205.25\ J\ K^{-1}\ mol^{-1}$ (Tinoco, Table A.5)

$\Delta_r H^ø = \Delta_r G^ø + T\Delta_r S^ø = -451.5\ kJ\ mol^{-1}\ + 298.15\ K \bullet (-205.25\ J\ K^{-1}\ mol^{-1}) = \underline{-512.7\ kJ\ mol^{-1}}$

(c) Upon an increase in temperature from 25 to 35^{o}C, it is very reasonable to assume that $\Delta_r S^ø$ does not change significantly (basically that the $\Delta_r C_p^ø$ doesn't change over this small temperature range), so the change in $\Delta_r G^ø$ is given by

Change in $\Delta_r G^ø$ = -(change in T) $\Delta_r S^ø = -10\ K\ (-205.25\ J\ K^{-1}\ mol^{-1}) = 2.05\ kJ\ mol^{-1}$

$\Delta_r G^ø$ (308.15 K) = change in $\Delta_r G^ø + \Delta_r G^ø = -451.5\ kJ/mol + 2.05\ kJ/mol = \underline{-449.5\ kJ\ mol^{-1}}$

- This assumes the overall reaction equilibrium is independent of pH and the temperature independence of $\Delta_r S^ø$ and $\Delta_r H^ø$ (i.e., temperature independent $\Delta_r C_p^ø$). BOTH these assumptions can be explicitly accounted for through C_p values of all components and temperature dependence of equilibrium and pH. If a student explicitly accounts for these small but yet measurable terms, extra credit will be given.

6. Calculate the standard Gibbs free energy change and the equilibrium constant for the oxidation of a formate ion to carbon dioxide at pH=7 and room temperature.

Overall reaction: ½ O_2 (g) + H^+ (aq) + $HCOO^-$ (aq) → H_2O (l) + CO_2 (g)

½ reactions: ½ O_2 (g) + $2H^+$ (aq) + $2e^-$ (aq) → H_2O (l) $E^ø = 0.815$ V

$HCOO^-$ (aq) → H^+ (aq) + CO_2 (g) + $2e^-$ $E^ø = 0.409$ V

- Atkins, Resource Section 3, Table 3 (p. 569-572).
- Wikipedia standard potentials.

Standard cell potential, $E^ø_{Cell} = E^ø_{red} + E^ø_{ox} = 0.815\text{ V} + 0.409\text{ V} = \underline{1.224\text{ V}}$

$\underline{\nu = 2}$

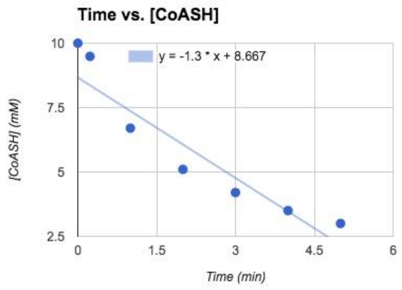
$\Delta_r G^ø = -\nu FE = -2\ (96.485\text{ kC/mol})\ (1.224\text{ kJ/kC}) = -\underline{236.2\text{ kJ/mol}}$

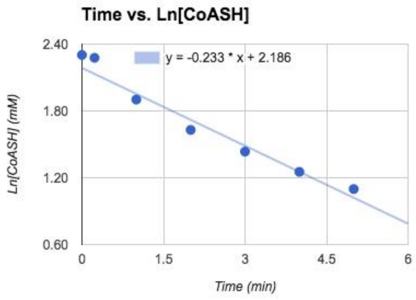
$K = \exp(-\Delta_r G^ø/RT) = e^{\Delta G/RT} = \exp(236.2\text{ kJ/mol} / 8.314\text{ J/Kmol x } 298.15\text{ K}) = \underline{e^{95.3} = 2.414\ x\ 10^{41}}$

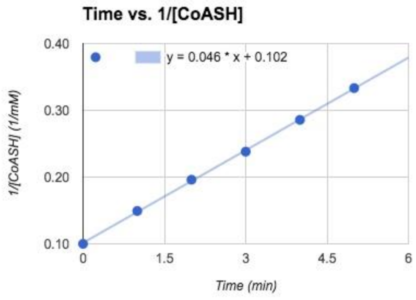
7. The important biochemical intermediate, acetyl CoA, may be prepared by reacting CoASH with acetyl chloride. The following data and plots of the corresponding were obtained for this reaction when CoASH and acetyl chloride were mixed in a 1:1 ratio:

Time (min)	0	1.0	2.0	3.0	4.0	5.0
[CoASH] (mM)	10.0	6.7	5.1	4.2	3.5	3.0

Determine the order of the overall reaction and the associated rate constant (remember to include the units on the rate constant).


Time vs. [CoASH]


Time vs. Ln[CoASH]


Time vs. 1/[CoASH]

Time (min)	[CoASH] (mM)	1/[CoSAH] (1 / mM)	Slope	Ln[CoSAH] (mM)
0	10	0.10	0.05	2.30
1	6.7	0.15	0.05	1.90
2	5.1	0.20	0.04	1.63
3	4.2	0.24	0.05	1.44
4	3.5	0.29	0.05	1.25
5	3	0.33		1.10

rate between 0.04 and 0.05 mM^{-1} min^{-1}

$$\frac{1}{[CoASH]_t} - \frac{1}{[CoASH]_o} = kt$$

2^{nd} Order
rate = k = 0.046 mM^{-1} min^{-1}

This shows that the rxn is overall 2^{nd} order. However, as [CoASH] = [acetyl chloride] this is consistent with any of the following rate laws:

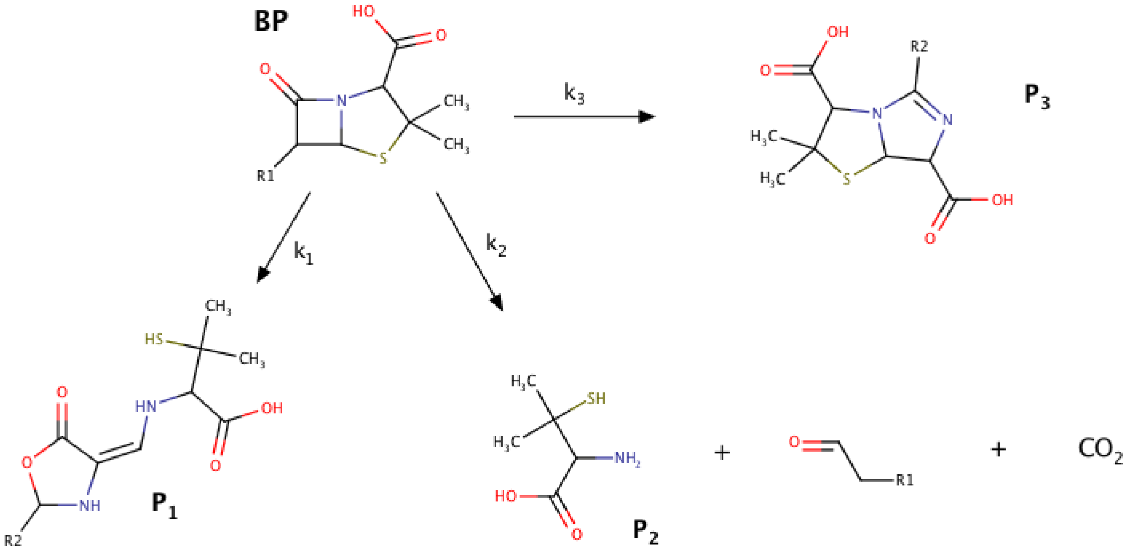
$$-\frac{d[CoASH]}{dt} = k[CoASH]^2$$

$$-\frac{d[CoASH]}{dt} = k[acetyl\,chloride]^2$$

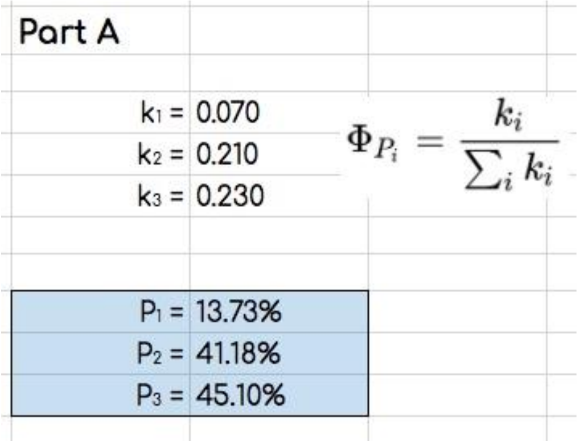
$$-\frac{d[CoASH]}{dt} = k[CoASH][acetyl\,chloride]$$

The only way to distinguish between these is to measure concentration as a function of time with $[CoASH]_o$ **NOT** equal to $[acetyl\ chloride]_o$

8. In acidic conditions, benzyl penicillin (BP) undergoes the following parallel reaction:



In the molecular structures, R_1 and R_2 indicate alkyl substituents. In a solution where pH=4, the rate constants for the processes at 22°C are $k_1 = 0.070\ s^{-1}$, $k_2 = 0.210\ s^{-1}$, $k_3 = 0.230\ s^{-1}$. **(A)** What are the percent yields for P_1, P_2, and P_3 formation?



Part A

k_1 = 0.070
k_2 = 0.210
k_3 = 0.230

$$\Phi_{P_i} = \frac{k_i}{\sum_i k_i}$$

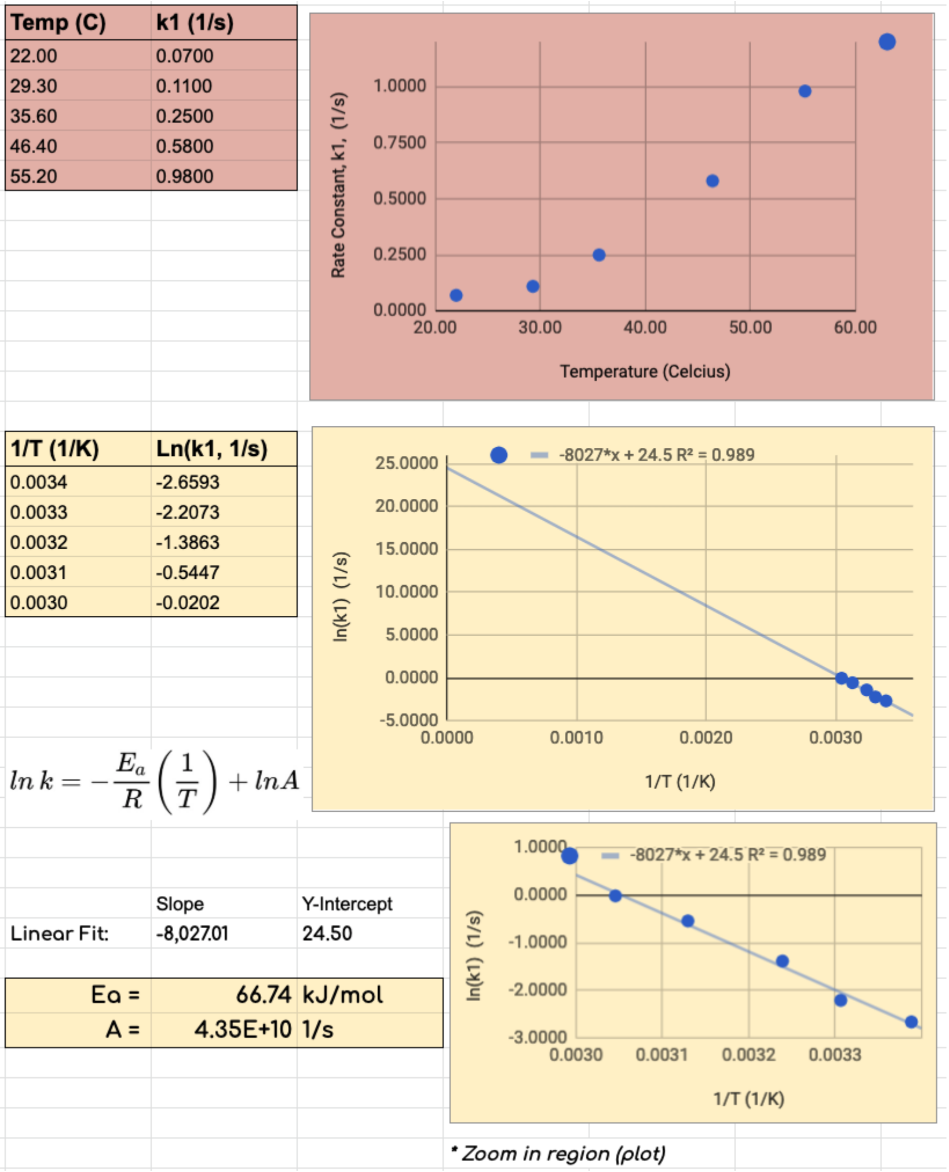
P_1 = 13.73%
P_2 = 41.18%
P_3 = 45.10%

** *Google Sheets* *Used to calculate*

(B) The temperature dependence of the acid-catalyzed hydrolysis of penicillin is investigated, and the dependence of k_1 on temperature is given in the following table:

Temperature (ºC)	**k_1 (s^{-1})**
22.0	0.070
29.3	0.110
35.6	0.250
46.4	0.580
55.2	0.980

What is the activation energy (E_a) and Arrhenius pre-exponential factor (*A*) for this branch (P_1) of the hydrolysis reaction? [Put a box around your final answers. Express your answer for E_a in units of kJ/mol and your answer for *A* in units of s^{-1}]



Temp (C)	k1 (1/s)
22.00	0.0700
29.30	0.1100
35.60	0.2500
46.40	0.5800
55.20	0.9800

1/T (1/K)	Ln(k1, 1/s)
0.0034	-2.6593
0.0033	-2.2073
0.0032	-1.3863
0.0031	-0.5447
0.0030	-0.0202

$$ln\, k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + lnA$$

	Slope	Y-Intercept
Linear Fit:	-8,027.01	24.50

Ea =	66.74	kJ/mol
A =	4.35E+10	1/s

* Zoom in region (plot)

*** Google Sheets Used to plot and calculate*