Information:

\[ \Delta G_{rxn} = -nF \Delta \mathcal{G} \]
\[ \mathcal{G} = 96,500 C / \text{mol} - e = 96.5 kJ / V \]
\[ \frac{RT}{F} \ln(10) = 0.06V \]

Acetic Acid (CH₃COOH) \( K_a = 1.8 \times 10^{-5} \)
\( pK_a = 4.74 \)
Phosphoric Acid (H₃PO₄)
\( K_{a1} = 7.3 \times 10^{-3}; K_{a2} = 6.3 \times 10^{-8}; K_{a3} = 4.2 \times 10^{-13} \)
\( pK_{a1} = 2.14; \ pK_{a2} = 7.2; \ pK_{a3} = 12.38 \)

Ammonia (NH₃) \( K_b = 1.76 \times 10^{-5} \)

Methylamine (CH₃NH₂) \( K_b = 4.4 \times 10^{-4} \)
\( pK_b = 3.36 \)

STP is 298°K, and 1 Atm

There are 23 problems on eight (8) pages, not counting this page; be sure you have all pages, numbered 1 through 8. To receive full credit on a problem you must explain your answer and be clear on what calculations you performed.

Point values:

Pg 1) 1 through 5 each 6 pts
Pg 2) 6: 26 pts;
Pg 3) 7: 13 pts;
Pg 4) 8: 10 pts; 9: 8 pts
Pg 5) 10 through 17, 5 points each.
Pg 6) 18 12 pts 19: 10 pts
Pg 7) 20: 10 pts; 21: 5 pts
Pg 8) 22: 18 pts 23: 18 pts
1a) At STP what is the volume occupied by each molecule of an ideal gas in a box (this is the
volume/molecule). \( V = \frac{22.4}{6.022 \cdot 10^{23}} \) L/molecule=3.7*10^{-23}dM^3/molecule.

b) Consider the volume each molecule occupies in part a) to be a cube. What is the length of the a side of the cube that each molecule occupies? L=33Ang.

c) If each of the ideal gas molecules is physically also a cube with a length of 1Å on a side, what is the molar entropy of the ideal gas molecules at STP?

\[
\bar{S} = R \ln \left( \frac{V}{V_o} \right) = 8.3 * 3 \ln \left( \frac{33}{1} \right) = 87 eu
\]

2a) What is the law of mass action, in a few words?
At equilibrium, a system will readjust concentrations, following the stoichiometric constraints, so that the products of the concentrations, raised to the appropriate signed stoichiometric powers, is always the same constant.

b) What mathematical expression best summarizes the law of mass action?

K = \( \prod [S_i]^{c_i} \), where S are the species of the reaction and c are the signed stoic. coefficients.

c) What is the origin or fundamental physical reason for the law of mass action?
The entropy of mixing, or the free energy minimization.

The rate laws show how a system comes to equilibrium.

3) In a chemical reaction, when K=Q, Circle all statement that are known to be true (not those that might by accident be true)

\( \Delta G^0 = 0, \ \Delta G^0 = \Delta G, \ \Delta S > 0, \ \Delta G > 0, \ \Delta H < 0, \ \Delta H_{\text{universe}} = 0, \ Q = 1, \)

K=1 \( \Delta G_{\text{universe}} = \Delta G_{\text{universe}}, \ \Delta G_{\text{universe}} = 0, \ \Delta G_{\text{universe}} < 0, \ \Delta S_{\text{universe}} > 0 \)

4) A system is composed of molecules of type A and B, which can introvert: \( A \xleftarrow{K} B \). At time t the [A]=4M and [B]=2M. At another time, t', [A]=2M and [B]=4M. K-equilibrium=0.1

a) Is the system in equilibrium at either times, t or t'? Explain
No, because Q=B/A=2/4 at time t, and Q=4/2 at time t'. At neither time is Q=K.

b) Is the time t<t' or the other way around? Explain.
Because Q at t is closer to K than Q at t', the system must have moved from t' to t at later time, so t'<t.

5a) What is one difference between \( \Delta G_{\text{universe}} \) and \( \Delta G^0_{\text{universe}} \)

They differ by Q, the equilibrium ratio. \( \Delta G_{\text{universe}} = 0 \) is the criterion for equilibrium (unlike \( \Delta G^0_{\text{universe}} \)).

b) What is one difference between \( \Delta G_{\text{universe}} \) and \( \Delta G \)

\( \Delta G_{\text{universe}} \) dX= \( \Delta G \), where dX is the change in reaction advancement. \( \Delta G_{\text{universe}} \) is intensive, and \( \Delta G \) is extensive.
6) In the reaction \(2N_2H_4(g) + N_2O_4(g) \leftrightarrow K \rightarrow 3N_2(g) + 4H_2O(g)\), the initial concentration of each species is 1M.

a) What should the sign of the entropy, \(\Delta S^{o}_{rxn}\), be for this reaction, and why?

Positive increase in entropy because the reaction goes from 3 to 7 moles of gas per mole of reaction.

Use the following table.

<table>
<thead>
<tr>
<th>Species</th>
<th>(S^o_f) J/mol-K</th>
<th>(\Delta G^o_f) kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2H_4(g))</td>
<td>121.2</td>
<td>149.2</td>
</tr>
<tr>
<td>(N_2O_4(g))</td>
<td>304.3</td>
<td>97.7</td>
</tr>
<tr>
<td>(N_2(g))</td>
<td>191.5</td>
<td>0.0</td>
</tr>
<tr>
<td>(H_2O(g))</td>
<td>188.72</td>
<td>-201.6</td>
</tr>
</tbody>
</table>

b) Compute the standard enthalpy of reaction, \(\Delta H^{o}_{rxn}\), at \(T=298°K\)

\[
\Delta H^{o}_{rxn} = \Delta G^{o}_{rxn} + T\Delta S^{o}_{rxn} = -969\text{kJ/mole}
\]

c) What is the standard molar entropy, \(\Delta S^{o}_{rxn}\),

\[
\Delta S^{o}_{rxn} = 4\times188.72 + 3\times191.5 - 1\times304.3 - 2\times121.2 = 0.782 \text{kJ/mol-K}
\]

d) What is the free energy, \(\Delta G^{o}_{rxn}\) for the reaction.

\[
\Delta G^{o}_{rxn} = 4\times(-201.6) - 97.7 - 2\times149.2 = -1,202 \text{kJ/mol}
\]

e) What is the equilibrium constant (at S.T.P.).

\[
K = \exp(-\Delta G^{o}_{rxn} / RT) = \exp(1,202/2.5) \text{ this is an exceedingly large number.}
\]

f) (Based on your numbers) is the system initially at equilibrium?

The system cannot be near equilibrium as \(Q=1\) at the start, and \(K >> 1\).

g) The reaction proceeds until there is 0.2M \(N_2H_4\), at which point the reaction is stopped (or quenched). Is this the direction of spontaneity? Explain

The reaction is proceeding from 1M to 0.2M in a reactant, so it is going in the direction of products.

h) The reaction proceeds until there is 0.2M \(N_2H_4\), at which point the reaction is stopped (or quenched). What is the concentration of \(H_2O(g)\) at this point?

\[
S=S_0+cX, \text{ so } 0.2=1.0-2X, \text{ so } X=0.4, \text{ For water } [H_2O(g)]=1+4X=1+1.6=2.6\text{M}.
\]
When studying enzyme mediated reactions, the kinetics are reasonably well explained by the following mechanism:

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td># 1</td>
<td>( E + B \xrightarrow{k_1f,k_{1b}} EB )</td>
<td>Fast</td>
</tr>
<tr>
<td># 2</td>
<td>( EB \xrightarrow{k_2} E + P )</td>
<td>Slow</td>
</tr>
</tbody>
</table>

Here B is the reactive molecule that can go on to make product, P, with the assistance of the enzyme E, which is a protein.

a) What is the net reaction for this mechanism?

\[ B \rightarrow P. \] (2 pts)

b) What rate law does the above mechanism predict for the rate of generation of product, P, written in terms of the concentrations of the reactants E and B? (3 pts)

For step 1: \[ [E][B]k_{1f} = k_{1b}[EB] \]

rate = \( \frac{dP}{dt} = k_2[EB] = k [E][B] \), where \( k = \frac{k_2k_{1f}}{k_{1b}} \)

c) The rate law can be written in terms of the total amount of enzyme: \( E_t = E + (EB) \), rather than the amount that is free. How does this change expression for the rate of generation of product, P? (3 pts)

From step 1: \( E_t[EB] = k_{1f}[EB] \), solve for \( [EB] = \frac{E_t[EB]}{k_{1f} + k_{1b}} \), substitute this into the expression for the rate: \( \frac{dP}{dt} = k_2 E_t[EB] \). The new expression has an extra term in the denominator that is proportional to [B], the substrate or reactant.

d) If the amount of B becomes very large what does the rate of production of P (\( \Delta P/\Delta t \)) become as a function of the rate constants and the total enzyme concentration? (2 pts)

As B becomes large, in part c, the rate limits out to rate = \( k_2 E_t \).

e) The above result is called the enzyme limited result. Compare the prediction of the maximum, enzyme limited, rate from part d) with that from part b). How do they seem different and why are they different? (3 pts)

The prediction in part b) is that the rate will appear to continue without bounds as the [B] increases, but in part d) we see that the rate must level off to a finite value depending on the total amount of enzyme. The flaw in the analysis of part b is that we imply that the rate increases proportional to [B] IF the amount of free enzyme is kept fixed. This of course implies we keep throwing more and more enzyme in as we add more B, which is NOT how an experiment is done.
8) The decomposition of N\textsubscript{2}O\textsubscript{5} (a heterodimer) into NO\textsubscript{2} and NO\textsubscript{3} is thought to be either first order in N\textsubscript{2}O\textsubscript{5} or second order. 

The (scant) data (right) was collected:

a) Estimate the rate constant for the loss of N\textsubscript{2}O\textsubscript{5} if the reaction is first order.

\( \ln(A) = \ln(A_o) - kt \). Solve for \( k = \ln(0.004/0.01)/20 = 0.046 \text{ sec}^{-1} \).

b) What quantity of the concentration do you plot as a function of time to obtain a straight line if the reaction is first order? (3 pts) Plot \( \ln(A) \) vs \( t \), the slope is \(-k\), and the intercept is \( \ln(A_o) \).

c) Find the rate constant for the loss of N\textsubscript{2}O\textsubscript{5} if the reaction is second order.

\( \frac{1}{A} = \frac{1}{A_o} + kt \). Solve for \( k = (1/0.004 - 1/0.01)/20 = 7.5 \text{ (mole-sec)}^{-1} \).

9a) Cyclopropane, when heated, rearranges to propene in a first order reaction. If the initial concentration is 0.05M and the rate-constant is 0.03 hr\(^{-1}\), how many hours will elapse before the concentration drops to 0.01M? (4 pts) \( t = \ln(0.05/0.01)/0.03 = 53 \text{ hours} \).

b) What is the half-life of the reaction in part a)? (4 pts) the half life=\( \ln(2)/0.03 = 23 \text{ hours} \).
10) Estimate the pH of a 0.015M solution of NaOCl, $K_a(\text{HOCl})=2.9\times10^{-8}$, $pK_a=7.54$

a) 4.2  
 b) 4.6  
 c) 9.4  
 d) 9.9 

pH = 14 + $\log_{10}(\sqrt{1e-14 \times 0.015 / 2.9e-8})$

11) Circle all of the following that are relatively constant with temperature:

a) $\Delta G_{rxn}^0$  
 b) $\Delta S_{rxn}^0$  
 c) $\Delta E$ (electrical potential)  
 d) $\Delta H_{rxn}^0$

12) Which of the following is a conjugate acid/base pair?

a) $H_3PO_4$ and $PO_4^{3-}$  
 b) $H_2PO_4^{-}$ and $HPO_4^{2-}$  
 c) $H_3PO_4$ and $H_3O^+$  
 d) $H_3O^+$ and $OH^-$

13) What is the best rate law for the two-step mechanism for the oxidation of NO:

step 1) $2NO(g) \rightarrow N_2O_2(g)$ fast;  
step 2) $N_2O_2(g)+ O_2(g) \rightarrow 2 NO_2(g)$ slow

rate = a) = $k[NO]$  
 b) = $k[NO]^2$  
 c) = $k[NO][O_2]$  
 d) = $k[NO]^2[O_2]$

14) A $1.0\times10^{-3}$M solution of lactic acid ($\text{CH}_3\text{CHOHCOOH}$) has a pH=3.5. What is the value of $K_a$?

a) $1.0\times10^{-3}$  
 b) $1.0\times10^{-4}$  
 c) $1.5\times10^{-3}$  
 d) $3.1\times10^{-4}$  

$X=10^{-3.5}$  
$K = \frac{X^2}{C-X}$  

15) For the reaction: $2\text{SO}_2(g) + O_2(g) \rightarrow 2\text{SO}_3(g)$, the equilibrium concentrations were measure to be $[\text{SO}_2]=3.6\times10^{-3} \text{ M}$, $[O_2]=6.1\times10^{-4} \text{ M}$, and $[\text{SO}_3]=1.0\times10^{-2} \text{ M}$. What is $K_C$ for this reaction?

a) $7.8\times10^{-3}$  
 b) $2.2\times10^{-2}$  
 c) $4.6\times10^3$  
 d) $1.3\times10^4$

$K_C = (1e-2^2)/(3.6e-3^2 \times 6.1e-4)$

16) In what temperature range is the reaction $\text{CaCO}_3(s) \rightarrow \text{CaO}(s)+ \text{CO}_2(g)$ spontaneous at unit concentration of each species? $\Delta S_{rxn}^0 = 158 J/molK$ and $\Delta H_{rxn}^0 = 178.3 kJ/mol$

A) At any temperature  
B) Above 1122K  
C) Below 1122K  
D) Above 890K  
E) Below 890K  
F) At No temperature.

17) Arrange the following reactions in order of decreasing entropy change at 25C. Decreasing order goes from the most positive $\Delta S$ to the most negative $\Delta S$.

1) $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l)$
2) $\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
3) $4\text{FeCl}_3(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)+6\text{Cl}_2(g)$
4) $\text{CH}_4(g)+2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O(g)}$

a) $2 > 1 > 3 > 4$  
 b) $2 > 3 > 1 > 4$  
 c) $3 > 2 > 4 > 1$  
 d) $3 > 4 > 2 > 1$

dn = 1) -3  
2) -1  
3) +3  
4) +1 so 3 is the most positive
18a) A solution of 0.02M Acetic Acid is titrated with 1M NaOH. What volume of base will be needed to bring 150 mls of the acid to the equivalence point?
(4 pts)
\[ V_a[A] = V_b[B]; \quad 0.02 \times 100/1 = 2 \text{ ml} \]

b) What is the pH at the equivalence point.
(4 pts)
\[ [A^-] = 0.02 \text{ initially, but } \frac{X}{C-X} ; \quad \text{and} \quad X=[OH^-] \]
\[ [OH^-] = X = \sqrt{K_H(C-X)} \]
pH=8.5

c) Compare the pH at the equivalence point of the titration with that of a solution of 0.02 M NaAcetate. (Neglect any volume dilution effects in the titration.)
(4 pts)
They are identical.

19) The titration curve is shown for 100 mls of acid in a beaker titrated against 0.025M NaOH in the burette. For all three parts (a,b and c) Be sure to draw construction lines on the graph and explain how you arrived at your answer.
a) What is the analytic concentration of the acid in the beaker
(4 pts)
\[ V_a[A] = V_b[B]; \quad C \times 100 = 0.25 \times 20 \]
C=0.05M
Drop a vertical line at 20mls
b) What is the \( K_a \) of the acid from the titration curve shown at right? (4 pts)
Drop a vertical line at \( 20/2=10 \text{ mls.} \)
Draw a horizontal line that intersects the intersection of the vertical and the graph.
\( PK_{A} = 7 \)
c) What two values of the pH bound the buffer region of the acid? (2 pts)
P\( H=6 \) and 8 bound the buffer region.
20) The alternative titration curve is shown for 100 mls of acid (different from the one above) in a beaker titrated against 0.025M NaOH in the burette.  \[ E(H) = \left[ Na^+ \right] + \left[ H^+ \right] - \left[ OH^- \right] \] Be sure to draw construction lines on the graph and explain how you arrived at your answer.

a) What is the analytic concentration of the acid in the beaker?

Draw a horizontal line at 0.06M,
That is the analytic or initial acid concentration (2pts)

b) What is the Ka of the acid from the titration curve shown at right?

Draw a horizontal line at 0.06/2
Where this intersects the curve
Drop a vertical line. This is the pH=pK
The pK=6 (3pts)

c) What two values of the pH bound the buffer region of the acid?
The pH is bounded by 5 and 7. (2pts)

21) Can an electrochemical cell do work when Q<K or when Q>K? Explain.

Yes, and it doesn’t matter which way Q is different from K, the system will move to Make Q=K, and electrical work can be done, by a concentration gradient battery. (5pts)

22) Use the following half cell reactions to write 3 spontaneous reactions, calculate \( \Delta \varepsilon_{\text{cell}} \) (Problem 21.46 in Text).

<table>
<thead>
<tr>
<th>Number</th>
<th>Half Reaction</th>
<th>( \varepsilon_{\text{half}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( Al^{3+}(aq) + 3e^- \rightarrow Al(s) )</td>
<td>-1.66V</td>
</tr>
<tr>
<td>2</td>
<td>( N_2O_4(g) + 2e^- \rightarrow 2NO_2^-(aq) )</td>
<td>0.867V</td>
</tr>
<tr>
<td>3</td>
<td>( SO_4^{2-}(aq) + 2e^- + H_2O \rightarrow SO_3^{2-}(aq) + 2OH^-(aq) )</td>
<td>0.93V</td>
</tr>
</tbody>
</table>

Reaction 1 (4pts), each reaction

\( Al(s) \rightarrow Al^{3+}(aq) + 3e^- \)  \( \text{Cell Potential} = 1.66 + 0.867 = 2.52V \)

\( N_2O_4(g) + 2e^- \rightarrow 2NO_2^-(aq) \)  \( \text{Net Reaction} \)
(Problem 22 continued) Reaction 2

\[ \text{Al(s)} \rightarrow \text{Al}^{3+} (aq) + 3e^- \quad \text{Cell Potential} = 1.66+0.93=2.6V \]

\[ \text{SO}_4^{2-} (aq) + 2e^- + H_2O \rightarrow \text{SO}_3^{2-} (aq) + 2\text{OH}^- (aq) \]

\[ 3\text{SO}_4^{2-} (aq) + 2\text{Al}(s) + 3H_2O \rightarrow 3\text{SO}_3^{2-} (aq) + 6\text{OH}^- (aq) + 2\text{Al}^{3+} (aq) \]

Reaction 3

\[ 2\text{NO}_2^- (aq) \rightarrow N_2\text{O}_4(g) + 2e^- \quad \text{Cell Potential} = 0.93-0.867=0.063V \]

\[ \text{SO}_4^{2-} (aq) + 2e^- + H_2O \rightarrow \text{SO}_3^{2-} (aq) + 2\text{OH}^- (aq) \]

\[ \text{SO}_4^{2-} (aq) + 2\text{NO}_2^- (aq) + H_2O \rightarrow \text{SO}_3^{2-} (aq) + 2\text{OH}^- (aq) + N_2\text{O}_4(g) \quad \text{Net Reaction} \]

Which is the strongest oxidizing agent, and why? (6 pts)

\[ \text{SO}_4^{2-} (aq) \]

Is the strongest oxidizing agent because it has the largest positive half cell potential

23) Some half reactions in from the table.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Half-cell potential (in Volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2\text{O} )</td>
<td>+1.23</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^- )</td>
<td>+0.40</td>
</tr>
<tr>
<td>( 2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g) )</td>
<td>0.00</td>
</tr>
<tr>
<td>( 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- )</td>
<td>-0.83</td>
</tr>
</tbody>
</table>

a) Using the above half reactions, determine the standard cell potential for a fuel cell in which \( \text{H}_2(g) \) and \( \text{O}_2(g) \) are reacted to produce water and electricity. (4pts)

You must choose any two so that they sum without leaving any acid or base unbalanced.

You can used reaction 1 and 3 together, or reaction 2 and 4 together. Either way the standard cell potential to make water is 1.23V; net reaction: \( \text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) \)

b) Use the above half reactions to determine the \( K_w \) for water. Please show your work, clearly.

(4 pts) For water the net reaction is: \( \text{OH}^- (aq) + \text{H}^+(aq) \rightarrow \text{H}_2\text{O}(l) \) This net reaction can be gotten by subtracting reaction 4 from reaction 3, or by subtracting reaction 2 from reaction 1. In both cases you get the net reaction has a potential fo 0.83V.

(10pts) For the net reaction as written, \( n=1 \). The connecting ideas are then:

\[
\ln(K) = -\frac{\Delta G_{\text{rxn}}^0}{RT} = \frac{n\text{RT}}{RT} = \frac{96.48 \cdot 0.8314}{2.478} 
\]

\[
\ln(K)=32.24 \text{ or } K=1.00 \times 10^{-14}, \text{ which is the value used in chapter 18.} 
\]