Answer all the questions on this paper. Continue overleaf if necessary. Show all work to get full credit. Remember, if you can’t do the problem write down as much as you can that is of relevance to solving the problem.

Section I: Multiple choice questions (28 points) (circle the correct answer(s))—points as indicated. Please show any relevant calculations otherwise you may lose credit.

1. For the cell Pt | F⁻ (aq) | F₂(g, 1 bar) || MnO₂(s), Pt, which of the following answers correctly gives the electrode reactions (2 points)
   (a) Anode: 2F⁻ → F₂
   (b) Anode: 2F⁻ → F₂ + 2e⁻
   (c) Cathode: MnO₂ + 2H₂O → Mn²⁺ + 4H⁺ + 3e⁻
   (d) Cathode: 2F⁻ + 2e⁻ → F₂
   (e) Anode: MnO₂ + 2H₂O → MnO₄⁻ + 4H⁺ + 3e⁻

2. Using your answer to question (1), write the overall cell reaction for this cell. (3 points)
   \[ \text{Zn}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

3. Which of the following ions likely has a ΔG° closest to that predicted by Born’s model, when a value of ε = 78 is used for the relative permittivity of H₂O? (2 points)
   (a) Li⁺
   (b) Cs⁺
   (c) Mg²⁺
   (d) Ca²⁺
   (e) Al³⁺

4. For your answer above, give a brief explanation of your choice. (3 points)

   [Least charge & large radius is likely to perturb the H₂O solvate shell the least; i.e., lead to something that will be best described using \( \varepsilon = 78 \) - Born’s model.]

5. The rate law for the reaction \( A + 2B \rightarrow C + D \) is found experimentally to be \( v = k[A]^2 \). If the concentration of \( A \) is doubled and the concentration of \( B \) is halved, the reaction rate will (2 points)
   (a) stay the same
   (b) increase by a factor of 2
   (c) increase by a factor of 4
   (d) decrease by a factor of 2
   (e) decrease by a factor of 4

6. Which of the following quantities will be doubled if the half-reaction \( A + e^- \rightarrow Y \) is doubled to give \( 2A + 2e^- \rightarrow 2Y \) (circle all that apply)? (2 points)
   (a) \( \Delta G° \)
   (b) \( E° \)
   (c) \( k \)
   (d) \( k' \)

7. Using the phase diagram to the right, if we have a solution of \( X_0 = 0.20 \), the solution will boil at (2 points)
   (a) 45°C
   (b) 55°C
   (c) 65°C
   (d) 68°C
   (e) 75°C

8. (see additional equation sheet for key equations & physical constants)

   PLEASE BE SURE YOU HAND IN YOUR INDEX CARD AT THE END OF THE EXAM

9. (93 points)
8. Using the phase diagram on the previous page, we’d expect the following to be TRUE - circle all that apply (2 points)
(a) Pure A has a lower vapor pressure than pure B
(b) Boiling a solution of mole fraction \(x_A = 0.5\) will give a vapor that is richer in B than the liquid
(c) Boiling a solution of mole fraction \(x_A = 0.1\) will give a vapor that is richer in B than the liquid
(d) Starting from a mole fraction \(x_A = 0.1\), repeated distillation provides azotropic composition in the
liquid phase
(e) The vapor phase is at the bottom of the plot

9. Using the diagram from the previous page, which of the following statements is FALSE? Circle all
that apply. (2 points)
(a) This is an example of a high boiling azeotrope
(b) Pure A boils at a higher temperature than pure B
(c) A P versus mole fraction composition plot for the same system would show an azetrope that has
a vapor pressure that is the difference between the vapor pressures of the two pure components
(d) The region enclosed by the curves are regions which consist of two phases
(e) The point marked with a *, three phases are in equilibrium

10. For the reaction \(2NO(g) + 4NO_2(g) \rightarrow 4N_2O(g)\), if the rate of consumption of \(NO_2\) is determined to be
\(1.9 \times 10^{-3} \text{ M s}^{-1}\), the rate of formation of \(N_2O\) is (2 points)
(a) \(1.0 \times 10^{-3} \text{ M s}^{-1}\)
(b) \(2.0 \times 10^{-3} \text{ M s}^{-1}\)
(c) \(5.0 \times 10^{-3} \text{ M s}^{-1}\)
(d) \(4.0 \times 10^{-3} \text{ M s}^{-1}\)

11. The correct expression for the solubility product of the sparingly soluble salt \(Ag_2SO_4\) is (2 points)
(a) \(K_{sp} = [Ag]^2[SO_4]^-\)
(b) \(K_{sp} = [Ag][SO_4]^2\)
(c) \(K_{sp} = [Ag]^2[SO_4]^2\)
(d) \(K_{sp} = [Ag][SO_4]^2\)

12. Which of the following values is NOT defined to be zero by convention for H (aq)? (2 points)
(a) \(\Delta H^\circ\)
(b) \(\Delta S\)
(c) \(\Delta G^\circ\)
(d) \(\Delta S^\circ\)

None, they are all defined to be zero.

13. Circle any statement which is FALSE in relation to the Debye-Hückel limiting law (DHL). (2 points)
(a) The value of \(\gamma\) predicted using DHL will always be less than one.
(b) The deviation from DHL increases as the ionic strength of the solution increases
(c) Perfect agreement with experiment can be obtained if the DHL is corrected for both finite ionic
size and for the orientation of the solvent molecules
(d) It is possible for experimental \(\gamma\) values to be greater than one.
(e) The value of \(\gamma\) will approach a value of 1 as the ionic strength goes to zero

\[\log \gamma \approx \text{constant} \times \frac{1}{\sqrt{I}}\]
14. (a) Using the data in the Table 8.1 on your equation shee, calculate the standard electrode potential ($E^o$) for the half-reaction $Fe^2+ + 2e^- \rightarrow Fe$ (5 points)

(b) Using your answer to part (a) and data in Table 8.1, calculate the emf ($E$) at 25°C for the reaction $3Sn^2+ (aq) + 2Fe^2+ (aq) \rightarrow 2Fe(s) + 3Sn^2+ (aq)$ taking place in a cell with the following concentrations $[Sn^2+] = 0.1m, [Sn^2+] = 0.01m, [Fe^2+] = 0.5m$ (5 points)
15. For the process $A + B \rightarrow 2Y$ it is found that a doubling of the concentration of $A$ results in a fourfold increase in the reaction rate while doubling the concentration of $B$ results in no change in the rate.

(a) Write the rate law for this reaction. Explain your logic. (4 points)

(b) If the rate constant is found to be $3.75 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and the initial concentration of the reactant $A$ is $1.0 \times 10^{-2} \text{ M}$, calculate the half-life (in seconds). (4 points)

(c) Make rough sketches of the following plots:

(i) $[A]$ against time (label the initial concentration of $A$ and also indicate the half-life on your diagram)

(ii) $[Y]$ against time (be sure to correctly indicate the initial concentration of this species)

(Your plots do not have to be drawn to scale). (4 points)

(a) $\text{Rate} = k[A]^2$ (since a doubling of $[A]$ quadruples the rate).

(b) $k = 3.75 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $[A]_0 = 1.0 \times 10^{-2} \text{ M}$

For 2nd order $k = \frac{1}{t^* a_0}$

So $t^* = \frac{1}{k a_0} = \frac{1}{3.75 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \times 1.0 \times 10^{-2} \text{ M}}$

$t^* = 266.7 \text{ sec}$

$t^* = 2.7 \times 10^3 \text{ seconds}$

(c) $\text{Note: there are no lines}$

(2 rate will change with time)

of formation of product or consumption of reactant.

Since $Y$ is a product, initial concentration will be zero.
16. A solution contains both of the following ionic compounds: 0.10 M LiNO₃ and 0.20 M Mg(NO₃)₂.
(a) Calculate the ionic strength of this solution. (4 points)

(b) Given that the solubility product of BaSO₄ is $9.2 \times 10^{-10}$ mol²·dm⁻⁶, calculate the solubility of BaSO₄ (in mol/L) in pure water. (4 points)

(c) Use the Debye-Hückel Limiting Law to calculate the mean activity coefficient ($\gamma_i$) of BaSO₄ in the solution of 0.10 M LiNO₃ and 0.20 M Mg(NO₃)₂ described above. (4 points)

(d) Calculate the solubility (mol/L) of BaSO₄ in the solution of 0.10 M LiNO₃ and 0.20 M Mg(NO₃)₂. How does this compare to the solubility in pure water that you calculated in part (b)? (6 points)

(a) $I = \frac{1}{2} \sum |z_i|^2$ where $z_i$ charge m ionic

0.10 M LiNO₃ $\rightarrow$ 0.10 M Li⁺ + 0.10 M NO₃⁻
0.20 M Mg(NO₃)₂ $\rightarrow$ 0.20 M Mg²⁺ + 0.40 M NO₃⁻

So $I = \frac{1}{2} \left[(0.10\text{M})(1)^2 + (0.10\text{M})(-1)^2 + (0.20\text{M})(2)^2 + (0.40\text{M})(-1)^2\right]

\[ I = \frac{1}{2} \left[0.10\text{M} + 0.10\text{M} + 0.80\text{M} + 0.40\text{M}\right] = \frac{1.40\text{M}}{2} = 0.70\text{M} \]

(b) $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 9.2 \times 10^{-10}$ M²

So $[\text{Ba}^{2+}] = \frac{9.2 \times 10^{-10}}{[\text{SO}_4^{2-}]} = 9.59 \times 10^{-6}$ M

So solubility BaSO₄ = $9.6 \times 10^{-6}$ mol/L

(c) $\log \gamma = -2z^2z (\frac{\gamma}{10}) \frac{I}{x}$

So $\gamma = -(2)(2)(0.51)\sqrt{0.70}$

$\log \gamma = -1.707 \Rightarrow \gamma = 0.0196$

(d) $K_{sp} = 9.2 \times 10^{-10}$ M² $= [\text{Ba}^{2+}][\text{SO}_4^{2-}]^2 \gamma^2$

$9.2 \times 10^{-10} = x^2 (0.0196)^2$

$x = 4.89 \times 10^{-5}$ M/L

So solubility in LiNO₃/Mg(NO₃)₂ solution is much higher than in pure water (act (b)).

≈ 50 times larger.
17. Calculate the mole fractions of water and hydrogen peroxide in (a) the liquid and (b) vapor phases for a solution that consists of only H₂O and H₂O₂ at 333.15 K and with a total pressure of 37.7 torr. You should assume that the solution behaves ideally. The vapor pressure of pure water at 333.15 K is 149.4 torr and the vapor pressure of pure hydrogen peroxide at 333.15 K is 17.6 torr. (6 points)

\[
\text{Use } X_w \text{ for mol. frac. H}_2\text{O (water)} \\
\text{and } X_p \text{ for mol. frac. H}_2\text{O}_2 \text{ (hydrogen peroxide)} \\

P_w^\circ = 149.4 \text{ torr} \quad P_p^\circ = 17.6 \text{ torr} \quad T = 333.15 \text{ K} \\

P_{\text{tot}} = 37.7 \text{ torr} = P_w + P_p \\

\text{Using Raoult's law: } P_w = X_w P_w^\circ \quad \text{and} \quad P_p = X_p P_p^\circ \\

\text{Since this is a 2-component mixture, } X_p = 1 - X_w \\

\text{So } P_{\text{tot}} = P_w X_w + P_p X_p (1 - X_w) \\

\text{For in what we know:} \\

37.7 \text{ torr} = 149.4 \text{ torr} (X_w) + 17.6 \text{ torr} (1 - X_w) \\

37.7 \text{ torr} = 149.4 \text{ torr} (X_w) + 17.6 \text{ torr} - 17.6 \text{ torr} (X_w) \\

20.1 \text{ torr} = (149.4 \text{ torr} - 17.6 \text{ torr}) (X_w) = 131.8 \text{ torr} (X_w) \\

(a) \quad \frac{X_w}{X_w} = 0.1525 \quad \text{and} \quad X_p = 1 - 0.1525 = 0.8475 \\

(b) \text{Need to use} \quad \text{Duhem's law: } P_w = X_w P_{\text{tot}} \quad \text{and} \quad P_p = X_p P_{\text{tot}} \\

P_w = 0.1525 (149.4 \text{ torr}) = 22.78 \text{ torr} \quad \text{and} \quad P_p = 0.8475 (17.6 \text{ torr}) = 14.92 \text{ torr} \\

\text{then, } Y_w = \frac{22.78 \text{ torr}}{37.7 \text{ torr}} = 0.604 \quad \text{or, } Y_w = \frac{X_w}{X_w} \\

Y_p = \frac{14.92 \text{ torr}}{37.7 \text{ torr}} = 0.396
Section III. True/False questions (21 points) For each of the following questions state whether the statement is TRUE or FALSE. In each case, explain your choice of answer and show the relevant logic behind your answer. If the statement is FALSE, explain what it should read for it to be TRUE.

The next two questions refer to the following half-reactions:

\[
\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s) \quad E^\circ = -2.71V \\
\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \quad E^\circ = +1.69V
\]

18. If these two half cells were combined to make an electrochemical cell following the standard conventions, the Na | Na⁺ system should form the cathode. (2 points)

\[ \begin{array}{l}
\text{The correct halfreaction is the reduction by convention. It must be} \\
\text{the one that has the most positive } E^\circ. \text{ Hence, this is} \\
\text{false since the Ag⁺/Ag half-cell will be the reduction.} \\
\end{array} \]

19. The standard electrode potentials indicate that the Na⁺ species is much more likely to be oxidized than the Ag⁺ species. (2 points)

\[ \begin{array}{l}
\text{Since the } E^\circ \text{ for the Na⁺/Na } \text{ half-cell is more negative, this} \\
\text{is the one that will be forced to run in reverse (i.e., the} \\
\text{oxydation, process).} \\
\end{array} \]

20. In the cell shown below, with the semi-permeable membrane allowing passage only of the M⁺ ion from one cell to another, if the initial concentrations of both M⁺ and Cl⁻ are 0.1 M and 1.0 M on the left and right, respectively (as indicated), there will initially be a potential difference between the two cells; this potential difference will decrease gradually until the concentrations on both sides are exactly equal, at which point the potential difference between the two cells is zero. (3 points)

\[ \begin{array}{l}
\text{Since only M⁺ ions can move through the membrane,} \\
\text{a buildup of charge will very quickly prevent any} \\
\text{further passage of M⁺ across the membrane. Hence,} \\
\text{this happens very rapidly after the cells have equilibrated.} \\
\text{In fact, the concentration will not change significantly} \\
\text{before the passage of none M⁺ is stopped.} \\
\end{array} \]

21. In a cell represented by the diagram below, electrons would flow from left to right when the two halves of the cell are connected to an external circuit and electrodes (made of the material M) are immersed in each solution. (3 points)

\[ \begin{array}{l}
\text{Since the goal is to balance } [\text{M}^+] \text{on both sides,} \\
\text{we need } [\text{M}^+] \text{left to increase & } [\text{M}^+] \text{right to decrease.} \\
\text{So we'll see} \\
\text{Loss: } M \rightarrow M^+ + e^- \quad \text{(increases } [\text{M}^+]) \\
\text{Gains: } M^+ + e^- \rightarrow M \quad \text{(decreases } [\text{M}^+]) \\
\text{So } e^- \text{ are generated on the right & used up on the left.} \\
\end{array} \]
22. Doubling the coefficients in a chemical reaction will square the value of the equilibrium constant. Will double $\Delta G^\circ$. Will not change $E^\circ$, and will change the value of the rate constant, $k$. (2 points)

23. The rate activity coefficient, $\gamma^+$, is equal to $(\gamma \gamma^+)$ for a 1:1 electrolyte. (2 points)

24. If the rate law for the reaction $A + 3B \rightarrow 2C$ is given by $v = \frac{k[A]^3[B]}{[C]}$, the overall reaction order $1 + [C]^{-1}$ during the initial stages of the reaction would appear to be 2. (3 points)

25. For a zeroth order reaction, changing the initial concentration of the reactant will have no effect on the value of the half-life of the reaction. (2 points)

26. A zeroth order reaction changes in rate, the initial concentration of the reactant will have no effect on the value of the rate of the reaction. (2 points)

BONUS question (3 points)

27. Explain the two main factors that are responsible for retarding the motion of ions towards electrodes in an electrolyte solution when an electric potential is applied to that solution.

Electrophoretic effect
Relaxation effect

See note 11 and 281 for details.