- please answer all **5 questions** in the spaces provided
- this is a **1-hour test** (but you have *2 hours to write it!*)
- a calculator and the equation sheets provided may be used

- all questions are of equal value
- no books or notes are allowed
- no marks for unreadable answers

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1. a) Carbonated water for soda drinks is made by dissolving CO_2 gas at about 2 bar and 25 °C in water. Why is it impractical to use Raoult's law for aqueous CO_2 solutions <u>under these conditions</u>? *Data*: The vapor pressure of liquid CO_2 is 64 bar at 25 °C.

Raoult's Law

$P_{CO_2} = X_{CO_2} P^*_{CO_2}$ ← (vapor pressure of pure liquid CO_2)

but liquid CO_2 does not exist at 25°C, 2 bar!

b) Use Henry's law to calculate the mole fraction of CO_2 in an aqueous solution saturated with CO_2 gas at 2.00 bar pressure at 25 °C. How many grams of CO_2 are dissolved in 1000 g water? *Data*: $k_{CO_2} = 3560$ bar. H_2O and CO_2 molecular weights are 18.0 g mol^{-1} and 44.0 g mol^{-1}.

$$P_{CO_2} = k_{CO_2} X_{CO_2} \qquad X_{CO_2} = \frac{P_{CO_2}}{k_{CO_2}} = \frac{2.00 \text{ bar}}{3650 \text{ bar}} = \boxed{5.48 \times 10^{-4}}$$

(dilute! in CO_2)

$$\frac{\text{moles } CO_2}{\text{moles } H_2O} = \frac{X_{CO_2}}{X_{H_2O}} = \frac{5.48 \times 10^{-4}}{1 - 5.48 \times 10^{-4}} = 5.48 \times 10^{-4}$$

$$\text{moles } CO_2 = 5.48 \times 10^{-4} \frac{1000 \text{ g}}{18.0 \text{ g mol}^{-1}} = 0.0305 \text{ mol}$$

$$\text{mass } CO_2 = (0.0305 \text{ mol})(44.0 \text{ g mol}^{-1}) = \boxed{1.34 \text{ g}}$$

(identical intermolecular interactions)

c) CO_2 and water do not form (ideal solutions) Why? (*Hint*: O=C=O is a linear molecule)

$CO_2 - CO_2$, $H_2O - H_2O$ interactions different

CO_2 is nonpolar H_2O is extensively H-bonded and polar

$$|\epsilon_{H_2O-H_2O}| > |\epsilon_{H_2O-CO_2}| > \epsilon_{CO_2-CO_2}$$

d) CO_2 and water do not form ideal solutions, but the solubility of CO_2 in water calculated in part **b** <u>without activity coefficients</u> is very accurate! Why?   Henry's Law applies

as $X_{CO_2} \rightarrow 0$, $P_{CO_2} \rightarrow k_{CO_2} X_{CO_2}$ and $\gamma^{(HL)}_{CO_2} \rightarrow 1$

$X_{CO_2} = 0.0000548 \approx 0$ (very dilute CO_2 solution)

2. a) For a liquid benzene(1) + toluene(2) mixture with a total vapor pressure of 50.0 Torr at 60 °C:

i) calculate the mole fraction of benzene in the liquid mixture. $(p_1^* = 96.4$ Torr, $p_2^* = 28.9$ Torr)

total pressure $p = P_1 + P_2 = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1-x_1)P_2^*$

$p = P_2^* + x_1(P_1^* - P_2^*)$ $\qquad x_1 = \dfrac{p - P_2^*}{P_1^* - P_2^*} = \dfrac{(50.0 - 28.9)\text{Torr}}{(96.4 - 28.9)\text{Torr}} = \boxed{0.312}$

**ii)** calculate the mole fraction of benzene in the vapor in equilibrium with the liquid

$y_1 = \dfrac{P_1}{P_1 + P_2} = \dfrac{P_1}{P} = \dfrac{x_1 P_1^*}{P} = \dfrac{0.312(96.4\,\text{Torr})}{50.0\,\text{Torr}} = \boxed{0.603}$

(vapor richer in more-volatile benzene)

b)

i) Using the phase diagram, give the solubility (in mole fraction units) of biphenyl in liquid naphthalene at 60 °C.

biphenyl solubility at 60 °C

read down from point A

$\boxed{X_1 = 0.82}$

biphenyl(1) + naphthalene(2) solid-liquid phase diagram at 1 bar

0.600 mole fraction biphenyl
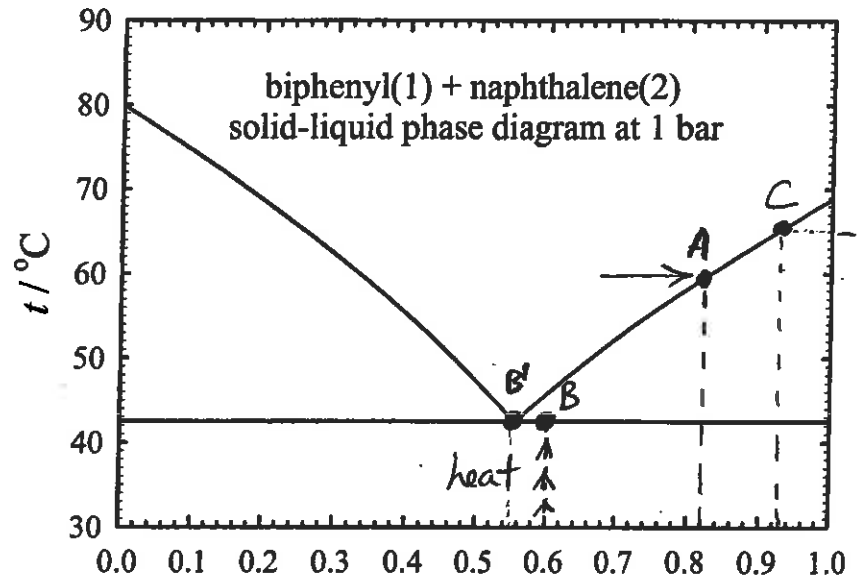
ii) 0.300 mol solid biphenyl and 0.200 mol solid naphthalene initially at 25 °C are heated. Give the temperature and the number of degrees of freedom when the first liquid appears. What is the mole fraction of biphenyl in the first liquid?

First liquid appears when the temperature at point B is reached, the eutectic temperature $\boxed{42.5\,°C}$

The first liquid has the eutectic composition (B') $x = 0.55$.
liquid + solid naphth. + solid biphen.

$F'(const. \ p) = C + 1 - P = 2 + 1 - 3 = \boxed{0}$

iii) To check the purity of a commercial sample of biphenyl, a small portion of the solid product is slowly heated, starting at 20 °C. The last solid melts at 65 °C. Give the purity of the biphenyl sample in mole fraction units. Why is this purity estimate reliable even if the impurity is not naphthalene?

point C $\boxed{x_1 = 0.93}$ (purity)

The freezing point depression is a colligative property, does not depend on the nature of the impurity molecules, only the number of molecules. 2

3. **a)** The osmotic pressure of a 0.045 mol L^{-1} aqueous dichloroacetic solution is 1.90 bar at 25 °C. Assuming the solution is ideal:
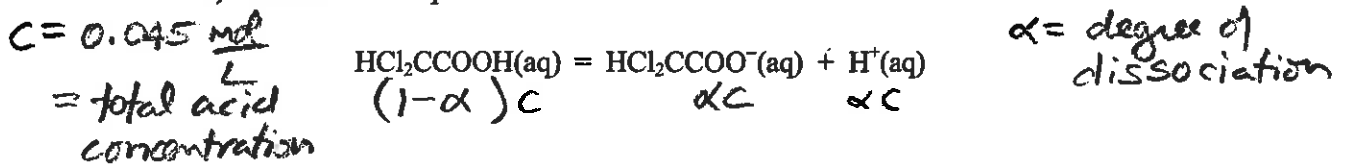
i) use the osmotic pressure to show dichloroacetic acid is a weak electrolyte

If HCl_2CCOOH is a strong electrolyte, then 0.045 mol L^{-1} acid gives 0.045 mol L^{-1} HCl_2COO^- ions and 0.045 mol L^{-1} H^+ ions (complete dissociation)

$$\Pi = (C_{HCl2COO^-} + C_{H^+})RT = (0.045+0.045)\frac{mol}{L}\left(0.08314\frac{L\,bar}{K\,mol}\right)(298K)$$

$$\Pi = 2.23 \; bar$$

ii) calculate the equilibrium constant for the dissociation of dichloroacetic acid

$C = 0.045 \frac{mol}{L}$
= total acid concentration

α = degree of dissociation

$$HCl_2CCOOH(aq) = HCl_2CCOO^-(aq) + H^+(aq)$$
$$(1-\alpha)c \qquad\qquad \alpha c \qquad\quad \alpha c$$

$$\Pi = \left(C_{HCl_2CCOOH} + C_{HCl_2CCOO^-} + C_{H^+}\right)RT = [(1-\alpha)c + \alpha c + \alpha c]\,RT$$

$$\Pi = (1+\alpha)cRT$$

$$1+\alpha = \frac{\Pi}{cRT}$$

$$= \frac{1.90}{0.045\,(0.08314)(298)}$$

$$1+\alpha = 1.70$$
$$\alpha = 0.70$$

$$K = \frac{C_{HCl_2CCOO^-}\,C_{H^+}}{C_{HCl_2CCOOH}}$$

$$= \frac{(\alpha c)(\alpha c)}{1-\alpha} = \frac{\alpha^2 c}{1-\alpha}$$

$$= \frac{(0.70)^2 0.045}{1-0.70}$$

$$\boxed{K = 0.0735}$$

iii) calculate the freezing point of the solution. *Data:* K_f = 1.86 K kg mol^{-1}, the density of water is 1.00 g cm^{-3}

dilute aqueous solution: $0.045 \frac{mol}{L} \approx 0.045 \frac{mol}{kg}$
(solution)   (water)

$\left(\begin{array}{l} 1\,L\;solution\;(almost\;pure\;water) \\ \approx 1000\;cm^3\;water \\ \approx 1.00\;kg\;water \end{array}\right)$

$\Delta T = K_f(1+\alpha)m \leftarrow$ total acid molality

$$= 1.86\,(1.70)\,0.045$$

$$\boxed{\Delta T = 0.142\;K}$$

b) Explain why the expression $\pi = RTc_2$ is analogous to the ideal gas law.

$$\Pi = c_2 RT = \frac{n_2}{V}RT$$

volume of solution

$$P_2 = \frac{n_2}{V}RT$$

3

$z_+ = 2$ $z_- = -1$ $m_+ = m_{Ca^{2+}} = 0.0050 \frac{mol}{kg}$ $m_- = m_{Cl^-} = 0.0100 \frac{mol}{kg}$

4.   **a)** Use Debye-Huckel theory to calculate the ionic strength (I) and the activity (a_{CaCl_2}) of $CaCl_2$ in a 0.0050 mol kg^{-1} aqueous $CaCl_2$ solution at 25 °C. $\boxed{\nu = 3}$

$$I = \frac{z_+^2 m_+ + z_-^2 m_-}{2} = \frac{2^2(0.0050) + (-1)^2 0.0100}{2} = 0.0150 \frac{mol}{kg}$$

$$(= 3m)$$

$\ln \gamma_\pm = -1.173 |z_+ z_-| \sqrt{I}$

$\quad = -1.173 \, (2)(1) \sqrt{0.0150}$

$\ln \gamma_\pm = -0.287$

$\gamma_\pm = e^{-0.287} = 0.750$

$a_{CaCl_2} = a_{Ca^{2+}} \, a_{Cl^-}^2$

$\quad = \gamma_+ m_+ (\gamma_- m_-)^2$

$\quad = \gamma_+ \gamma_-^2 \, m_+ m_-^2 = \gamma_\pm^3 m_+ m_-^2$

$\quad = 0.750(0.005)(0.010)^2$

$\boxed{a_{CaCl_2} = 2.11 \times 10^{-7} \, mol^3 \, kg^{-3}}$

b) Why does the formation of bisulfate ions ($H^+ + SO_4^{2-} \rightarrow HSO_4^-$) reduce the activity of aqueous H_2SO_4?

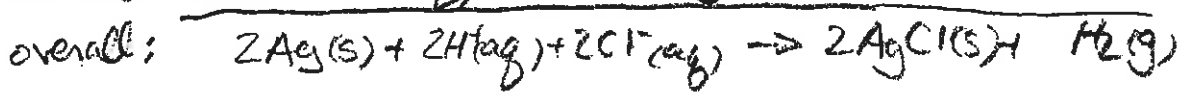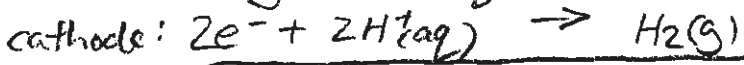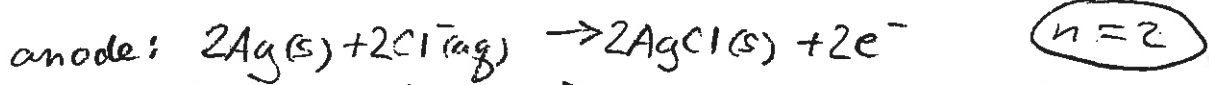the association reaction reduces the molalities of the H^+ and SO_4^{2-} ions

$$\left(a_{H_2SO_4} \propto m_{H^+}^2 \, m_{SO_4^{2-}} \right)$$

c) Measurements for the reversible cell

Ag(s) | AgCl(s) | HCl (aq) | H$_2$(g) | Pt(s)

give $E^° = -0.2224$ volt and $dE^°/dT = 0.00045$ volt K^{-1} at 25 °C.

Write the overall cell reaction and calculate $\Delta G^°$ $\Delta S^°$ and $\Delta H^°$ at 25 °C.

anode: $2Ag(s) + 2Cl^-(aq) \rightarrow 2AgCl(s) + 2e^-$ $\boxed{n=2}$

cathode: $2e^- + 2H^+(aq) \rightarrow H_2(g)$

overall: $2Ag(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow 2AgCl(s) + H_2(g)$

$\Delta G^° = -nFE^° = -(2 \, mol)(96485 \, C \, mol^{-1})(-0.2224 \, V)$

$\boxed{\Delta G^° = 42920 \, J}$

$\Delta S^° = -\frac{d\Delta G^°}{dT} = nF \frac{dE^°}{dT} = (2)(96485 \frac{C}{mol})(+0.00045 \frac{V}{K})$

$\boxed{\Delta S = +86.8 \, J \, K^{-1}}$

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

$\Delta H^° = \Delta G^° + T\Delta S^°$

$\quad = 42920 + (298.15)(86.8)$

$\boxed{\Delta H^° = 68810 \checkmark}$

4

5. This question refers to the electrochemical cell

$$\text{Zn(s)} \mid \text{ZnSO}_4(\text{aq, 0.001 mol kg}^{-1}) \parallel \text{CuSO}_4(\text{aq, 0.001 mol kg}^{-1}) \mid \text{Cu(s)}$$

a) Describe the device indicated by "∥". Give two reasons why it is essential for cell operation.

A salt bridge a porous barrier, such as a glass frit.
1) prevents $Cu^{2+}(aq)$ from contacting the $Zn(s)$ electrode by preventing the two electrolytes from mixing ("short circuit!")
2)

b) Give the overall cell reaction.

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

or

$$Zn(s) + Cu^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Zn^{2+}(aq) + SO_4^{2-}(aq) + Cu(s)$$
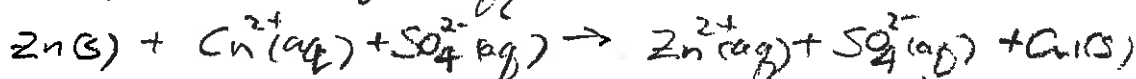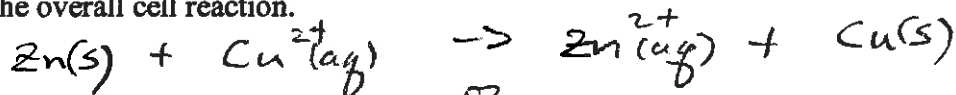
c) Write the Nernst equation for the cell. (Do not assume ideal solution behavior.)

$$E = E^0 - \frac{RT}{2F} \ln\left(\frac{a_{Zn^{2+}(aq)}}{a_{Cu^{2+}(aq)}}\right)$$

$$= E^0 - \frac{RT}{2F} \ln \gamma_{Zn^{2+}} m_{22}$$

d) Use the table of standard reduction potentials to calculate the standard cell voltage E^0.

$$E^0 = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$$

$$= 0.3394 \text{ V} - (-0.763 \text{ V})$$

$$\boxed{E^0 = 1.102 \text{ V}}$$

e) Calculate the cell voltage E using Debye-Huckel theory for the ionic activity coefficients.

$$\ln \gamma_{Zn^{2+}} = -1.173(-2)^2 \sqrt{I} = \ln \gamma_{Cu^{2+}}$$

same charge on Zn^{2+} and Cu^{2+}, same ionic strength Left and Right

$$E = E^0 - \frac{RT}{2F} \ln\left[\left(\frac{\gamma_{Zn^{2+}}}{\gamma_{Cu^{2+}}}\right)\left(\frac{m_{Zn^{2+}}}{m_{Cu^{2+}}}\right)\right]$$

$$\frac{0.0050}{0.0050} = 1$$

$$= 1$$

$$E = E^0 - \frac{RT}{2F} \ln[(1)(1)] = E^0 - 0 = E^0 = \boxed{1.102 \text{ V}}$$

f) The measured cell voltage is slightly lower (by about 0.01 volt) than the cell voltage calculated from the Nernst equation. Account for this discrepancy.

The cell is not reversible due to irreversible mixing in the salt bridge. As a result $\Delta G < w_e$

$$-nFE_{rev} < -nF E_{irrev}$$

$$E_{rev} > E_{irrev}$$

Standard Reduction Potentials at 25°C

Electrode	$E°/V$	Electrode Reaction
$F^- \mid F_2(g) \mid Pt$	2.87	$\frac{1}{2}F_2(g) + e^- = F^-$
$Au^{3+} \mid Au$	1.50	$\frac{1}{3}Au^{3+} + e^- = \frac{1}{3}Au$
$Pb^{2+} \mid PbO_2 \mid Pb$	1.455	$\frac{1}{2}PbO_2 + 2H^+ + e^- = \frac{1}{2}Pb^{2+} + H_2O$
$Cl^- \mid Cl_2(g) \mid Pt$	1.3604	$\frac{1}{2}Cl_2(g) + e^- = Cl^-$
$H^+ \mid O_2(g) \mid Pt$	1.2288	$H^+ + \frac{1}{4}O_2(g) + e^- = \frac{1}{2}H_2O$
$Ag^+ \mid Ag$	0.7992	$Ag^+ + e^- = Ag$
$Fe^{3+}, Fe^{2+} \mid Pt$	0.771	$Fe^{3+} + e^- = Fe^{2+}$
$I^- \mid I_2(s) \mid Pt$	0.5355	$\frac{1}{2}I_2 + e^- = I^-$
$Cu^+ \mid Cu$	0.521	$Cu^+ + e^- = Cu$
$OH^- \mid O_2(g) \mid Pt^b$	0.4009	$\frac{1}{4}O_2(g) + \frac{1}{2}H_2O + e^- = OH^-$
$Cu^{2+} \mid Cu$	0.3394	$\frac{1}{2}Cu^{2+} + e^- = \frac{1}{2}Cu$
$Cl^- \mid Hg_2Cl_2(s) \mid Hg^c$	0.268	$\frac{1}{2}Hg_2Cl_2 + e^- = Hg + Cl^-$
$Cl^- \mid AgCl(s) \mid Ag$	0.2224	$AgCl + e^- = Ag + Cl^-$
$Cu^{2+}, Cu^+ \mid Pt^d$	0.153	$Cu^{2+} + e^- = Cu^+$
$Br^- \mid AgBr(s) \mid Ag$	0.0732	$AgBr + e^- = Ag + Br^-$
$H^+ \mid H_2(g) \mid Pt$	0.0000	$H^+ + e^- = \frac{1}{2}H_2(g)$
$D^+ \mid D_2(g) \mid Pt$	−0.0034	$D^+ + e^- = \frac{1}{2}D_2(g)$
$Pb^{2+} \mid Pb$	−0.126	$\frac{1}{2}Pb^{2+} + e^- = \frac{1}{2}Pb$
$Sn^{2+} \mid Sn$	−0.140	$\frac{1}{2}Sn^{2+} + e^- = \frac{1}{2}Sn$
$Ni^{2+} \mid Ni$	−0.250	$\frac{1}{2}Ni^{2+} + e^- = \frac{1}{2}Ni$
$Cd^{2+} \mid Cd$	−0.4022	$\frac{1}{2}Cd^{2+} + e^- = \frac{1}{2}Cd$
$Fe^{2+} \mid Fe$	−0.440	$\frac{1}{2}Fe^{2+} + e^- = \frac{1}{2}Fe$
$Zn^{2+} \mid Zn$	−0.763	$\frac{1}{2}Zn^{2+} + e^- = \frac{1}{2}Zn$
$OH^- \mid H_2(g) \mid Pt$	−0.8279	$H_2O + e^- = \frac{1}{2}H_2(g) + OH^-$
$Mg^{2+} \mid Mg$	−2.37	$\frac{1}{2}Mg^{2+} + e^- = \frac{1}{2}Mg$
$Na^+ \mid Na$	−2.714	$Na^+ + e^- = Na$
$Li^+ \mid Li$	−3.045	$Li^+ + e^- = Li$

[a] All ions are at unit activity (on the molal scale) in water, and all gases are at 1 bar.