

- Enter your answers into a blue or green Composition Book. Perform only the number of problems required.

Useful Constants and Conversions

Universal Gas Constant= $R = 8.31 J / mole \cdot K = 0.0821 L \cdot atm / mole \cdot K$

Faraday's Constant= $\mathfrak{F} = 96,458 Coulombs / mole$

gravitational constant= $g = 9.8 m/s^2$

Avagadro's Number= $N_A = 6.02 \times 10^{23} molecules/mole$

1 atm = 101,325 Nt/m² = 760 torr

1 bar = 10⁵ Nt/m² = 0.986923 atm = 750.052 torr

1 Nt/m² = 1 Pascal (=1Pa)

1 torr = 1 mmHg

1000L = 1m³

Part 1 (18 points) Give 3 out of 6 definitions.

1.1) State the Gibbs-Duhem equation. Explain its use in the theory of real solutions.

Answer: For a two component system: $n_1 d\mu_1 + n_2 d\mu_2 = 0$.

or $d \ln a_2 = -\frac{n_1}{n_2} d \ln a_1 \dots$ from $d\mu = d(\mu^0 + RT \ln a) = RT d \ln a$. It means the solvent

activity can be used to determine the solute activity and hence the solute's activity coefficient. From this equation the properties of the solvent, measured from the properties of its vapor or from other colligative properties like freezing point depression or osmotic pressure, can be used to obtain the activity coefficient of a non-volatile solute.

1.2) The Gibbs Phase Rule. Define and give the equation for the degrees of freedom in a multi-component, multi-phase system. What is the physical meaning of degrees of freedom, as the term is used in the phase rule?

Answer: The Gibbs Phase Rule gives a relationship between the degrees of freedom f of the system, the number of components c , and the number of phases p . The relationship is $f = c - p + 2$. The number of degrees of freedom f is the number of intensive variables required to specify the state of the system. Their values can be altered independently without changing the number of phases.

1.3) Colligative properties: Define. Give an example of a colligative property and explain how colligative measurements provide information on solute activity coefficients. An equation might be helpful but a calculation is unnecessary.

Answer:

- 1.4) Molal Osmotic Coefficient, also called the Practical Osmotic Coefficient. Define and describe how this quantity is used in the theory of solutions and colligative properties. Give an example.

Answer: Formally defined as $\phi = -\frac{m_1}{m_2} \ln a_1$, the osmotic coefficient can be

obtained from colligative data, e.g. from osmotic pressure data where $\phi = \frac{m_1}{m_2} \frac{\pi \bar{V}_1}{RT}$

, from vapor pressure data where $\phi = -\frac{m_1}{m_2} \ln \frac{P_1}{P_1^0}$, or from freezing point

depression data where $j = 1 - \phi = 1 - \frac{\Delta T}{\nu m_2 K_f}$. When measured over a range of

solute molalities, ϕ is used to evaluate the solute activity coefficient at some m_2

from $\ln \gamma_{m_2} = \phi_{m_2} - 1 + \int_0^{m_2} \frac{\phi - 1}{m'_2} dm'_2$

- 1.5) State the Gibbs Adsorption Isotherm Equation. Explain.

Answer: $\Gamma_{2,1} = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_2} \right)$. This equation relates the change in surface tension ($d\gamma$) of

a solution with solute chemical potential (i.e. $d \ln a_2$) to the solute adsorption $\Gamma_{2,1}$, which is the moles of solute per unit area of surface relative to the component 1...usually the solvent.

- 1.6) Homogeneous Function of Rank 1: Define and give an example of such a function in thermodynamics, explain why the thermodynamic function is homogeneous, and give at least one important consequence of this fact.

Answer: A rank 1 homogeneous function has the properties

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_k) = \lambda f(x_1, x_2, \dots, x_k) \text{ and } f(x_1, x_2, \dots, x_k) = \sum_i x_i \left(\frac{\partial f}{\partial x_i} \right)_{x_{j \neq i}}$$

Energy, which is a function of S, V, and n, i.e. $dE(S, V, \{n_i\}) = TdS - PdV + \sum_i \mu_i dn_i$ is

rank 1 because S, V, and n are all extensive and when increased each by a factor of λ will increase E by a factor of λ . Then as a consequence of the second property

$$E(S, V, \{n_i\}) = S \left(\frac{\partial E}{\partial S} \right)_{V, n} + V \left(\frac{\partial E}{\partial V} \right)_{S, n} + \sum_i n_i \left(\frac{\partial E}{\partial n_i} \right)_{V, S, n_{j \neq i}} = TS - PV + \sum_i \mu_i n_i$$

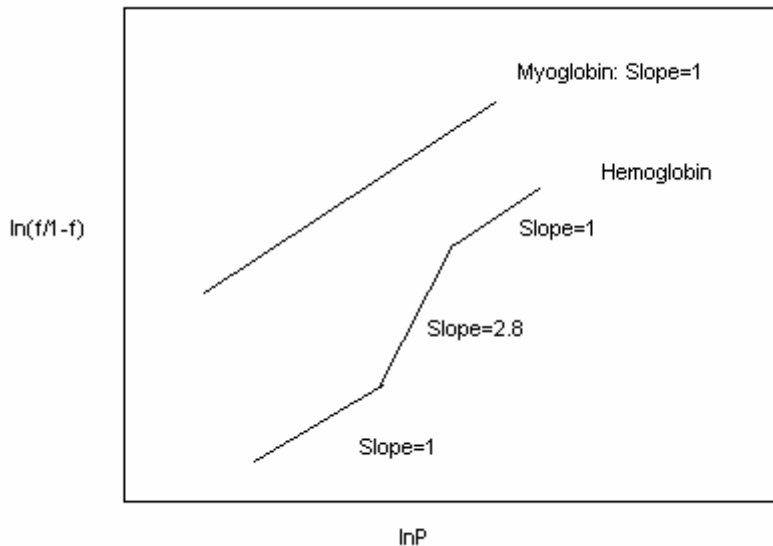
and so $dE = d(TS) - d(PV) + \sum_i d(\mu_i n_i)$. An important consequence of this last

relationship is the Gibbs-Duhem equation: $SdT - VdP + \sum_i n_i d\mu_i = 0$ or at constant P and

$$T, \sum_i n_i d\mu_i = 0$$

Part 2: (20 points total) Topics for discussion. Answer 2 out of the 4 questions.

- 2.1) Myoglobin and hemoglobin are oxygen transport proteins. Myoglobin binds a single oxygen molecule while each hemoglobin molecules binds four oxygen molecules. Hemoglobin's oxygen binding has been described by the MWC model of cooperative binding. Sketch Hills plots for the binding of oxygen to myoglobin and to hemoglobin. Explain any differences in these plots in terms of models of binding between the oxygen and these two transport proteins.



Myoglobin has a single oxygen binding site so its Hill plot is a straight line with slope =1. On the other hand, hemoglobin (Hb) has four oxygen binding sites. At low oxygen pressure the system is dominated by an equilibrium between free Hb and Hb with a single site occupied. This part of the plot has a slope of 1. at high oxygen pressure Hb with three sites bound is in equilibrium with fully bound Hb, and again the slope is 1. At intermediate pressures there occurs partly cooperative binding which produces a slope of 2.8.

- 2.2) Large quantities of sugar are used in the canning of jams. The presence of the sugar is partly responsible for killing bacteria that cause botulism. Explain.

Solution: Bacteria are immersed in a concentrated sugar solution. Water flows into the bacteria producing a strong osmotic pressure which eventually causes the bacterial cell wall to burst. The bacteria die in a sea of sugar.

- 2.3) If half of the oxygen binding sites in person's hemoglobin is saturated by breathing carbon monoxide, the person will likely die. On the other hand if half the hemoglobin is inactive in a person due to sickle cell anemia, the

person lives a normal life. Explain these observations in terms of models for binding of oxygen to hemoglobin.

Solution:

- 2.4) Dipalmitoyl lecithin is a naturally-occurring detergent that is found at the air-water interface of the alveoli, which are the smallest air compartments in the lung. Explain the function of dipalmitoyl lecithin in the lung. Explain your answer in terms of surface tension and the effect of detergents on the surface tension of water.

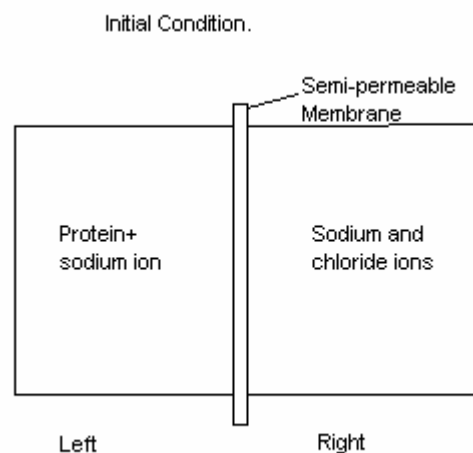
Solution: The alveoli are small air sacs in the lungs that are surrounded by tissue fluid. The pressure difference between the inside of an alveolus and the surrounding fluid is

$$\Delta P = P_{inside} - P_{outside} = \frac{2\gamma}{r}$$
 where γ is the surface tension and r is the radius of the alveolus.

Because the alveoli are interconnected, an alveolus with small radius will have a higher internal pressure than a alveolus with a larger radius. The tendency will be for air to move from the small alveoli to larger alveoli, a process called coarsening. If coarsening occurs breathing will be difficult and the lungs will eventually collapse. To avoid this the pressure gradients between alveoli are diminished by lowering the surface tension with a lipid surfactant. The lower surface tension makes it easier to expand the lungs.

Part 3: (30 points total) Short Calculations. Perform 3 out of the 5 calculations.

- 3.1) Consider a 0.001M solution of the sodium salt of an anionic protein NaP, which is separated by a semi-permeable from a 0.01M NaCl solution. See diagram below for the situation before equilibrium is reached.



The membrane is permeable to sodium and chloride ions but is impermeable to the protein. Assuming the protein salt dissociates completely to Na^+ and P^- , calculate the final concentrations of Na^+ , Cl^- and P^- in both solutions and the net osmotic pressure.

Solution. This is the Donnan effect: The concentration of chloride in the protein compartment is

$$[\text{Cl}^-]_{\text{Left}}^{\text{final}} = x = \frac{([\text{Cl}^-]_{\text{Right}}^{\text{initial}})^2}{[\text{Protein}] + 2 \times [\text{Cl}^-]_{\text{Right}}^{\text{initial}}} = \frac{b^2}{a + 2b} = \frac{(0.01)^2}{0.001 + 0.02} = 0.0048M$$

$$[\text{Protein}] = a = 0.001M$$

$$[\text{Na}^+]_{\text{Left}}^{\text{final}} = a + x = 0.001M + 0.0048M = 0.0058M$$

$$[\text{Cl}^-]_{\text{Right}}^{\text{final}} = [\text{Na}^+]_{\text{Right}}^{\text{final}} = b - x = 0.01 - 0.0048 = 0.0052M$$

$$\pi_{\text{net}} = RT [C_2^L - C_2^R] = (0.0821 \text{Latm mol}^{-1} \text{K}^{-1})(293K)[(2)(0.0058) - (2)(0.0052)] = 0.029 \text{atm.}$$

3.2) Calculate the vapor pressure for a mist of water droplets, where the droplets are spherical with radius 10^{-9} m. Assume $T=293K$. The vapor pressure of water with a flat interface is 0.023 atm at $T=293K$. Assume the surface tension of water is 0.0727Nm^{-1} .

Solution: Use the Kelvin equation

$$\ln\left(\frac{P}{P^0}\right) = \frac{2M\gamma}{RT\rho r} = \frac{(2)(0.018 \text{kg mol}^{-1})(0.0727 \text{Nm}^{-1})}{(8.31 \text{Jmol}^{-1} \text{K}^{-1})(293K)(10^3 \text{kgm}^{-3})(10^{-9} \text{m})} = 1.08$$

$$P = P_0 e^{1.08} = (0.023 \text{atm})(2.93) = 0.067 \text{atm}$$

3.3) For the oxidation-reduction

$\text{AgCl}(s) + \frac{1}{2} \text{H}_2(g) \rightarrow \text{Ag}(s) + \text{H}^+(aq) + \text{Cl}^-(aq)$ the standard cell potential is 0.2225V. Calculate the activity coefficient of a 0.00914M molar solution of HCl if the cell potential is 0.4686V and the pressure of hydrogen is 1 atm.

Solution:

$$E = E^0 - \frac{RT}{nF} \ln a_{\text{H}^+} a_{\text{Cl}^-} = E^0 - \frac{RT}{nF} \ln \gamma_{\pm}^2 C^2$$

$$-\ln \gamma_{\pm} = \ln C + (E - E_0) \frac{nF}{2RT} = \ln(0.00914) + (0.4686V - 0.2225V) \left(\frac{96485 \text{Cmol}^{-1}}{(2)(8.31 \text{Jmol}^{-1} \text{K}^{-1})(298K)} \right)$$

$$= -4.695 + 4.794 = 0.099 \Rightarrow \gamma_{\pm} = e^{-0.099} = 0.905$$

3.4) The virial equation of state for a real gas at low pressure has the form

$PV = nRT + BP$ where B is a constant called the virial coefficient. All other symbols have their usual definitions. For the gas trimethylamine ($N(\text{CH}_3)_3$)

$B = -1.192 \text{ Lmol}^{-1}$ between 0.2 atm and 0.8 atm at $T=273\text{K}$. At $P=0.4$ atm and $T=273\text{K}$, a gram of triethylamine occupies 0.927L. Calculate the fugacity and fugacity coefficient of trimethylamine under these conditions.

Solution:

$$P\bar{V} = RT + BP \Rightarrow B = \bar{V} - \frac{RT}{P} = \frac{0.927 \text{ Lg}^{-1}}{1 \text{ mole} / 59 \text{ g}} - \frac{(0.0821 \text{ Latm mol}^{-1} \text{K}^{-1})(273 \text{ K})}{0.4 \text{ atm}}$$

$$= 54.693 \text{ Lmol}^{-1} - 56.033 \text{ Lmol}^{-1} = -1.34 \text{ Lmol}^{-1}$$

$$\int_{p^0}^f d \ln f = \frac{1}{RT} \int_{p^0}^P \frac{V}{n} dP = \frac{1}{RT} \int_{p^0}^P \left(\frac{RT}{P} + B \right) dP \approx \ln P + \frac{BP}{RT}$$

$$f = P \exp \left\{ \frac{BP}{RT} \right\} = (0.4 \text{ atm}) \exp \left\{ \frac{(-1.34 \text{ Lmol}^{-1})(0.4 \text{ atm})}{(0.0821 \text{ Latm mol}^{-1} \text{K}^{-1})(273 \text{ K})} \right\} = (0.4 \text{ atm})(0.98)$$

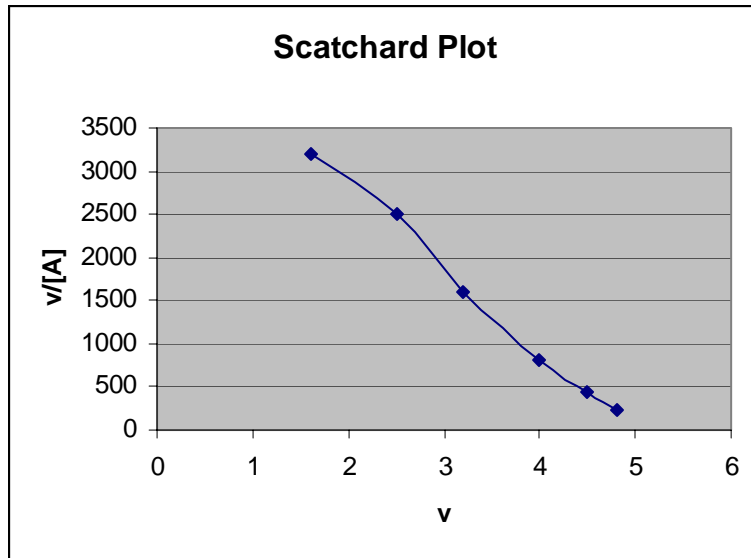
3.5) Consider the data for the binding of a ligand A to a macromolecule

Concentration of A (moles/L)	\bar{v}
0.0005	1.6
0.0010	2.5
0.0020	3.2
0.0050	4.0
0.0100	4.1
0.0200	4.8

From a Scatchard plot of the data determine the number of binding sites and the binding constant K

Solution:

Answer: The x intercept is 5 so $N=5$. The intercept is $NK=4800$...so $K=960$.



Part 4 (32 points total) Perform one of the two multi-step problems given below.

4.1 The concentration of sodium ion in a nerve cell is $[Na^+]_{in}=0.010$ M and the concentration outside the cell is $[Na^+]_{out}=0.140$ M. The concentration of potassium ion in a cell is $[K^+]_{in}=0.100$ M and the concentration outside the cell is $[K^+]_{out}=0.005$ M. Assume $T=310K$. Faraday's constant is $96,485$ C/mole.

- a) Assume that the difference in electrostatic potential between the inside of the cell and the outside of the cell is $\Delta\psi = \psi_{in} - \psi_{out} = -0.070V$, calculate the change in chemical potential that occurs when one mole of sodium ion is transported from the interior of the cell to the exterior.

$$\begin{aligned} \text{Solution: } \Delta\mu &= \mu_{out} - \mu_{in} = RT \ln \left(\frac{[Na^+]_{out}}{[Na^+]_{in}} \right) + (+1) \cdot \mathfrak{F} \cdot (\psi_{out} - \psi_{in}) \\ &= (8.31J \cdot K^{-1} \cdot mol^{-1})(310K) \cdot \ln \left(\frac{0.140}{0.01} \right) + (96,485C \cdot mol^{-1})(0.070J/C) \\ &= (6,799 + 6,754)J/mole = 13,553 J/mole. \end{aligned}$$

- b) Calculate the change in chemical potential that occurs when one mole of potassium ion is transported from the exterior of the cell to the interior. Explain any difference in your answers for parts b and c.

$$\begin{aligned} \text{Solution: } \Delta\mu &= \mu_{in} - \mu_{out} = RT \ln \left(\frac{[K^+]_{in}}{[K^+]_{out}} \right) + (+1) \cdot \mathfrak{F} \cdot (\psi_{in} - \psi_{out}) \\ &= (8.31J \cdot K^{-1} \cdot mol^{-1})(310K) \cdot \ln \left(\frac{0.100}{0.005} \right) + (96,485C \cdot mol^{-1})(-0.070J/C) \\ &= (7717 - 6754)J/mole = 963J/mole. \end{aligned}$$

Even more work is required because the concentration gradient is greater than the sodium case. But the concentration gradient is offset somewhat by a favorable electrostatic gradient.

- c) In the cell, three moles of sodium ion and two moles of potassium ion are transported for every mole of ATP that is hydrolyzed to ADP and inorganic phosphate P_i . Assuming the ratio $\frac{[ATP]}{[ADP]}$ in the cell is 100 and the concentration of inorganic phosphate is 0.005 M, calculate the change in chemical potential that occurs when three moles of sodium and two moles of potassium are actively transported across the cell membrane as a result of the hydrolysis of one mole of ATP. The standard chemical potential change for the hydrolysis of ATP is -31 kJ/mole. Assume $T=310K$.

Solution:

$$\begin{aligned}\Delta\mu &= 3\Delta\mu(\text{part } a) + 2\Delta\mu(\text{part } b) + \Delta\mu_{ATP \rightarrow ADP+P_i}^0 + RT \ln Q \\ &= 3\Delta\mu(\text{part } a) + 2\Delta\mu(\text{part } b) + \Delta\mu_{ATP \rightarrow ADP+P_i}^0 + RT \ln \left\{ \frac{[ADP][P_i]}{[ATP]} \right\} \\ &= (3)(13,553J/mole) + (2)(963J/mole) - 31,000J/mole + (8.31J/mole)(310K) \ln\left(\frac{0.005}{10^2}\right) \\ &= 40,659 J/mole + 1,926 J/mole - 31,000 J/mole + 2576J/mole \times \ln(5 \times 10^{-5}) = -13,926 J/mole\end{aligned}$$

- d) The electrostatic potential of the cell membrane $\Delta\psi$ is dependent upon the permeability of the membrane to transport of various ions. In nerve cells, local ion permeabilities can suddenly change, causing a drastic change in the local potential difference, called the action potential. Using the ion concentrations given above, calculate the action potential necessary to bring the Na^+ ions inside and outside the membrane to equilibrium.

$$\begin{aligned}\text{Solution: } \Delta\mu &= \mu_{out} - \mu_{in} = 0 = RT \ln \left(\frac{[Na^+]_{out}}{[Na^+]_{in}} \right) + (+1) \cdot \mathfrak{F} \cdot (\psi_{out} - \psi_{in}) \\ 0 &= (8.31J \cdot K^{-1} \cdot mol^{-1})(310K) \cdot \ln \left(\frac{0.140}{0.01} \right) + (96,485C \cdot mol^{-1}) \Delta\psi \\ \Delta\psi &= \frac{6799J}{96485C} = 0.07V\end{aligned}$$

4.2) For extremely accurate work with buffers, the dissociation constant K_a for the weak acid dissociation $HA \xrightleftharpoons{K_a} H^+ + A^-$ should be written using activities:

$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}} = \frac{\gamma_{H^+} [H^+] \gamma_{A^-} [A^-]}{\gamma_{HA} [HA]}$$

- a) Using the definitions $pH = -\log a_{H^+}$ and $pK_a = -\log K_a$, and assuming the weak acid HA behaves ideally, i.e. $\gamma_{HA} = 1$, the Henderson-Hasselbach (H.-H.) equation is obtained by taking the logarithm of both sides of the equation for K_a . Show that

the H.-H. equation is
$$pH = pK_a + \log \frac{[A^-]}{[HA]} + \log \gamma_{A^-}.$$

Solution:
$$K_a = \frac{a_{H^+} a_{A^-}}{a_{HA}} \rightarrow a_{H^+} = K_a \frac{a_{HA}}{a_{A^-}} \rightarrow pH = -\log a_{H^+} = -\log \left(K_a \frac{a_{HA}}{a_{A^-}} \right)$$

$$pH = -\log a_{H^+} = -\log \left(K_a \frac{a_{HA}}{a_{A^-}} \right) \rightarrow pH = -\log K_a + \log \frac{a_{A^-}}{a_{HA}} = pK_a + \log \frac{\gamma_{A^-} [A^-]}{\gamma_{HA} [HA]}$$

$$pH = pK_a + \log \frac{\gamma_{A^-} [A^-]}{\gamma_{HA} [HA]} \xrightarrow{\gamma_{HA}=1} pH = pK_a + \log \frac{\gamma_{A^-} [A^-]}{[HA]} = pK_a + \log \frac{\gamma_{A^-} [A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{\gamma_{A^-} [A^-]}{[HA]} = pK_a + \log \frac{[A^-]}{[HA]} + \log \gamma_{A^-}$$

- b) Suppose a buffer solution is produced by dissolving 0.40 moles of acetic acid and 0.55 moles of sodium acetate in 1 liter of water. For acetic acid $K_a = 1.76 \times 10^{-5}$. Calculate the activity coefficient for acetate ion if the pH of the solution is 4.5.

Solution:

$$pH \approx pK_a + \log \left(\frac{C_b}{C_a} \right) + \log \gamma_{OAc^-}$$

$$4.52 = -\log (1.76 \times 10^{-5}) + \log \left(\frac{0.55}{0.40} \right) + \log \gamma_{A^-}$$

$$\log \gamma_{A^-} = 4.52 - 4.76 - 0.14 = -0.4$$

$$\therefore \gamma_{A^-} = 10^{-0.4} = 0.40$$

- c) Using Debye-Huckel theory, calculate the ionic strength and the mean activity coefficient for the solution in part b. Assume $T = 298K$.

$$\mu = \frac{1}{2} (z_+^2 [Na^+] + z_-^2 [OAc^-]) = \frac{1}{2} ((+1)^2 (0.55) + (-1)^2 (0.55)) = 0.55$$

$$\log \gamma_{\pm} = -0.51 |z^+ z^-| \sqrt{\mu} = -0.51 \times 0.74 = -0.378$$

$$\gamma_{\pm} = 10^{-0.378} = 0.419$$