Useful Constants and Conversions
Universal Gas Constant: \( R = 8.31 J \text{ mole} \cdot K = 0.0821 L \cdot \text{atm} \cdot \text{mole} \cdot K \)
Faraday’s Constant: \( \mathcal{F} = 96,458 \text{ Coulombs/mole} \)
gravitational constant: \( g = 9.8 m/s^2 \)
Avagadro’s Number: \( N_A = 6.02 \times 10^{23} \text{ molecules/mole} \)
1 atm = 101,325 Nt/m\(^2\) = 760 torr
1 bar = 10\(^5\) Nt/m\(^2\) = 0.986923 atm = 750.052 torr
1 Nt/m\(^2\) = 1 Pa
1 torr = 1 mmHg
1000 L = 1 m\(^3\)

Part 1: (18 points total) Topics for discussion and definition. Answer 3 out of the 5 questions.

1.1) 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 ligand and the 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.
1.2) Explain how the surface pressure is measured with a Langmuir film balance. Sketch the experimental apparatus. What is the physical origin of the surface pressure?

The Langmuir film balance is a trough with a float in the middle which separates pure water from water and surfactant. The surfactant layer is compressed by a moveable arm and the resulting force against the float is measured. The surface pressure is the measured force divided by the length of the float and yields the difference between the surface tension of pure water $\gamma_0$ and the surface tension of the solution $\gamma$:

$$P_{\text{surface}} = \frac{F}{L} = \gamma_0 - \gamma$$

![Langmuir Film Balance Diagram](image)

1.3) 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

$$\Delta P = P_{\text{inside}} - P_{\text{outside}} = \frac{2\gamma}{r}$$

where $\gamma$ 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.
1.4) Fugacity. Define and describe two methods for measuring the fugacity coefficient.

Answer: The fugacity is a measurement of general escape tendency from a system and is related to the pressure $P$ by $f = \gamma_f P$ where $\gamma_f$ is the fugacity coefficient, which measures the deviation of a gas from ideal behavior. If $PV = nRT$ then $\gamma_f = 1$. The fugacity coefficient $\gamma_f = \exp \left\{ \frac{1}{RT} \int_{0}^{P} \alpha \, dP \right\}$ where $\alpha = \frac{P - RT}{P}$. The quantity $\alpha$ can therefore be obtained by independent measurements of $V$, $P$, and $T$...or can be calculated from the equation of state.

1.5) Henry’s Law Solution. Explain the Henry’s Law Solution Model. In particular explain the manner in which the physical behavior of the Henry’s Law solute differs from the components of an ideal solution. Explain how the Henry’s Law solute standard state differs from the standard state of a component of an ideal solution.

Solution: In a Henry’s Law solution, the partial pressure of the solute vapor is related to the solution composition by $P = k_i \chi$ where $k_i = \exp \left[ \frac{\mu_{\text{sol}}^0 - \mu_{\text{ad}}^0}{RT} \right]$. In an ideal solution the standard state of a component is the pure liquid form of the component. The solute standard state is defined as a situation where the solute is energetically equivalent to being surrounded by solvent molecules.

1.6) State the Gibbs Adsorption Isotherm Equation. Explain.

Answer: $\Gamma_{2,1} = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln \chi} \right)$. This equation relates the change in surface tension ($d\gamma$) of a solution with solute chemical potential (i.e. $d\mu_{\text{sol}}$) 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.

Part 2: (20 points total) Answer two out of four questions

2.1 Hemoglobin is a protein that transports oxygen from the lungs to actively metabolizing tissue. There are four oxygen binding sites on each hemoglobin molecule. Carbon monoxide poisoning occurs when a person is exposed to CO and as a result, CO binds to hemoglobin instead of oxygen. Death can occur when 50% of the total binding sites on hemoglobin are occupied by CO. On the other hand, a person with sickle cell anemia can have up to half of their hemoglobin inactive and still live. Explain.

Answer: Sickle cell anemia inactivates half the hemoglobin molecules, but the other half can function normally. On the other hand, oxygen binding to hemoglobin is cooperative. Binding to a given site enhances binding to other sites on the same protein. CO will not do this and so if half the hemoglobin sites are saturated with CO, the other half do not have normal oxygen binding affinities.
2.2) Consider a compass needle, fixed at one end but free to rotate clockwise or counter clockwise on the surface of water, which has surface tension $\gamma_1=0.07 \text{ N m}^{-1}$. A surfactant is added to the region to the right of the needle, changing the surface tension to $\gamma_2 < \gamma_1$. In response to this surface tension gradient, will the needle rotate clockwise, counter-clockwise, or remain stationary? Explain.

Answer:

2.3) Suppose you represent the “melting” of a structured or “native” protein N into the unstructured, denatured D form by the equilibrium $N \rightleftheadarrow D$. You can use differential scanning calorimetry (DSC) to measure the enthalpy of melting...call this enthalpy measurement $\Delta H_{\text{DSC}}$. Suppose you next calculate the enthalpy of melting from the equation

$$
\Delta H = R \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \ln \left( \frac{K(T_2)}{K(T_1)} \right)
$$

where the equilibrium constant at temperature $T$ is assumed to be $K(T) = \frac{C_D}{C_N}$, where $C_D$ is the concentration of denatured protein and $C_N$ is the concentration of native protein. Suppose the calculated enthalpy turns out to be less than the experimentally measured enthalpy. Which of your assumptions might have produced this discrepancy? Explain.

Answer:

$\Delta H_{\text{calc}} < \Delta H_{\text{DSC}}$ means the equilibrium is more complex and includes other species than D and N. DSC measures all heat produced/absorbed from all species...not just N and D. The theory underestimates the enthalpy because it assumes only a single equilibrium.
2.4) “Time release” drugs have the advantage of releasing the drug to the body at a constant rate so that the drug concentration at any time is not high enough to have harmful side effects or so low as to be ineffective. A schematic diagram of a time-release capsule is shown below. Explain how it works, thermodynamically.

Answer: Due to the lower concentration of salts in the tissue fluids, water moves through the semi-permeable membrane. Osmotic pressure builds up in the compartment and exerts force on the elastic membrane. The solution with drug is expelled through the holes.

Part 3: (30 points total) Short Calculations. Perform 2 out of the 4 calculations.

3.1) The flow of electrons down the electron transport chain in the cellular mitochondrion results in the expulsion of protons from inside the inner mitochondrial membrane to the outer side. This produces a pH gradient across the membrane of \( \Delta pH = pH_{in} - pH_{out} = 0.5 \). If the electrostatic potential across this membrane is \( \Delta \psi = \psi_{in} - \psi_{out} = -0.15V \), calculate the change in chemical potential when one mole of protons move from outside the membrane back to the inside. Note \( \ln(x) = 2.3 \log(x) \). Assume \( T = 310K \).

Solution:

\[
\Delta \mu = \mu_{in} - \mu_{out} = RT \ln \left( \frac{c_{H^+}_{in}}{c_{H^+}_{out}} \right) + F(\psi_{in} - \psi_{out}) \\
= RT \left[ \ln c_{H^+}_{in} - \ln c_{H^+}_{out} \right] + F(\psi_{in} - \psi_{out}) = 2.303RT \left[ \log c_{H^+}_{in} - \log c_{H^+}_{out} \right] + F(\psi_{in} - \psi_{out}) \\
= 2.303RT \left( pH_{out} - pH_{in} \right) + F(\psi_{in} - \psi_{out}) \\
= 2.303 \left( 8.31JK^{-1}mol^{-1} \right) \left( 310K \right) (-0.5) + \left( 96485Cmol^{-1} \right)(-0.15V) \\
= -2966Jmol^{-1} - 14473Jmol^{-1} = 17439Jmol^{-1}
\]
3.2) The data show, as a function of temperature, the pressures of carbon monoxide required to adsorb 10cm³ (corrected to P=1 atm and T=273K) of gas onto charcoal. Calculate the differential heat of adsorption for CO on charcoal. A graph is useful but not necessary.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>200</th>
<th>210</th>
<th>220</th>
<th>230</th>
<th>240</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(kPa)</td>
<td>4.00</td>
<td>4.95</td>
<td>6.03</td>
<td>7.20</td>
<td>8.47</td>
<td>9.85</td>
</tr>
</tbody>
</table>

Solution: The equation is
\[
\left( \frac{\partial \ln P}{\partial T} \right)_\theta = -\frac{\Delta H_a}{RT^2} \quad \text{or} \quad \left( \frac{\partial \ln P}{\partial (1/T)} \right)_\theta = \frac{\Delta H_a}{R}.
\]
This means the slope of the graph of \( \ln P \) versus \( 1/T \) gives the heat of adsorption divided by R. If the student chooses to do a graph it should appear as above. Note the x axis is reversed so the slope is actually negative. The slope is
\[
\frac{\Delta H_a}{R} = -902 K^{-1} \Rightarrow \Delta H_a = (8.31 J / mole \cdot K)(-902 K^{-1}) = -7496 J.
\]

If a graph is not used the correct integrated equation is
\[
\ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

3.3) Suppose crystalline glycine is in equilibrium with glycine dissolved in aqueous solution: \( \text{glycine} (cr) \rightleftharpoons \text{glycine} (aq) \). The standard Gibbs energy of formation of crystalline glycine is \( \Delta G^\circ_f = -377.7 \text{kJmol}^{-1} \). The solubility of glycine in water is 3.4 moles per 1000 g of water, and the activity coefficient for glycine under these conditions is about 0.73. Calculate \( \Delta G^\circ_f \) glycine in aqueous solution. Assume T-298K.
Solution The two forms of glycine are in equilibrium so that
\[ \Delta G_f^i (\text{glycine, cr}) = \Delta G_f^i (\text{glycine, aq}) + RT \ln \gamma_m \]
\[ \therefore \Delta G_f^i (\text{glycine, aq}) = \Delta G_f^i (\text{glycine, cr}) - RT \ln \gamma_m \]
\[ = -377700 \text{Jmol}^{-1} - (8.31 \text{JK}^{-1} \text{mol}^{-1})(298K) \ln(0.73 \times 3.4) \]
\[ = -377700 \text{Jmol}^{-1} - 2250 \text{Jmol}^{-1} = -379950 \text{Jmol}^{-1} \]

3.4) For nitrogen gas at T=273K, the equation of state is
\[ \frac{PV_m}{Latm} \approx 22.414 - 10.281 \times 10^{-3} P + 65.189 \times 10^{-6} P^2, \] pressure P is in units of atmospheres and molar volume \( V_m \) is in liters per mole. Calculate the fugacity of nitrogen at T=273K and P=200 atm.
Solution \( \ln \left( \frac{f}{P} \right) = \frac{1}{RT} \int_0^P \alpha dP \) where \( \alpha = V_m - \frac{RT}{P}. \) Then
\[ \alpha = V_m - \frac{RT}{P} \approx 22.414 P^{-1} - 10.281 \times 10^{-3} + 65.189 \times 10^{-6} P - \left( \frac{0.0821 \text{LatmK}^{-1} \text{mol}^{-1}}{P} \right)(273K) \]
\[ = -10.281 \times 10^{-3} + 65.189 \times 10^{-6} P \]
\[ \ln \left( \frac{f}{P} \right) = \frac{1}{RT} \int_0^P \alpha dP = \frac{1}{(0.0821 \text{LatmK}^{-1} \text{mol}^{-1})(273K)} \int_0^{200} \left( -10.281 \times 10^{-3} + 65.189 \times 10^{-6} P \right) dP \]
\[ = \frac{1}{22.41 \text{Latm}} \left( -10.281 \times 10^{-3} \times 200 + 65.189 \times 10^{-6} \times \frac{200^2}{2} \right) \text{Latm} \]
\[ = -2.056 + 1.304 = -0.0336 \]
\[ \therefore f = 200 \text{atm} \times e^{-0.0336} = 193 \text{atm} \]

4) Part 3 (32 points total) Perform two of the three problems given below.

4.1) Heptane and 2-methylpentane are liquids at T=315K which form ideal solutions when mixed. Suppose you mix one mole of heptane and three moles of 2-methylpentane at T=315K.
- Calculate the entropy of mixing, the Gibbs free energy of mixing, and the enthalpy of mixing for this process.
- Also, calculate the vapor pressures of heptane and 2-methylpentane above the resulting solution. At 315K the vapor pressure of pure heptane is 0.13 atm and the vapor pressure of pure 2-methylpentane is 0.53 atm.
• What are the mole fractions of heptane and 2-methylpentane in the vapor phase?

Solution:
• For an ideal solution $\Delta H_{\text{mix}} = 0$.

\[
\chi_{\text{hept}} = \frac{n_{\text{hept}}}{n_{\text{hept}} + n_{\text{2MP}}} = \frac{1}{1+3} = 0.25
\]

\[
\chi_{\text{2MP}} = \frac{n_{\text{2MP}}}{n_{\text{hept}} + n_{\text{2MP}}} = \frac{3}{1+3} = 0.75 \quad \text{or} \quad \chi_{\text{2MP}} = 1 - \chi_{\text{hept}} = 0.75
\]

\[
\Delta S_{\text{mix}} = -R \left( \chi_{\text{hept}} \ln \chi_{\text{hept}} + \chi_{\text{2MP}} \ln \chi_{\text{2MP}} \right)
\]

\[
= -(8.31 \text{ J/mole}\cdot \text{K})(0.25 \ln(0.25) + 0.75 \ln(0.75))
\]

\[
= -(8.31 \text{ J/mole}\cdot \text{K})((0.25)(-1.38) + (0.75)(-0.28))
\]

\[
= -(8.31 \text{ J/mole}\cdot \text{K})(-0.345 - 0.21) = -(8.31 \text{ J/mole}\cdot \text{K})(-0.56)
\]

\[
= 4.65 \text{ J/mole}\cdot \text{K}
\]

• There are 4 moles total so

\[
\Delta S_{\text{mix}} = (4 \text{ moles}) \Delta S_{\text{mix}} = (4)(4.65 \text{ J/K}) = 18.61 \text{ J/K}
\]

• $\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}} = -(315 \text{ K})(18.61 \text{ J/K}) = -5862 \text{ J}$

• $P_{\text{hept}} = \chi_{\text{hept}} P^0_{\text{hept}} = (0.25)(0.13 \text{ atm}) = 0.0325 \text{ atm}$

• $P_{\text{2MP}} = \chi_{\text{2MP}} P^0_{\text{2MP}} = (0.75)(0.53 \text{ atm}) = 0.4 \text{ atm}$

• Dalton’s Law of Partial Pressure states

\[
P_T = P_{\text{hept}} + P_{\text{2MP}} = 0.0325 + 0.4 = 0.4325 \text{ atm}
\]

\[
\therefore \chi_{\text{hept}} = \frac{P_{\text{hept}}}{P_T} = \frac{0.0325}{0.4325} = 0.075
\]

\[
\chi_{\text{2MP}} = 1 - \chi_{\text{hept}} = 1 - 0.075 = 0.925
\]

4.2) I. Langmuir measured the following data for the adsorption of methane onto 1 gram of mica at T=90K:

<table>
<thead>
<tr>
<th>P (bars)</th>
<th>V (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.4</td>
<td>85.0</td>
</tr>
<tr>
<td>11.1</td>
<td>80.4</td>
</tr>
<tr>
<td>9.6</td>
<td>75.9</td>
</tr>
<tr>
<td>8.55</td>
<td>71.6</td>
</tr>
<tr>
<td>7.4</td>
<td>67.9</td>
</tr>
<tr>
<td>6.68</td>
<td>64.2</td>
</tr>
<tr>
<td>5.85</td>
<td>61.2</td>
</tr>
</tbody>
</table>
Where $P$ is the pressure of the methane above the mica surface at equilibrium, and $V$ is the volume of gas adsorbed onto the surface, measured at $T=293K$ and at a pressure of 1 atm.

a) If adsorption of methane onto mica at $T=90K$ occurs without interactions between methane molecules on the surface, all surface sites are equivalent, and adsorption cannot proceed beyond monolayer coverage, show that
\[ \frac{P}{V} = \frac{1}{V_m K} + \frac{P}{V_m}, \]
where $V_m$ is the volume of gas adsorbed at $T=293K$ and $P=1$ atm to form a monolayer, and $K$ is the equilibrium constant for adsorption.

Solution: From the conditions mentioned the appropriate isotherm equation is the Langmuir isotherm. Then...
\[
V = \frac{V_m K P}{1 + K P} \Rightarrow V + V K P = V_m K P \Rightarrow P = \frac{V}{V_m K} + \frac{V P}{V_m}
\]
\[
\therefore \frac{P}{V} = \frac{1}{V_m K} + \frac{P}{V_m}
\]

b) From an appropriate graph of the data in the Table, determine $V_m$ and $K$. Note: You do not have to graph all the data...but you must graph enough data to establish linear behavior (i.e. more than two points). Express $V_m$ in units of meters$^3$.

Solution: Slope=$1/V_m=0.008$mm$^{-3}$. So $V_m=124$mm$^3=1.24\times10^{-7}$ m$^3$. The $y$ intercept is 0.0484 bars/mm$^3$. Therefore
\[
\frac{1}{V_m K} = 0.0484 \text{ bars/mm}^3 \Rightarrow K = \frac{1}{\left(0.0484 \text{ bars/mm}^3\right)(124\text{mm}^3)} = 0.167 \text{ bars}^{-1}
\]
c) From the information determined in part b, determine the pressure of methane at which the surface is half covered at $T=90K$. Gives you answer in bars. Hint: Use the equation from part a.

Solution:

$$\frac{P}{V} = \frac{1}{V_m K} + \frac{P}{V_m} \Rightarrow V = \frac{V_m}{2} \Rightarrow 2P = \frac{1}{V_m K} + \frac{P}{V_m} \Rightarrow P = \frac{1}{K}$$

$$\therefore P = \frac{1}{0.167\text{bars}^{-1}} = 6\text{ bars}$$

d) Suppose the cross sectional area of a methane molecule is $\sigma=10^{-19}m^2$. Use the information obtained in part b to determine the surface area of one gram of mica. Assume the methane vapor behaves ideally.

Solution: You need the molar volume at $T=293K$ and $P=1\text{ atm}$. This is

$$V = \frac{RT}{P} = \frac{(0.0821L \cdot \text{atm} / \text{mole} \cdot K)(293K)}{1\text{ atm}} = 24L = 0.024m^3$$

Then the surface area per gram is

$$A = \frac{\sigma N_A V_m}{V} = \left(10^{-19}m^2\right) \left(6.02 \times 10^{23} \text{mole}^{-1}\right) \left(1.24 \times 10^{-7}m^3 / \text{gm}\right)$$

$$= 0.311m^2 / \text{gm}$$