• Universal gas constant \( R = 8.31 \text{J/mole-K} = 0.0821 \text{L-atm/mole-K} \)
• \( 1 \text{Joule} = 1 \text{J} = 1 \text{Nt-m} = 1 \text{kg-m}^2/\text{s}^2 = 1 \text{C-V} \)
• \( 101 \text{J} = 1 \text{L-atm} \)
• \( 1 \text{Pa} = 1\text{J/m}^3 = 1\text{N/m}^2 \)
• \( 1 \text{atm} = 1.01 \times 10^5 \text{Pa} = 1.01 \text{bar} \)
• \( 1 \text{L} = 10^{-3} \text{m}^3 \)
• Faraday’s constant \( F = 96,485 \text{C/mole} \)

• **Give all answers in MKS units: energy in Joules, pressure in Pascals, volume in m\(^3\), etc.**

**Part 1: (18 points)** Define three out of the six terms given below. Limit your definitions to less than 200 words.

1.1) Define fugacity, as the term is used in thermodynamics.

1.2) Define buoyancy and discuss its relevance to an equilibrium centrifugation experiment.

1.3) Define the Henry’s Law model for dilute solutions and in particular discuss the solute standard state.

1.4) Define activity, as the term is used in thermodynamics.

1.5) Define an ideal solution. How is vapor pressure related to solution composition in this case.

1.6) Define the Donnan effect. How is this effect relevant to ionic equilibria?

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

2.1). “Time release” capsules 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.
2.2) It has been suggested that energy could be produced by digging a canal between the Mediterranean Sea, whose water is 3% salt, and the Dead Sea, whose water is 28% salt. The Dead Sea is almost 500 m below sea level. Using the data given, discuss at least two ways that energy could, in principle, be produced by this scheme.

2.3) Explain why a macromolecular solution would be centrifuged in a salt density gradient. To support your arguments, sketch a density profile for the salt and the macromolecule, at the instant the macromolecular solution reaches equilibrium in the spinning centrifuge rotor. When would you use such an experiment?

2.4) A steel needle will float on a water surface because of surface tension. Suppose a needle floats on the surface of water with one end fixed but leaving the needle free to rotate, as shown below. The surface tension on one side of the needle is $\gamma_1$ and the surface tension on the other side is $\gamma_2$. Suppose $\gamma_1 > \gamma_2$. As a result of this surface tension difference will the needle rotate: clockwise, counterclockwise, or will the needle not rotate at all? Explain your answer.

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

3.1) Calculate the mean activity coefficient of a 0.005M aqueous solution of CaCl$_2$ at 298K. Assume CaCl$_2$ dissociates completely in water at 298K.
3.2) A virus is studied by equilibrium centrifugation. The rotor speed is 800 rpm. 
\[ T = 277 K, V_2 = 0.65 \text{cm}^3/\text{gm}, \rho = 1.002 \text{gm/cm}^3. \] 
At equilibrium a graph of \( \ln C \) versus \( r^2 \), is linear and the ratio \( \frac{C_b}{C_a} = 8.53 \), where \( C_b \) is the concentration of virus at \( r_b = 7.30 \text{ cm} \) and \( C_a \) is similarly the concentration at \( r_a = 7.00 \text{ cm} \). Calculate the molecular weight of the virus.

3.3) A satisfactory equation of state for ammonia is \( P(V - b) = RT \) where \( b = 0.0379 \text{ L mol}^{-1} \). Calculate the fugacity and the fugacity coefficient of the gas when the pressure is 50 atm. Assume \( T = 298 K \).

3.4) Consider the redox reaction \( \text{NADH}(aq) + H^+(aq) \rightarrow \text{NAD}^+(aq) + H_2(g) \). At \( T = 298 K \) the standard free energy change \( (\Delta G^0)_s = 18.12 \text{kJ}/\text{mole} \), where a standard state definition for \( H^+ \) is \([H^+]_0 = 10^{-7} \text{ M} \) has been used. All other aqueous species have standard state concentrations of 1M. For gases the standard state is defined as \( P = 1 \text{ atm} \). If \([\text{NADH}] = 0.015 \text{ M}, [\text{NAD}^+] = 0.0046 \text{ M}, P_{H_2} = 0.01 \text{ atm} \), calculate the free energy change \( \Delta G \) at \( pH = 5 \).

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

4.1 The respiratory system is an exergonic process with the net reaction:
\[ C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(\ell) \]
a) Calculate the Gibbs energy change for this process under standard conditions. The data in the Table will be useful.

<table>
<thead>
<tr>
<th>( \Delta G^0 ) (kJ mol(^{-1}))</th>
<th>( C_6H_{12}O_6(s) )</th>
<th>( O_2(g) )</th>
<th>( CO_2(g) )</th>
<th>( H_2O(\ell) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-910.56</td>
<td>0.0</td>
<td>-394.38</td>
<td>-237.19</td>
<td></td>
</tr>
</tbody>
</table>

| \( S^0 \) (JK\(^{-1}\) mol\(^{-1}\)) | 212.13 | 205.03 | 213.64 | 69.94 |

b) Using your result in part a and the information in the table, calculate the Gibbs energy change at \( T = 310 \text{ K} \). Assume the entropies listed are constant between 298K and 310K.

c) The energy released by the respiratory system is stored by creating a proton gradient across the inner membrane of a cellular organelle called the mitochondrion. The pH inside the inner membrane is 0.75 units higher than the pH outside the inner membrane, i.e. \( pH_\text{inside} - pH_\text{outside} = 0.75 \). The electrostatic potential across the membrane is \( \Delta \psi = \psi_\text{out} - \psi_\text{in} = 0.168V \). With these data calculate the work required to move one mole of protons from inside the inner mitochondrial membrane to outside the inner membrane. Using the data from parts b and c, calculate the moles of protons that can be moved across the inner mitochondrial membrane by the process described in part a. Assume all activity coefficients are unity. Assume \( T = 310 \text{ K} \).
d) Discharge of the pH gradient across the inner mitochondrial involves moving protons back into the inside of the inner mitochondrial membrane. This pH discharge is coupled to ATP synthesis: \( ADP + P_i \rightarrow ATP \) for which \( \Delta G^0 \approx 31kJmol^{-1} \). How many moles of protons must be in principle discharged to synthesize a mole of ATP? In fact 38 moles of ATP are synthesized per mole of glucose metabolized. Given this fact and your results in part c, what is the % efficiency of ATP production by the respiratory system?

4.2) The data below show the binding of NADH to beef heart LDH, taken from data of S. Anderson and G. Weber, *Biochemistry*, 4, 1948 (1965). The NADH binding sites on beef heart LDH act independently and bind NADH with equal affinities. \( T=293K \).

<table>
<thead>
<tr>
<th>( \nu )</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>3.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NADH]</td>
<td>0.50</td>
<td>1.21</td>
<td>2.21</td>
<td>3.51</td>
<td>5.81</td>
<td>9.09</td>
<td>17.5</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Note: [NADH] is tabulated in units of \( 10^{-7}M \)

a) From a Scatchard plot, determine \( N \), the number of NADH binding sites on beef heart LDH and the affinity constant \( K \). You must plot enough data to establish linear behavior. Two points is insufficient. The data are noisy so plot as many points as time allows.

b) From the data in part a, calculate the Gibbs binding energy at \( T=293K \).

c) If the binding experiment is repeated at \( T=310K \), the y intercept is half the value at \( T=293K \). Calculate the enthalpy of binding assuming it is constant between \( T=293K \) and \( T=310K \).

d) At \( T=293K \) calculate the binding entropy, the entropy of the surroundings and the entropy of the universe. Is this result consistent with the result obtained in part a? Explain.