1. For any process in a closed system of constant composition that can only perform pressure-volume work, the first and second laws of thermodynamics may be combined to obtain

$$dU = TdS - PdV \quad \text{(where } U \text{ is internal energy)}$$

In addition, there are three properties; H, A, G defined in terms of Enthalpy, Helmholtz energy, Gibbs energy, respectively. From the above equation we may express in three other ways by use of

$$H = U + PV$$
$$A = U - TS$$
$$G = U + PV - TS.$$

Please show that $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$, $\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$.

2. A cell is set up as follows:

$$Fe / Fe^{2+}(a=0.1) \,\|\, Cd^{2+}(a=0.001) / Cd$$

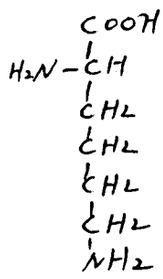
(a) Write the cell reaction.

(b) Calculate the voltage of the cell, the polarity of the electrodes, and the direction of spontaneous reaction.

(c) Calculate the equilibrium constant of the cell reaction.

$$\left(\begin{array}{ll} Cd^{2+} + 2e \rightleftarrows Cd & E^\circ = -0.40\,V \\ Fe^{2+} + 2e \rightleftarrows Fe & E^\circ = -0.44\,V \end{array} \right)$$

3. At what pH is the average net charge on a lysine molecule zero? That is, what is its isoelectric point?



(lysine)

$pK_1 = 2.16$ ($-COOH$)

$pK_2 = 9.18$ ($\alpha-NH_3^+$)

$pK_3 = 10.79$ ($\varepsilon-NH_3^+$)

4. Derive the integrated rate equation for a reversible first-order reaction. (Assume, only A is present initially)