Name:______________________________
Seating Number (not UID #): __________

BE 100: BIOENGINEERING FUNDAMENTALS
FALL 2019

Midterm 1

November 6, 2019

1. (26 points) Let's consider a two-dimensional surface comprised of 1 mole of water. Note that the surface is comprised of only one component (*i.e.*, water). For such a two-dimensional system, the surface tension (γ) multiplied by the differential area stretched ($d\underline{a}$) replaces the conventional $P\underline{V}$ work. The Fundamental Equation (*i.e.*, Combined 1st and 2nd Laws) for this two-dimensional system comprised of 1 mole can therefore be written as:

$$dU = \delta Q + \delta W = TdS + \gamma da$$

when considering a closed system. Unlike $P\underline{V}$ work, $\gamma d\underline{a}$ is positive in the Fundamental Equation because performing work on the system (*i.e.*, increasing the energy of the system) corresponds to stretching the surface. Here are the analogous equations in two-dimensions for the molar enthalpy, the molar Helmholtz free energy, and the molar Gibbs free energy:

$$H \equiv U - \gamma a$$
$$A \equiv U - TS$$
$$G \equiv H - TS$$

The molar heat capacity at constant area, C_a, for the surface has been measured, and it is defined as:

$$C_a \equiv \left(\frac{\delta Q}{\partial T}\right)_a$$

This heat capacity can be treated as a constant in this problem. The same is true for the molar heat capacity at constant surface tension, C_γ, and it is defined as:

$$C_\gamma \equiv \left(\frac{\delta Q}{\partial T}\right)_\gamma$$

The following model represents an equation of state for the surface:

$$\gamma = \frac{\zeta T^4 n}{\underline{a}}$$

where ζ is a constant, n is the number of moles, $\underline{a}$ is the total area, and T is the absolute temperature.

The surface rapidly increases area from (T_1,a_1) to (T_2,a_2). This process is so fast that you can assume it is adiabatic. Do you expect the molar entropy change of the surface for this process to be greater than, less than, or equal to 0? Please explain. Derive an expression for this entropy change for this 1 mole of surface. In addition, derive an expression for the work done on the surface for this rapid area expansion process.

2. Consider a gas, where the following equation of state applies:

$$\mathrm{P} = \frac{\lambda \mathrm{n} \mathrm{T}^2}{\underline{\mathrm{V}}}$$

where λ is a constant, P is the pressure, $\underline{\mathrm{V}}$ is the total volume, n is the number of moles, and T is the absolute temperature. The heat capacities of the gas are also known, and they are constants ($C_V = \beta$ J/(mol*K) and $C_P = \gamma$ J/(mol*K).

a. (8 points) For the equation of state and heat capacities stated above, derive an expression for the following partial derivative in terms of some or all of the parameters β, γ, and λ, and the measurable properties T and P.

$$\left(\frac{\partial H}{\partial U}\right)_V$$

b. (10 points) For the equation of state and heat capacities stated above, derive an expression for the following partial derivative in terms of some or all of the parameters β, γ, and λ, and the measurable properties T and P.

$$\left(\frac{\partial G}{\partial H}\right)_T$$

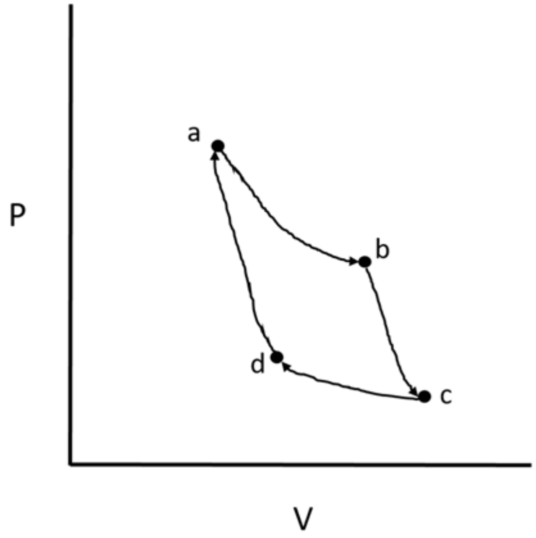
3. (26 points) Consider 1 mole of an ideal gas going through the cycle shown below. From a→b, the ideal gas undergoes a reversible, isothermal expansion at a temperature of T_2 Kelvins. From b→c, the ideal gas undergoes a reversible, adiabatic expansion. In this step, the ideal gas drops to a temperature of T_1 Kelvins. From c→d, the ideal gas undergoes a reversible, isothermal compression at a temperature of T_1 Kelvins. From d→a, the ideal gas undergoes a reversible, adiabatic compression, and the temperature increases back to T_2 Kelvins. The C_V and C_P for this ideal gas are known constants. Please derive an expression for the thermal efficiency of this cycle, where the thermal efficiency is defined as follows:

$$\eta \equiv 1 + \frac{heat\ transferred\ to\ the\ gas\ from\ c \rightarrow d}{heat\ transferred\ to\ the\ gas\ from\ a \rightarrow b}$$

The final expression should only have numbers and T_1 and T_2. In this problem, you will **not** need to prove the following equality for an ideal gas undergoing a reversible, adiabatic expansion/compression

$$PV^{(C_P/C_V)} = constant$$

but you probably want to use the equality.



4. Short answer questions (Part I)

   a. (5 points) Consider a liquid solution comprised of two types of molecules (a pentamer and water). The pentamer is made up of 5 monomer units, and each monomer unit is the size of a water molecule. There are N_p number of indistinguishable pentamer molecules and N_w number of indistinguishable water molecules, where N_p and N_w are both greater than 10^{20}. Each lattice site has z nearest neighbors, which is also known as the coordination number of the lattice. Let's just consider the 4th segment of the (n-1)th pentamer. How many different ways can this 4th segment of the (n-1)th pentamer be placed into the lattice that already contains (n-2)th pentamers but no water molecules. Also assume that the pentamer extends out instead of folding back on itself.

   b. (2 points) You have a 20-sided die and a regular 6-sided die. How many possible configurations are there for rolling both of these dice at the same time?

   c. (2 points) In a process of a gas being compressed in a piston-cylinder setup, the gas in the cylinder has an initial pressure of 1 atm while the gas outside the cylinder has an initial pressure of 3 atm. Will this compression process be reversible or irreversible? Please explain.

d. (2 points) What thermodynamic potential function is maximized or minimized at constant internal energy, volume, and moles? Is it maximized or minimized?

e. (4 points) Consider a surface that has ψ antibodies immobilized on it. Each antibody has 2 binding sites, and on each site, there can be any one of η different antigens bound or no antigens bound. Derive an expression for the entropy of this system. You do not need to worry about the number of molecules of each antigen, since you have way more of each type of antigen molecule than binding sites.

5. Short answer questions (Part 2)

   a. (5 points) Consider a molecule with only one ionizable group. This group is the carboxylic acid, and its pKa is γ. In a particular experiment, the pH is β, and the concentration of the molecule is η mol/L. Derive an expression for the concentration of the neutral form of the molecule.

   b. (1 point) You are considering the process of antigen molecules in an aqueous solution binding to antibody molecules that are immobilized on a surface as the aqueous solution flows over the surface. During this short period of time, some of the antigen molecules bind to the antibodies and an increase in the number of bound antigen molecules is observed as a function of time. Are you investigating an equilibrium or kinetic phenomenon?

c. (4 points) What are the single-letter and three-letter abbreviations for methionine? In addition, although you do not need to do any calculations, please draw methionine at a pH value of 5. Please also label the non-hydrogen side-chain atoms as α, β, etc. Note that the pKa values of the main carboxylic acid and amine groups are 2.28 and 9.21, respectively.

d. (1 point) Consider a protein, where three side chains are given flexibility. The side chain at amino acid residue position 1 has 3 rotamers (a, b, and c), that at position 2 has 3 rotamers (a, b, and c), and that at position 3 has 2 rotamers (a, b). The relevant table of energies is given below. Considering **only** the first round of dead-end elimination, determine the best case scenario for rotamer b in position 3.

		1			2			3		
		a	b	c	a	b	c	a	b	
	a				-1	0	2	6	3	2
1	b				3	1	-7	2	-5	-3
	c				5	2	4	4	-2	-8
	a	-1	3	5				1	-2	1
2	b	0	1	2				4	2	4
	c	2	-7	4				7	-6	-6
	a	6	2	4	1	4	7			0
3	b	3	-5	-2	-2	2	-6			1
		2	-3	-8	1	4	-6	0	1	

e. (1 point) What program do we use in this class to align the sequence of the protein of interest with the sequence of the template protein?

f. (2 points) Does the entropy of a protein increase, decrease, or stay the same when it denatures? Please explain qualitatively in words.

g. (1 point) Give a definition of pharmacodynamics.

1.

Since the system is closed and the process is adiabatic, the molar entropy change of the surface is greater than 0 since the process is irreversible due to being so rapid.

To determine the molar entropy change, let's use the following:

$$(T_1, a_1) \xrightarrow[\text{reversible, isothermal}]{} (T_1, a_2) \xrightarrow[\text{reversible, constant area}]{} (T_2, a_2)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_a dT + \left(\frac{\partial S}{\partial a}\right)_T da \quad \text{Eq. (1)}$$

$$\delta Q = T dS \quad \text{Eq. (2)}$$

$$\left(\frac{\delta Q}{\partial T}\right)_a = T\left(\frac{\partial S}{\partial T}\right)_a \quad \text{Eq. (3)}$$

$$C_a = T\left(\frac{\partial S}{\partial T}\right)_a$$

$$\left(\frac{\partial S}{\partial T}\right)_a = \frac{C_a}{T} \quad \text{Eq. (4)}$$

Combining Eqs. (1) and (4):

$$dS = \frac{C_a}{T} dT + \left(\frac{\partial S}{\partial a}\right)_T da \quad \text{Eq (5)}$$

$$A \equiv U - TS \quad \text{Eq. (6)}$$

$$dA = dU - TdS - SdT \quad \text{Eq. (7)}$$

$$dA = \overbrace{TdS + \gamma da} - TdS - SdT \quad \text{Eq. (8)}$$

$$dA = -SdT + \gamma da \quad \text{Eq (9)}$$

$$\left(\frac{\partial(-S)}{\partial a}\right)_T = \left(\frac{\partial \gamma}{\partial T}\right)_a \quad \text{Eq. (10)}$$

$$\left(\frac{\partial s}{\partial a}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_a \quad \text{Eq (11)}$$

Combining Eqs. (5) and (11):

$$dS = \frac{C_a}{T}\,dT - \left(\frac{\partial \gamma}{\partial T}\right)_a da \quad \text{Eq. (12)}$$

$$\Delta S = \Delta S_{\substack{\text{rev,}\\ \text{isothermal}}} + \Delta S_{\substack{\text{rev,}\\ \text{constant } a}} \quad \text{Eq. (13)}$$

$$\Delta S_{\substack{\text{rev,}\\ \text{isothermal}}} = -\int_{a_1}^{a_2} \underbrace{\left(\frac{\partial \gamma}{\partial T}\right)_a}_{\uparrow\ \text{If T appears, it is constant at } T_1} da \quad \text{Eq. (14)} \quad \text{since } dT = 0$$

$$\Delta S_{\substack{\text{rev,}\\ \text{constant } a}} = C_a \int_{T_1}^{T_2} \frac{dT}{T} \quad \text{Eq. (15)}$$

since C_a is a constant in this problem
<u>and</u> $da = 0$

Combining Eqs. (13) - (15):

$$\Delta S = -\int_{a_1}^{a_2} \left(\frac{\partial \gamma}{\partial T}\right)_a da + C_a \int_{T_1}^{T_2} \frac{dT}{T} \quad \text{Eq. (16)}$$

$$\Delta S = -\int_{a_1}^{a_2} \left(\frac{\partial \gamma}{\partial T}\right)_a da + C_a \ln\left(\frac{T_2}{T_1}\right) \quad \text{Eq. (17)}$$

$$\gamma = \frac{\zeta T^4 n}{\underline{a}} \cdot \frac{\frac{1}{n}}{\frac{1}{n}}$$

$$\gamma = \frac{\zeta T^4}{a} \quad \text{Eq. (18)}$$

$$\left(\frac{\partial \gamma}{\partial T}\right)_a = \frac{4\xi T^3}{a} \quad \text{Eq. (19)}$$

combining Eqs. (17) and (19)

$$\Delta S = -\int_{a_1}^{a_2} \frac{4\xi \overset{\text{constant at } T_1}{T^3}}{a}\,da + C_a \ln\left(\frac{T_2}{T_1}\right) \quad \text{Eq. (20)}$$

$$\Delta S = -4\xi (T_1)^3 \int_{a_1}^{a_2} \frac{da}{a} + C_a \ln\left(\frac{T_2}{T_1}\right) \quad \text{Eq. (21)}$$

$$\Delta S = -4\xi (T_1)^3 \ln\left(\frac{a_2}{a_1}\right) + C_a \ln\left(\frac{T_2}{T_1}\right) \quad \text{Eq. (22)}$$

Let's now derive an expression for the work done on the surface.

$$\Delta U = Q + W \quad \text{Eq. (23)}$$

$Q = 0$ Eq. (24) since adiabatic

$$W = \Delta U \quad \text{Eq. (25)}$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_a dT + \left(\frac{\partial U}{\partial a}\right)_T da \quad \text{Eq. (26)}$$

$$dU = \delta Q + \gamma\, da \quad \text{Eq. (27)}$$

$$\left(\frac{\partial U}{\partial T}\right)_a = \left(\frac{\delta Q}{\partial T}\right)_a + \gamma \underset{\uparrow\, 0}{\left(\frac{\partial a}{\partial T}\right)_a} \quad \text{Eq (28)}$$

$$\left(\frac{\partial U}{\partial T}\right)_a = C_a \quad \text{Eq. (29)}$$

Combining Eqs. (26) and (29):

$$dU = C_a\, dT + \left(\frac{\partial U}{\partial a}\right)_T da \quad \text{Eq (30)}$$

$$dU = T\,dS + \gamma\,da \quad \text{Eq (31)}$$

$$\left(\frac{\partial U}{\partial a}\right)_T = T\left(\frac{\partial S}{\partial a}\right)_T + \gamma \underset{1}{\left(\frac{\partial a}{\partial a}\right)_T} \quad \text{Eq. (32)}$$

$$\left(\frac{\partial U}{\partial a}\right)_T = T\left(\frac{\partial S}{\partial a}\right)_T + \gamma \quad \text{Eq. (33)}$$

Combining Eqs. (11) and (33):

$$\left(\frac{\partial U}{\partial a}\right)_T = -T\left(\frac{\partial \gamma}{\partial T}\right)_a + \gamma \quad \text{Eq (34)}$$

Combining Eqs. (19) and (34):

$$\left(\frac{\partial U}{\partial a}\right)_T = -T \cdot \frac{4\xi T^3}{a} + \gamma \quad \text{Eq (35)}$$

Combining Eqs. (18) and (35)

$$\left(\frac{\partial U}{\partial a}\right)_T = -\frac{4\xi T^4}{a} + \frac{\xi T^4}{a}$$

$$\left(\frac{\partial U}{\partial a}\right)_T = \frac{-3\xi T^4}{a} \quad \text{Eq (36)}$$

Combining Eqs. (30) and (36):

$$dU = C_a\,dT - \frac{3\xi T^4}{a}\,da \quad \text{Eq (37)}$$

Will again choose the reversible, isothermal step followed by the reversible, constant area step

$$\Delta U = \Delta U_{\substack{\text{rev,}\\ \text{isothermal}}} + \Delta U_{\substack{\text{rev,}\\ \text{constant } a}} \quad \text{Eq. (38)}$$

$$\Delta U_{\substack{\text{rev,}\\ \text{isothermal}}} = -3\xi \int_{a_1}^{a_2} \frac{\overset{\text{constant at } T_1}{T^4}}{a}\,da \quad \text{Eq. (39) Since } dT=0$$

$$\Delta U_{\substack{\text{rev,}\\ \text{isothermal}}} = -3\xi (T_1)^4 \int_{a_1}^{a_2} \frac{da}{a} = -3\xi (T_1)^4 \ln\left(\frac{a_2}{a_1}\right) \quad \text{Eq (40)}$$

$$\Delta U_{\text{rev, constant } a} = C_a \int_{T_1}^{T_2} dT \quad \text{Eq. (41)}$$ since C_a is a constant in this problem and $da = 0$

$$\Delta U_{\text{rev, constant } a} = C_a (T_2 - T_1) \quad \text{Eq. (42)}$$

Combining Eqs. (38), (40), and (42):

$$\Delta U = -3\xi (T_1)^4 \ln\left(\frac{a_2}{a_1}\right) + C_a (T_2 - T_1) \quad \text{Eq. (43)}$$

Combining Eqs. (25) and (43):

$$W = -3\xi (T_1)^4 \ln\left(\frac{a_2}{a_1}\right) + C_a (T_2 - T_1)$$

*Note that your expressions will look a little different if you proceeded with a reversible, constant area step followed by a reversible, isothermal step since I made up this equation of state. As long as you did your work correctly, you will get all the points.

2.

a.

$$\left(\frac{\partial H}{\partial U}\right)_V = ?$$

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{\left(\frac{\partial H}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial T}\right)_V} \quad \text{Eq. (1)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{Eq. (2)}$$

Combining Eqs. (1) and (2):

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{\left(\frac{\partial H}{\partial T}\right)_V}{C_V} \quad \text{Eq (3)}$$

$$dH = TdS + VdP \quad \text{Eq. (4)}$$

$$\left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V \quad \text{Eq (5)}$$

$$\delta Q = TdS \quad \text{Eq. (6)}$$

$$\left(\frac{\delta Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{Eq. (6)}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \text{Eq. (7)}$$

Combining Eqs. (3), (5), and (7)

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{C_V + V\left(\frac{\partial P}{\partial T}\right)_V}{C_V} \quad \text{Eq. (8)}$$

$$P = \frac{\lambda n T^2}{\underline{V}} \cdot \frac{\frac{1}{n}}{\frac{1}{n}}$$

$$P = \frac{\lambda T^2}{V} \quad \text{Eq. (9)}$$

$$V = \frac{\lambda T^2}{P} \quad \text{Eq. (10)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = 2 \frac{\lambda}{V} T$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{2\lambda T}{V} \quad \text{Eq. (11)}$$

Combining Eqs. (8) and (11)

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{C_V + V\left(\frac{2\lambda T}{V}\right)}{C_V}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{C_V + 2\lambda T}{C_V} \quad \text{Eq. (12)}$$

Since $C_V = \beta$

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{\beta + 2\lambda T}{\beta} \quad \text{Eq. (13)}$$

Another Approach:

$$H \equiv U + PV \quad \text{Eq (14)}$$

$$dH = dU + PdV + VdP \quad \text{Eq. (15)}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = \underset{\overset{\uparrow}{1}}{\left(\frac{\partial U}{\partial U}\right)_V} + P \underset{\overset{\uparrow}{0}}{\left(\frac{\partial V}{\partial U}\right)_V} + V\left(\frac{\partial P}{\partial U}\right)_V \quad \text{Eq. (16)}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = 1 + \frac{V}{\left(\frac{\partial U}{\partial P}\right)_V} \quad \text{Eq. (17)}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = 1 + \frac{V}{\left(\frac{\left(\frac{\partial U}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial T}\right)_V}\right)} \quad \text{Eq. (18)}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = 1 + \frac{V\left(\frac{\partial P}{\partial T}\right)_V}{C_V} \quad \text{Eq. (19)}$$

$$\left(\frac{\partial H}{\partial U}\right)_V = \frac{C_V + V\left(\frac{\partial P}{\partial T}\right)_V}{C_V} \quad \text{Eq. (20)} \qquad \text{SAME AS EQ. (8)}$$

b.)

$$\left(\frac{\partial G}{\partial H}\right)_T = ?$$

$$G \equiv H - TS \quad \text{Eq.}(21)$$

$$dG = dH - TdS - SdT \quad \text{Eq.}(22)$$

$$\left(\frac{\partial G}{\partial H}\right)_T = \underset{\overset{\uparrow}{1}}{\left(\frac{\partial H}{\partial H}\right)_T} - T\left(\frac{\partial S}{\partial H}\right)_T - S\underset{\overset{\uparrow}{0}}{\left(\frac{\partial T}{\partial H}\right)_T} \quad \text{Eq.}(23)$$

$$\left(\frac{\partial G}{\partial H}\right)_T = 1 - T\left(\frac{\partial S}{\partial H}\right)_T \quad \text{Eq.}(24)$$

$$\left(\frac{\partial G}{\partial H}\right)_T = 1 - \frac{T}{\left(\frac{\partial H}{\partial S}\right)_T} \quad \text{Eq.}(25)$$

$$dH = TdS + VdP \quad \text{Eq.}(26)$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T\underset{\overset{\uparrow}{1}}{\left(\frac{\partial S}{\partial S}\right)_T} + V\left(\frac{\partial P}{\partial S}\right)_T \quad \text{Eq.}(27)$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T + V\left(\frac{\partial P}{\partial S}\right)_T \quad \text{Eq.}(28)$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T + \frac{V}{\left(\frac{\partial S}{\partial P}\right)_T} \quad \text{Eq.}(29)$$

$$dG = -SdT + VdP \quad \text{Eq.}(30)$$

$$\left(\frac{\partial(-S)}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{Eq.}(31)$$

Combining Eqs. (29) and (31):

$$\left(\frac{\partial H}{\partial S}\right)_T = T - \frac{V}{\left(\frac{\partial V}{\partial T}\right)_P} \quad \text{Eq. (32)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{2\lambda T}{P} \quad \text{Eq. (33)}$$

Combining Eqs. (10), (32), and (33)

$$\left(\frac{\partial H}{\partial S}\right)_T = T - \frac{\frac{\lambda T^2}{P}}{\frac{2\lambda T}{P}}$$

$$\left(\frac{\partial H}{\partial S}\right)_T = T - \frac{T}{2}$$

$$\left(\frac{\partial H}{\partial S}\right)_T = \frac{1}{2} T \quad \text{Eq. (34)}$$

Combining Eqs. (25) and (34):

$$\left(\frac{\partial G}{\partial H}\right)_T = 1 - \frac{T}{\frac{1}{2}(T)} = 1 - 2$$

$$\left(\frac{\partial G}{\partial H}\right)_T = -1 \quad \text{Eq (35)}$$

Another Approach:

$$\left(\frac{\partial G}{\partial H}\right)_T = \frac{\left(\frac{\partial G}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial P}\right)_T} \quad \text{Eq.(36)}$$

$$dG = -SdT + VdP \quad \text{Eq. (30) repeat}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{Eq. (37)}$$

Combining Eqs. (36) and (37)

$$\left(\frac{\partial G}{\partial H}\right)_T = \frac{V}{\left(\frac{\partial H}{\partial P}\right)_T} \quad \text{Eq. (38)}$$

$$dH = TdS + VdP \quad \text{Eq. (4) repeat}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\underset{\uparrow 1}{\left(\frac{\partial P}{\partial P}\right)_T} \quad \text{Eq. (39)}$$

Combining Eqs. (31) and (39):

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad \text{Eq.(40)}$$

Combining Eqs. (38) and (40):

$$\left(\frac{\partial G}{\partial H}\right)_T = \frac{V}{V - T\left(\frac{\partial V}{\partial T}\right)_P} \quad \text{Eq. (41)}$$

Combining Eqs. (10), (33), and (41)

$$\left(\frac{\partial G}{\partial H}\right)_T = \frac{\frac{\lambda T^2}{P}}{\frac{\lambda T^2}{P} - T\,\frac{2\lambda T}{P}} = \frac{1}{-1} = -1 \quad \text{SAME RESULT}$$

3.

$$\eta \equiv 1 + \frac{Q_{cd}}{Q_{ab}} \quad \text{Eq. (1)}$$

where Q_{cd} is the heat transferred to the gas from c→d

and Q_{ab} is the heat transferred to the gas from a→b

This problem is therefore focused on determining Q_{ab} and Q_{cd}

Consider a→b

$$\Delta U_{ab} = Q_{ab} + W_{ab} \quad \text{Eq. (2)}$$

$$Q_{ab} = \Delta U_{ab} - W_{ab} \quad \text{Eq. (3)}$$

$$W_{ab} = -\int_{V_a}^{V_b} P\,dV \quad \text{Eq. (4)} \qquad P = \frac{RT}{V} \quad \text{Eq. (4A)}$$

constant at T_2 is the reversible path

$$W_{ab} = -\int_{V_a}^{V_b} \frac{RT}{V}\,dV \quad \text{Eq. (5)}$$

$$W_{ab} = -RT_2 \ln\left(\frac{V_b}{V_a}\right) \quad \text{Eq. (6)}$$

Combining Eqs. (3) and (6)

$$Q_{ab} = \Delta U_{ab} + RT_2 \ln\left(\frac{V_b}{V_a}\right) \quad \text{Eq. (7)}$$

Need to now determine ΔU_{ab}

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{Eq. (8)}$$

↳Need T for an ideal gas since we expect an ideal gas to only depend on T and not V and P as ideal gas molecules have kinetic energies but no interactions and no size.

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \text{Eq. (9)}$$

Combining Eqs. (8) and (9):

$$dU = C_V\,dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{Eq. (10)}$$

$$dU = T\,dS - P\,dV \quad \text{Eq. (11)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \quad \text{Eq. (12)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \quad \text{Eq. (13)}$$

$$dA = -S\,dT - P\,dV \quad \text{Eq. (14)}$$

$$\left(\frac{\partial(-S)}{\partial V}\right)_T = \left(\frac{\partial(-P)}{\partial T}\right)_V \quad \text{Eq. (15)}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{Eq. (16)}$$

Combining Eqs. (13) and (16):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{Eq. (17)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \text{Eq (18)}$$

Combining Eqs. (4A), (17), and (18)

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - \frac{RT}{V} \quad \text{Eq. (19)}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{Eq. (20)}$$

Combining Eqs. (10) and (20):

$$dU = C_v dT + 0 \cdot dV \quad \text{Eq (21)}$$

$$dU = C_v dT \quad \text{Eq (22)}$$

$$\Delta U_{ab} = \int_{T_2}^{T_2} C_v \, dT = C_v (T_2 - T_2) \quad \text{Eq. (23)}$$

$$\Delta U_{ab} = 0 \quad \text{Eq. (24)}$$

Combining Eqs. (7) and (24):

$$Q_{ab} = RT_2 \ln\left(\frac{V_b}{V_a}\right) \quad \text{Eq. (25)}$$

Consider $c \rightarrow d$

$$\Delta U_{cd} = Q_{cd} + W_{cd} \quad \text{Eq. (26)}$$

$$Q_{cd} = \Delta U_{cd} - W_{cd} \quad \text{Eq. (27)}$$

$$W_{cd} = -\int_{V_c}^{V_d} P \, dV \quad \text{Eq. (28)}$$

constant at T_1 for this

$$W_{cd} = -\int_{V_c}^{V_d} \frac{RT}{V} dV \quad \text{Eq. (29)}$$

$$W_{cd} = -RT_1 \ln\left(\frac{V_d}{V_c}\right) \quad \text{Eq. (30)}$$

$$\Delta U_{cd} = \int_{T_1}^{T_1} C_v dT = C_v (T_1 - T_1) \quad \text{Eq (31)}$$

$$\Delta U_{cd} = 0 \quad \text{Eq. (32)}$$

Combining Eqs. (27), (30), and (32):

$$Q_{cd} = RT_1 \ln\left(\frac{V_d}{V_c}\right) \quad \text{Eq. (33)}$$

Combining Eqs. (1), (25), and (32):

$$\eta = 1 + \frac{RT_1 \ln\left(\frac{V_d}{V_c}\right)}{RT_2 \ln\left(\frac{V_b}{V_a}\right)} \quad \text{Eq (34)}$$

$$\eta = 1 + \frac{T_1}{T_2} \frac{\ln\left(\frac{V_d}{V_c}\right)}{\ln\left(\frac{V_b}{V_a}\right)} \quad \text{Eq. (35)}$$

We cannot have V_a, V_b, V_c, and V_d in the final answer.

Let's see if we can use the given equality for reversible, adiabatic expansions/compressions of an ideal gas to obtain a relationship between T and V.

$$PV^{c_p/c_v} = \text{constant} \quad \text{Eq. (36)}$$

Combining Eqs. (4A) and (36)

$$\frac{RT}{V} V^{c_p/c_v} = \text{constant} \quad \text{Eq. (37)}$$

$$T V^{\left(\frac{c_p}{c_v} - 1\right)} = \frac{\text{constant}}{R} \quad \text{Eq (38)}$$

Consider b → c

$$T_b V_b^{\left(\frac{c_p}{c_v} - 1\right)} = T_c V_c^{\left(\frac{c_p}{c_v} - 1\right)} \quad \text{Eq. (39)}$$

$$T_b = T_2 \quad \text{Eq. (40)}$$

$$T_c = T_1 \quad \text{Eq (41)}$$

Combining Eqs. (39)-(41):

$$T_2 V_b^{\left(\frac{c_p}{c_v}-1\right)} = T_1 V_c^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq. (42)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_b}{V_c}\right)^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq. (43)}$$

Consider $d \to a$

$$T_d V_d^{\left(\frac{c_p}{c_v}-1\right)} = T_a V_a^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq. (44)}$$

$$T_d = T_1 \qquad \text{Eq. (45)}$$

$$T_a = T_2 \qquad \text{Eq (46)}$$

$$T_1 V_d^{\left(\frac{c_p}{c_v}-1\right)} = T_2 V_a^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq (47)}$$

$$\frac{T_1}{T_2} = \left(\frac{V_a}{V_d}\right)^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq. (48)}$$

Combining Eqs. (43) and (48):

$$\left(\frac{V_b}{V_c}\right)^{\left(\frac{c_p}{c_v}-1\right)} = \left(\frac{V_a}{V_d}\right)^{\left(\frac{c_p}{c_v}-1\right)} \qquad \text{Eq (49)}$$

$$\frac{V_b}{V_c} = \frac{V_a}{V_d} \qquad \text{Eq (50)}$$

$$\frac{V_b}{V_a} = \frac{V_c}{V_d} \qquad \text{Eq (51)}$$

Combining Eqs. (35) and (51):

$$\eta = 1 + \frac{T_1}{T_2} \frac{\ln\left(\frac{V_d}{V_c}\right)}{\ln\left(\frac{V_c}{V_d}\right)} \quad \text{Eq (52)}$$

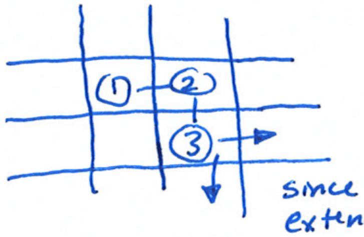
$$\eta = 1 + \frac{T_1 \ln\left(\frac{V_d}{V_c}\right)}{T_2 \ln\left[\left(\frac{V_d}{V_c}\right)^{-1}\right]} \quad \text{Eq (53)}$$

$$\eta = 1 + \frac{T_1 \ln\left(\frac{V_d}{V_c}\right)}{(-T_2) \ln\left(\frac{V_d}{V_c}\right)}$$

$$\eta = 1 - \frac{T_1}{T_2}$$

4.

a. For the 4th segment of the (n-1)th pentamer, there is a restriction because it must be placed next to the 3rd segment. Moreover, it can only be placed in a neighboring site that is empty since the 2nd segment of the (n-1)th pentamer is blocking a neighboring site <u>and</u> segments from the first (n-2) pentamers may be occupying a neighboring site.



max # of sites available to the 4th segment of the (n-1)th polymer $= (\overset{\text{\# of nearest neighbors}}{z} - 1)$

one of sites is occupied by the 2nd segment of the (n-1)th polymer

probability that any lattice site is empty $= \dfrac{N_{total} - \overbrace{5(n-2)}^{\text{sites occupied by first (n-2) polymers}} - 3}{N_{total} - 1}$

sites occupied by first 3 segments of the (n-1)th polymer

need to place next to the 3rd segment of the (n-1)th polymer, so the site where the 3rd segment is located is unavailable for consideration.

# of ways to place the 4th segment of the (n-1)th polymer $= (z-1)\left[\dfrac{N_{total} - 5(n-2) - 3}{N_{total} - 1}\right]$

where $N_{total} = N_W + 5N_p$

b.

$$\Omega = \Omega_{\substack{\text{20-sided} \\ \text{die}}} \, \Omega_{\substack{\text{6-sided} \\ \text{die}}}$$

$$\Omega = 20 \cdot 6 = 120$$

c. The compression will be irreversible since the pressure difference is more than differential in magnitude.

d.

$$d\underline{S} = \frac{1}{T}\, d\underline{U} + \frac{P}{T}\, d\underline{V} - \sum_{i=1}^{c} \frac{\mu_i}{T}\, dn_i$$

Entropy is maximized.

e.

$\underline{S} = k_B \ln \Omega$ Eq. (1)

$$\Omega = \underbrace{(\eta+1)(\eta+1)\ \ldots\ (\eta+1)}_{}$$

24 of these since each antibody has 2 binding sites

$\Omega = (\eta+1)^{24}$ Eq. (2)

Combining Eqs. (1) and (2):

$\underline{S} = k_B \ln\left[(\eta+1)^{24}\right]$ Eq. (3)

$\underline{S} = 24\, k_B \ln(\eta+1)$ Eq. (4)

5.

a.

deprotonated carboxylic acid group $= X^{\ominus}$

Let's use the Henderson – Hasselbalch equation

$$pH = pKa + \log\left(\frac{[X^{\ominus}]}{[HX]}\right) \quad Eq.(1)$$

$$\frac{[X^{\ominus}]}{[HX]} = 10^{pH-pKa} \quad Eq\ (2)$$

$$[HX] = \frac{[X^{\ominus}]}{10^{pH-pKa}} \cdot \frac{10^{pKa-pH}}{10^{pKa-pH}} \quad Eq(3)$$

$$[HX] = 10^{pKa-pH}[X^{\ominus}] \quad Eq\ (4)$$

$$[X^{\ominus}] + [HX] = \eta\ \frac{mol}{L} \quad Eq(5)$$

Combining Eqs. (4) and (5):

$$[X^{\ominus}]\left(1+10^{pKa-pH}\right) = \eta\ \frac{mol}{L} \quad Eq.(6)$$

$$[X^{\ominus}] = \frac{\eta\ \frac{mol}{L}}{1+10^{pKa-pH}} \quad Eq(7)$$

Combining Eqs. (4) and (7):

$$[HX] = \frac{10^{pKa-pH}}{1+10^{pKa-pH}}\ \eta\ \frac{mol}{L} \quad Eq(8)$$

$$[HX] = \frac{10^{(\gamma-\beta)}}{1+10^{(\gamma-\beta)}}\ \eta\ \frac{mol}{L} \quad Eq(9)$$

Another approach which is more logical is to solve Eq. (2) for $[X^{\ominus}]$ to get $[HX]$ more directly

$$[X^{\ominus}] = 10^{pH-pKa}[HX] \quad \text{Eq. (10)}$$

Combining Eqs. (5) and (10):

$$[HX]\left(10^{pH-pKa}+1\right) = \eta\,\frac{mol}{L} \quad \text{Eq (11)}$$

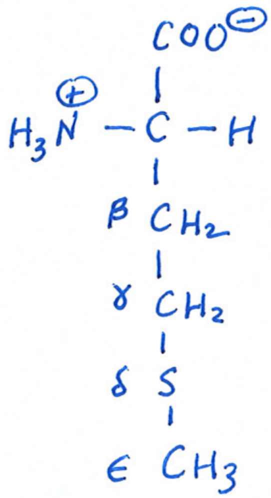
$$[HX] = \frac{\eta\,\frac{mol}{L}}{10^{pH-pKa}+1} \quad \text{Eq (12)}$$

Eq. (12) is the same as Eq. (8) if you multiply Eq. (12) by $\dfrac{10^{pKa-pH}}{10^{pKa-pH}}$, which is multiplying by 1

b. Kinetic phenomenon

c.

Methionine = Met = M



d.

Best case scenario for rotamer b in position 3

E(3b) + min[E(1a, 3b) or E(1b, 3b) or E(1c, 3b)]

+ min[E(2a, 3b) or E(2b, 3b) or E(2c, 3b)]

= 1 + min[3 or −5 or −2] + min[−2 or 2 or −6]

= 1 + (−5) + (−6)

= −10

e. CLUSTAL W

f. The entropy of a protein increases when it denatures because it now has major conformational changes, and for each major conformation, the protein has many rotational degrees of freedom. When the protein is folded, although it has many rotational degrees of freedom, it only has a single major conformation.

g. What the drug does to the body