Chem 440
Practice exam

Hour Exam 2

Useful numbers and formulas you may need are given at the end.
You must turn in your answer by 10:55 to get full credit.

1. (10 pts) Consider a bag containing three 1-dollar coins and six quarters. You are allowed to pull out exactly one coin in every draw.

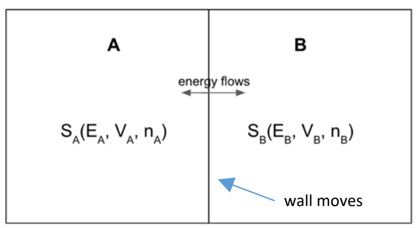
a. (1+1) If randomly chosen, **what is** the probability of pulling a single quarter? **Of pulling a** single 1-dollar coin?

b. (2) **What is** the probability of pulling a quarter, a 1-dollar coin, and then another quarter in that order in three draws?

c. (2+1) **What** is the average value *E* of a single draw? **Is it possible** to pull out that amount in one draw?

d. (2+1) Let's say we add a half dollar to the bag. **What is** the new average value of a single draw? **Is it possible** to pull out that amount in a single draw?

2. (10 pts) Consider an isolated system made up of two subsystems A and B divided by a moveable wall that also allows heat, but not particles, to pass through (dn_A=dn_B=0). We allow the subsystems to come to equilibrium:



a. (1+1) **Can** work be exchanged between A and B? **Is** entropy extensive (additive)?

b. (1+1) Based on part a., **what is** the change in total entropy dS_{tot} in terms of dS_A and dS_B? In equilibrium dS_{tot} =0, therefore **give** the simple relation between dS_A and dS_B when A and B are in equilibrium.

c. (1+1+1) **Write down** the general formula for dE when dn=0 [see 'Useful Information']. Solve for dS, and **write down** the **two** formulas for dS_A and dS_B, putting subscripts "A" or "B" on all variables to distinguish the two subsystems.

d. (1+1+1) **Insert** the two formulas from part c. into part b. at equilibrium. **Use** conservation of total energy $dE= dE_A + dE_B$ =0 and total volume $dV= dV_A + dV_B$ =0 to eliminate dE_B and dV_B from your formula. **Regroup** your formula to show that in equilibrium, since dE_A and dV_A are independent changes, therefore $T_A= T_B$ and $P_A= P_B$.

3. (10 pts) E is a function of S, V, and n. Therefore $dE = TdS - PdV + \mu dn$. F is a function of T, V, and n. Let's figure out what dF is equal to.

a. (2+1) Based on the above, **what** thermodynamic variable is $\frac{\partial E}{\partial S}$ equal to? **Is it** intensive or extensive?

b. (2) If F is the intercept of E as a function of slope $\frac{\partial E}{\partial S}$, **write** F in terms of E and simple extensive and intensive variables using your result in a. [Hint: you could look at 'Useful Information'.]

c. (2) **Write down** the total differential $dF = \cdots$ of your expression for F in part b., keeping in mind that in general the total differential of a product of two variables, AB, equals $d(AB) = AdB + BdA$.

d. (2+1) Substitute dE by $TdS - PdV + \mu dn$ into your result from c. and cancel terms to **write down** the formula for dF. **What is** the derivative $\frac{\partial F}{\partial T}$ equal to in terms of a simple variable?

4. (10 pts) Let us calculate the partition function $Z(T)$ for folding of a peptide with N=10 amino acids. Each amino acid has W_{AA}=3 microstates.

a. (2+1) How many total microstates W_{tot} does the whole peptide with N amino acids have? [Hint: W is a multiplicative quantity, not extensive.] Give a **formula** in terms of N and W_{AA}, and **numerical** value.

b. (1) The folded state has W_F=1 microstate. All the other microstates make up the unfolded macrostate. Given your answer in a., **what is** W_U, the number of microstates in the unfolded state?

c. (2) Assume the folded state has energy E_F=0, and the unfolded state has energy E_U=29 kJ/mole. **Write down** the canonical partition function $Z(T)$ for the peptide in terms of W_F, W_U, E_U, and T.

d. (1+1+1+1) **Calculate** the partition function at T=298 K. **Is** the peptide mostly folded or mostly unfolded? **Calculate** the partition function at T=350 K. **Is** the peptide mostly folded or mostly unfolded? [Hint: the partition function Z is the number of microstates accessible to the system at temperature T, and the folded state accounts for 1 microstate.]

Useful information:

Constants: 1 atomic mass unit ≈ 1.66 x 10^{-27} kg; mass of electron $m_e \approx 9.109 \times 10^{-31}$ kg; Planck's constant $h \approx 6.626 \times 10^{-34}$ J·s; $\hbar = h/2\pi$; Avogadro's number $N_A = 6.02214076 \cdot 10^{23}$; $k_B \approx 1.38 \cdot 10^{-23}$ J/K; gas constant $R \approx 8.31$ J/mole/K, or $R \approx -0.08205\ L \cdot atm \cdot mol^{-1} \cdot K^{-1}$; Faraday's number ≈ 96485 Coulombs/mole. $c \approx 3 \cdot 10^8$ m/s; e ≈ 1.6.10^{-19} Coulombs; Avogadro's number $N_A = 6.02214076 \cdot 10^{23}$; gas constant $R \approx 8.31$ J/mole/K = $k_B \cdot N_A$;

Partition functions and thermodynamic potentials: $\rho_j = 1/W_j$ (constant energy);
$\rho_j = W_j \exp(-E_j/RT)/Z$; $Z = \exp(-F/RT) = \Sigma\, W_j \exp(-E_j/RT)$ (constant temperature); average $A = \Sigma\, \rho_j A_j$;

$dE = TdS - PdV + \mu dn$, and this can be solved for dS, dV or dn.

$E(S,V,\ldots)$; $F(T,V,\ldots)=E-TS$; $H(S,P,\ldots)=E+PV$; $G(T,P,\ldots)=H-TS$ all contain the same information.

Conversions: 1 Å = 0.1 nm = 100 pm = 10^{-10} m; wavenumber (cm^{-1}) = $\frac{10^7}{\lambda\,(nm)}$

Math: $N! = N(N-1)(N-2) \cdots 3 \cdot 2 \cdot 1 \approx N^N - N\ln N$; $0! = 1$

Energy levels: $E(n) = -Ry/n^2$, where $Ry = 2.1798741 \cdot 10^{-18}$ J (H atom); $E_n = h\nu(n+1/2)$ (spring)

Color and wavelength: