Chem 440
Fall 2023

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.

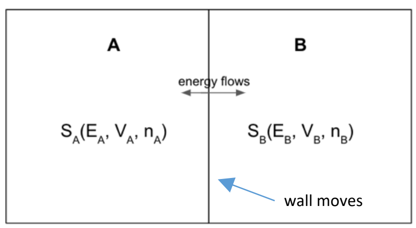
a. (1+1) If randomly chosen, **what is** the probability of pulling a single quarter? **Of pulling a** single 1-dollar coin?

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 energy (i.e. 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? At 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 $\mathrm{T}dS - PdV + \mu dn$ 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=25 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.]

<u>Useful information:</u>

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.

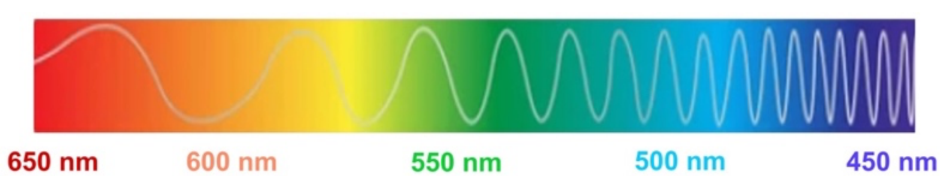
$E(S,V,\ldots)$; $F(T,V,\ldots)=E-TS$; $H(S,P, ,\ldots)=E+PV$; $G(T,P,\ldots)=H-TS$ all contain the same information.

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:



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Solutions:

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

a. (1+1) If randomly chosen, **what is** the probability of pulling a quarter? **Of pulling a** 1-dollar coin?
Solution: There are 3+6=9 total coins. P(one quarter) = $\frac{6}{9}$ =$\frac{2}{3}$; and P(one 1-dollar) = $\frac{3}{9} = \frac{1}{3}$.

b. (2) **What is** the probability of pulling a quarter, a 1-dollar coin, and then another quarter <u>in that order</u> in three draws?
P(quarter, 1-dollar, then quarter) = $\frac{6}{9} * \frac{3}{8} * \frac{5}{7} = 0.18 = 18\%$. Note that the denominator decreases by one in every successive draw because there is one less coin in the bag.

c. (2+1) What is the average value *E* of a single draw? Is it possible to pull out that amount in one draw?
Solution: $E(X) = \sum X_i P_i = \left(1 * \frac{3}{9}\right) + \left(\frac{1}{4} * \frac{6}{9}\right) = 0.50$
It is not possible to draw 50 cents from the bag in a single attempt. This goes to show that the average value does not necessarily correlate to any single value within a sample.

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?
Solution: $E(X) = \sum X_i P_i = \left(1 * \frac{3}{10}\right) + \left(\frac{1}{4} * \frac{6}{10}\right) + \left(\frac{1}{2} * \frac{1}{10}\right) = 0.3 + 0.15 + 0.05 = 0.50$
Yes, in this case you can pull the half-dollar to get 50 cents, the average value of the sample.

2. (10 pts) Consider an isolated system made up of two subsystems A and B divided by a <u>moveable</u> wall that also allows energy (i.e. heat), but not particles to pass through (dn_A=dn_B=0). We allow the sub-systems to come to equilibrium.

a. (1+1) Can work be exchanged between **A** and **B**? Is entropy extensive (additive)?
Solution: Yes, work can also be exchanged between the subsystems because the wall is moveable wall. (The same is true for heat, as stated in the problem.) Yes, entropy is 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? At equilibrium dS_{tot} =0, therefore **give** the simple relation between dS_A and dS_B when A and B are in equilibrium.
Solution: $dS_{tot} = dS_A + dS_B = 0$
$dS_A = -dS_B$

c. (1+1+1) **Write down** the general formula for dE when dn=0. 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 sub subsystems.
Solution: In general $dE = TdS - PdV + \mu dn$, so $dE = TdS - PdV$ when dn =0.
Solving for dS for each subsystem, $dS_A = \frac{1}{T_A} dE_A + \frac{P_A}{T_A} dV_A$ and $dS_B = \frac{1}{T_B} dE_B + \frac{P_B}{T_B} dV_B$

d. (1+1+1) **Insert** the two formulas from c. into 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 $P_A = P_B$.

Solution: $dS_A = -dS_B \Rightarrow \frac{1}{T_A}dE_A + \frac{P_A}{T_A}dV_A = -\frac{1}{T_B}dE_B - \frac{P_B}{T_B}dV_B$.

Since $dE_A = - dE_B = 0$ and $dV_A = - dV_B \Rightarrow = \frac{1}{T_A}dE_A + \frac{P_A}{T_A}dV_A = \frac{1}{T_B}dE_A - \frac{P_B}{T_B}dV_A$.

Collecting terms, $= \left(\frac{1}{T_A} - \frac{1}{T_B}\right)dE_A = -\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)dV_A$. Since dE_A an d dV_A are independent changes, this can only be true if $\left(\frac{1}{T_A} - \frac{1}{T_B}\right) = 0$ and thus $T_A = T_B$, and also $= -\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) = 0$ and thus $P_A = P_B$

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

Solution: $\frac{\partial E}{\partial S} = T$. Intensive

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'.]

Solution: $F = E - TS$

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

Solution: $dF = dE - TdS - SdT$

d. (2+1) Substitute dE by $dS - PdV + \mu dn$ 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?

Solution: $dF = (TdS - PdV + \mu dn) - TdS - SdT = -SdT - PdV + \mu dn$.

Since $dF \sim -SdT$, $\partial F/\partial T = -S$

4. (10 pts) Let us calculate the partition function $Z(T)$ for folding for 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.

Solution: $W_{tot} = W_{AA}^N = 3^{10} = 59049$.

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?

Solution: $W_U = W_{tot} - 1 = 59048$

c. (2) Assume the folded state has energy E_F=0, and the unfolded state has energy E_U=25 kJ/mole. **Write down** the canonical partition function $Z(T)$ for the peptide in terms of W_F, W_U, E_U, and T.

Solution: $Z(T) = W_F + W_U e^{-\frac{E_U}{RT}} = 1 + 59048 e^{-\frac{25\ \text{kJ/mole}}{0.00831 * T(K)}}$

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 has 1 microstate.]

Solution:

$Z(298) = 1 + 59048e^{-\frac{25\ \mathrm{kJ/mole}}{0.00831*298}} = 3.437$. Mostly unfolded because 2.437 (on average) of the unfolded microstates are populated, so there is almost 3 times as much unfolded peptide as there is folded peptide.

$Z(350) = 1 + 59048e^{-\frac{25\ \mathrm{kJ/mole}}{0.00831*350}} = 11.92$. Even more unfolded because now 10.92 (on average) of the unfolded microstates are populated, so there is almost 11 times as much unfolded peptide as there is folded peptide.