Discussion 10

Name and section: ______________________________

$$
\begin{aligned}
U(S,V,N) &= TS - pV + \mu N \\
S(U,V,N) &= \frac{U}{T} + \frac{p}{T}V - \frac{\mu}{T}N \\
F(V,T,N) &= U - TS \\
G(p,T,N) &= U + pV - TS \\
H(S,p,N) &= U + pV
\end{aligned}
$$

T	G	-p
F		H
V	U	-S

Good **P**hysicists **H**ave **S**tudied **U**nder **V**ery **F**ine **T**eachers

V	F	T
U		G
-S	H	-p

Valid **F**acts and **T**heoretical **U**nderstanding **G**enerate **S**olutions to **H**ard **P**roblems

1. Maxwell Relations

   (a) Derive the Maxwell relations from U, F, G, and H.

   (b) How are these Maxwell relations related to the squares above?

A general partition function Z for a Boltzmann distribution with discrete energy states is

$$Z = \sum_i \mathrm{e}^{-\beta E_i}$$

where $\beta = (k_B T)^{-1}$, E_i is the energy of microstate i, and the sum is over all possible microstates.

2. Consider a gas of N carbon monoxide (CO) molecules above a metallic surface. Treat each CO molecule as an independent, distinguishable two level system. Assume each CO molecule can exist in one of two energy states: free in the gas ($E_1 = 0$) and bound to the surface ($E_2 = -\epsilon$). Further assume there is a multiplicity of gas states γ_g and multiplicity of bound states γ_b available to each molecule, and that $\gamma_\mathrm{g} > \gamma_\mathrm{b} \gg N$.

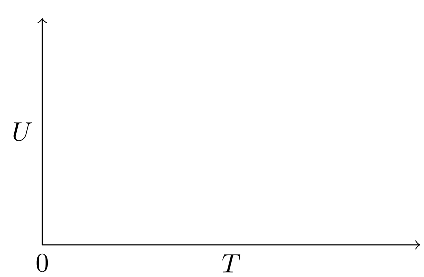
   (a) What is the partition function $q(T)$ for a single CO molecule in terms of ϵ, γ_g, γ_b, and $k_B T$?

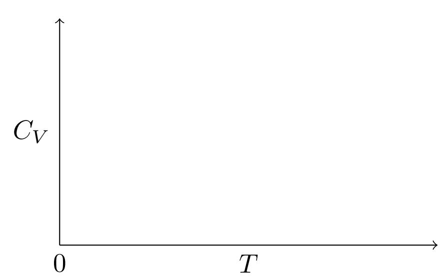
   (b) What is the partition function $Q(T)$ for N molecules of CO in terms of N, ϵ, γ_g, γ_b, and $k_B T$? Be sure to account for the indistinguishability of the CO molecules.

   (c) What is the average energy, $U = \langle E \rangle$ for N molecules of CO in terms of N, ϵ, γ_g, γ_b, and $k_B T$?

(d) What is the constant volume heat capacity, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ for N molecules of CO in terms of N, ϵ, $\gamma_{\rm g}$, $\gamma_{\rm b}$, and $k_B T$.

(e) Plot the energy $U(T)$ and constant volume heat capacity $C_V(T)$ as a function of temperature. Clearly indicate the high and low ($T = 0$) temperature limits.





3. Calculating changes in entropy

   Assume the following where needed: $T = 300\,\mathrm{K}$ and $C_V = \frac{5}{2}Nk_B$ for a diatomic ideal gas.

   (a) One mole of O_2 gas fills a room of $500\,\mathrm{m}^3$. What is the entropy change ΔS for squeezing the gas into $1\,\mathrm{cm}^3$ in the corner of the room?

   (b) One mole of O_2 gas is in a room of $500\,\mathrm{m}^3$. What is the entropy change ΔS for heating the room from $T = 270\,\mathrm{K}$ to $330\,\mathrm{K}$?

   (c) The free energy of a conformational motion of a loop in a protein is $\Delta G = 2\,\mathrm{kcal/mol}$. The enthalpy change is $\Delta H = 0.5\,\mathrm{kcal/mol}$. Compute ΔS.