

Discussion 10

Name and section: \_\_\_\_\_

$$U(S, V, N) = TS - pV + \mu N$$

$$S(U, V, N) = \frac{U}{T} + \frac{p}{T}V - \frac{\mu}{T}N$$

$$F(V, T, N) = U - TS$$

$$G(p, T, N) = U + pV - TS$$

$$H(S, p, N) = U + pV$$

T	G	-p
F		H
V	U	-S

**Good Physicists Have Studied Under Very Fine Teachers**

V	F	T
U		G
-S	H	-p

**Valid Facts and Theoretical Understanding Generate Solutions to Hard Problems**

1. Maxwell Relations

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

**Solution:**

$$\frac{\partial^2 H}{\partial S \partial p} = \frac{\partial^2 H}{\partial p \partial S}$$

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial p}\right)_S$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$

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

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T}$$

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

$$\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$$

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$$

as shown in class.

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

**Solution:** They are like drawing an “L” and then a backwards “L” sharing the bottom part of the “L” in any orientation. The overall sign will be negative if you have an odd number of negatives and positive for an even count of negatives.

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

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

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  $\gamma_g$  and multiplicity of bound states  $\gamma_b$  available to each molecule, and that  $\gamma_g > \gamma_b \gg N$ .

- (a) What is the partition function  $q(T)$  for a single CO molecule in terms of  $\epsilon$ ,  $\gamma_g$ ,  $\gamma_b$ , and  $k_B T$ ?

**Solution:**

$$q(T) = \gamma_g \exp\left(-\frac{0}{k_B T}\right) + \gamma_b \exp\left(-\frac{-\epsilon}{k_B T}\right)$$

$$q(T) = \gamma_g + \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)$$

- (b) What is the partition function  $Q(T)$  for  $N$  molecules of CO in terms of  $N$ ,  $\epsilon$ ,  $\gamma_g$ ,  $\gamma_b$ , and  $k_B T$ ? Be sure to account for the indistinguishability of the CO molecules.

**Solution:**

$$Q(T) = \frac{[q(T)]^N}{N!}$$

$$Q(T) = \frac{1}{N!} \left( \gamma_g + \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right) \right)^N$$

- (c) What is the average energy,  $U = \langle E \rangle$  for  $N$  molecules of CO in terms of  $N$ ,  $\epsilon$ ,  $\gamma_g$ ,  $\gamma_b$ , and  $k_B T$ ?

**Solution:** For a single particle, the expected energy  $U_s$  is

$$\begin{aligned} U_s &= 0 \cdot \frac{\gamma_g}{q(T)} + (-\epsilon) \cdot \frac{\gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)}{q(T)} \\ &= -\frac{\epsilon \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)}{\gamma_g + \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)} \end{aligned}$$

For the system of  $N$  particles,

$$U = \langle E \rangle = -\frac{N \epsilon \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)}{\gamma_g + \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)}$$

This problem can also be solved by recalling

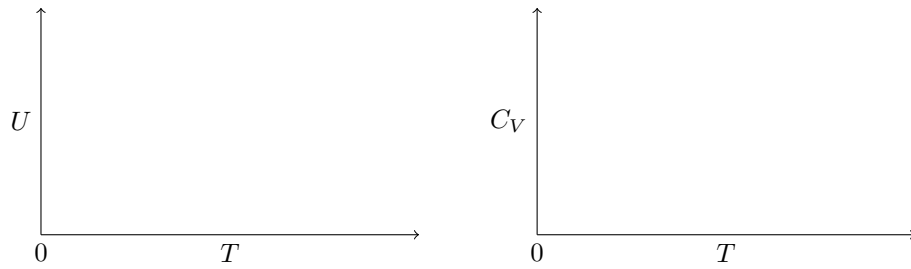
$$\langle E \rangle = U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta}$$

- (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  $N$ ,  $\epsilon$ ,  $\gamma_g$ ,  $\gamma_b$ , and  $k_B T$ .

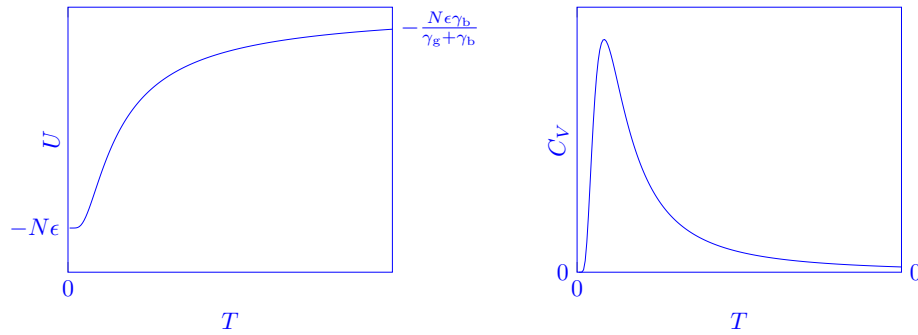
**Solution:**

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{k_B T^2} \frac{N \epsilon^2 \gamma_b \gamma_g \exp\left(\frac{\epsilon}{k_B T}\right)}{\left(\gamma_g + \gamma_b \exp\left(\frac{\epsilon}{k_B T}\right)\right)^2} \\ &= -\frac{\epsilon \gamma_g}{k_B T^2} \frac{U(T)}{q(T)} \end{aligned}$$

- (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.



**Solution:**



3. Calculating changes in entropy

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

- (a) One mole of  $\text{O}_2$  gas fills a room of  $500\text{ m}^3$ . What is the entropy change  $\Delta S$  for squeezing the gas into  $1\text{ cm}^3$  in the corner of the room?

**Solution:**

$$\begin{aligned} dS &= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \\ &= \frac{p}{T} dV \\ \Delta S &= RT \ln \frac{V_2}{V_1} \\ &= RT \ln \left( \frac{1\text{ cm}^3}{500\text{ m}^3} \right) \\ \Delta S &= -RT \ln \left( 5 \times 10^8 \right) \end{aligned}$$

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

**Solution:**

$$\begin{aligned}dS &= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN \\&= \frac{1}{T} dU \\&= \frac{1}{T} \frac{5}{2} R dT \\ \Delta S &= \frac{5}{2} R \ln \left( \frac{330}{270} \right)\end{aligned}$$

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

**Solution:**

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ \Delta S &= \frac{1}{T} (\Delta H - \Delta G) \\ &= \frac{1}{300\text{ K}} (0.5\text{ kcal/mol} - 2\text{ kcal/mol}) \\ \Delta S &= 5\text{ cal}/(\text{mol K})\end{aligned}$$