

Instructor: Subhadip Mitra

Date: MARCH 2, 2023

Time: 1 H 30 M

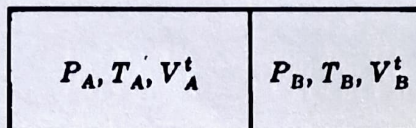
End Examination

Total Marks: 40

Instructions:

- Class notes or books are not permitted. But you may bring one A4 sheet of handwritten material (not photo-copy/printed) and a calculator.
- Illegible answers will not be graded. No 'benefit of doubt' because of bad notation/illegible hand-writing etc.

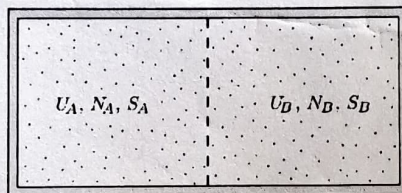
Q 1. (a) A rigid tank made with a heat insulating material is filled with an ideal gas. It is divided into two unequal parts A & B:



Find the equilibrium temperature and pressure once the partition is removed (assume C_V is constant).

- (b) Calculate the change in μ for ice at -10°C , with density $917\text{ kg}\cdot\text{m}^{-3}$, when the pressure is increased from 1.0 bar to 4.0 bar.
- (c) Why is the Helmholtz energy called the maximum work function? Why it is also called the Helmholtz free energy?
- (d) Show that in PT diagrams, the boundaries between the solid and liquid phases are approximately linear in general.
[2 + 2 + (2 + 1) + 3 = 10 CO: 1,2,3]

Q 2. (a) Consider two systems A & B that are free to exchange heat and particles (slowly):



Show/argue that one of the condition for equilibrium is

$$-T \left(\frac{\partial S_A}{\partial N_A} \right)_{U,V} = -T \left(\frac{\partial S_B}{\partial N_B} \right)_{U,V}$$

where there are N_A and N_B moles of A-types and B-type particles, respectively.

- (b) We can generalize the thermodynamic identity to include N -changing processes. Show that the total change in the entropy is given as

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \Rightarrow dU = TdS - PdV + \mu dN$$

where $\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V}$. The μdN term is called chemical work.

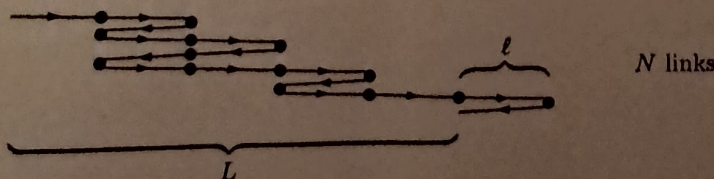
- (c) Gibbs energy of the gaseous phase of a substance is more sensitive to a change in temperature than its liquid and solid phases. Explain.

- (d) Show that for a van der Waals gas, $\left(\frac{\partial C_V}{\partial V} \right)_T = 0$. Does this mean C_V is a constant in this case?

Hint: For a state function, the order of partial differentiations does not matter.

[2 + 2 + 2 + (3 + 1) = 10 CO: 1,2,3]

Q 3. Consider a chain of rubber bands of N links (N is large), each of length ℓ . Imagine that each link has only two possible states, pointing either left or right. The total length L of the rubber band is the net displacement from the beginning of the first link to the end of the last link.



- (a) Show that the entropy of the configuration with N_R links pointing to the right can be written as

$$S = \left(N \ln \left(\frac{N}{N - N_R} \right) - N_R \ln \left(\frac{N_R}{N - N_R} \right) \right) k_B$$

Hint: $S = k_B \ln [\Omega(N_R)]$ and Stirling's approximation: $\ln(N!) \approx \ln(N) - N$ for large N .

- (b) Rewrite the above expression in terms of L/ℓ .
- (c) For a one-dimensional system such as this, the length L is analogous to the volume V of a three-dimensional system. Similarly, the pressure P is replaced by the tension force F . Taking F to be positive when the chain is pulling inward, write down and explain the appropriate thermodynamic identity (fundamental equation) for this system. Express the tension force F in terms of a partial derivative of the entropy. From this expression, compute the tension in terms of L , T , N , and ℓ .
- (d) Show that when $L/\ell \ll N$, the tension force is directly proportional to L (Hooke's law).

[2 + 2 + 4 + 2 = 10 CO: 1,2,3]

Q 4. (a) Derive the Maxwell relations.

(b) How can one measure $S(T) - S(0)$ in practice?

(c) Prove the Clausius inequality, $dS \geq \frac{\delta Q}{T}$.

(d) Prove that when an ideal gas changes adiabatically, $PV^{5/3} = \text{constant}$.

(e) What is enthalpy?

[2 + 2 + 2 + 2 + 2 = 10 CO: 1,2]

$N - N_R$