

This is a closed book, closed notes exam, to be taken in a single 75 minute period. The problems should be worked on separate pages and attached to this sheet when completed. There are four problems, which will be weighted equally. For full credit, be sure to show and explain all your work.

Name: _____

Signature: _____

Some useful information:

The entropy of an ideal gas is given by

$$S(T, V, N) = S_0 + Nk_B \log \left[\left(\frac{T}{T_0} \right)^\alpha \left(\frac{V}{V_0} \right) \right]$$

where $S_0 \equiv S(T_0, V_0, N_0)$ and the gas has $C_V = \alpha Nk_B$.

In a mixture of ideal gases, the Gibbs free energy of species i can be expressed

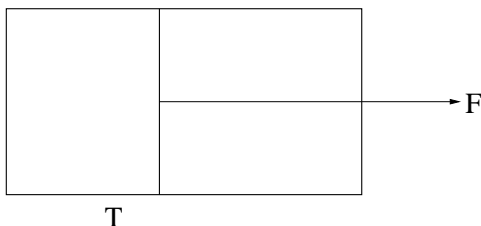
$$G_i = \mu_{i0}N_i + k_B T N_i \log x_i$$

where μ_{i0} is determined by the temperature T and total pressure P of the system.

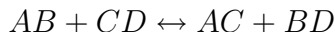
1. Explain clearly and in detail why the second law of thermodynamics forbids the existence of a heat engine more efficient than a Carnot engine.

2. The system shown below consists of a chamber of fixed volume V with two separate partitions, each of which contains an ideal gas. The separating wall between the partitions is free to move, and an attached string allows it to be displaced by an external force. The entire chamber is thermally connected to a reservoir at fixed temperature T .

Demonstrate explicitly that when the external force F reversibly does work W on the system, the Helmholtz free energy, A , of the system increases by W .



3. A chamber held at fixed temperature and pressure contains N atoms each of four atomic species, labelled A , B , C , and D . The atoms combine to form binary molecules, and the molecules undergo an exchange reaction



The total internal energy of a pair of (AC, BD) molecules is greater than that of a pair of (AB, CD) molecules by an amount ϵ . You can assume no free atoms are present. Define the “degree of reaction”

$$\xi = \frac{N_{AC}}{N_{AB} + N_{AC}}$$

as a measure of how far the reaction has proceeded towards the right-hand side.

(a) Express the Gibbs free energy of the total system as a function of ξ (and any other parameters that are needed). You may approximate the molecular gases as ideal.

(b) Determine the equilibrium value of ξ in terms of ϵ and the temperature T .

4. A monatomic gas satisfies the van der Waals equation of state,

$$\left(P - a\frac{N^2}{V^2}\right)(V - Nb) = Nk_B T$$

(a) Show that $(\partial C_V / \partial V)_{T,N} = 0$.

(b) Use physical reasoning (not a mathematical derivation) to deduce from (a) what the heat capacity C_V of the gas must be.

(c) Proceed from (b) to determine the internal energy E as a function of N , V , and T .