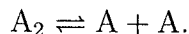


4

A gas is composed of an atomic species A. At low temperature the atoms mostly bind in pairs to form diatomic molecules A_2 , but at higher temperatures the molecules can thermally dissociate into individual atoms *via* the reversible process



The binding energy of the diatomic molecule is E_0 . The mass of an isolated A atom is m and that of a diatomic molecule is $2m$. We wish to compute the fraction of molecules that are thermally dissociated when N atoms of A are held in thermal equilibrium at temperature T in a container of volume V .

In working this problem you may assume that the temperature is high enough that we can use classical Boltzmann statistics, and that N and V are large enough that we are in the thermodynamic limit. You may also neglect any rotational or vibrational modes of the diatomic molecule.

- Write down the expression giving the partition function $Z_{N,\text{atoms}}$ of a gas of N identical atoms of mass m at temperature T in a container of volume V . Evaluate the integral it contains, and so express $Z_{N,\text{atoms}}$ as a product of powers of kT , m , the reduced Planck constant \hbar , V and $N!$. Here k is Boltzmann's constant.
- Write down the partition function Z_N for the partially dissociated gas of N atoms as a sum over terms, each corresponding to there being N_1 single atoms and N_2 diatomic molecules (with $N_1 + 2N_2 = N$).
- To deal with the constraint $N_1 + 2N_2 = N$, introduce a chemical potential μ and form the grand-canonical partition function

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} Z_N e^{\mu N/kT}.$$

Evaluate $\mathcal{Z}(\mu, V, T)$ in closed form.

- From your result in part (c) compute N_1 and N_2 in terms of μ , and hence show that

$$\frac{(N_1)^2}{N_2} = K e^{-E_0/kT}.$$

where K is a number, depending on m , kT , V and \hbar that you should evaluate explicitly.