

AN ELEMENTARY APPROACH TO QUANTUM STATISTICAL PROBLEMS

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In order to derive the relation between macroscopic thermodynamic quantities and the quantum mechanical properties of atoms or atomic unions, statistical thermodynamics is usually applied. It is considered a necessary means of solving problems of this type because "phenomenological thermodynamics as a *macroscopic* theory is fundamentally not able to make statements about atomic systems". The aim of this presentation is to correct this entrenched prejudice, which is even required by standardized exams. Various important results of quantum statistics (freezing of a molecular vibration, heat capacity of para hydrogen, Maxwell's distribution law of molecular velocities, etc.) can be derived for which, apart from the well-known relations of quantum mechanics, only the chemical potential and its concentration and energy dependence are needed:

$$\mu = \mu_0 + RT \ln \frac{c}{c_0} \quad (\text{"mass action formula"}),$$

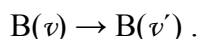
$$\mu(\varepsilon) = \mu(0) + N_A \varepsilon \quad (\text{"activation formula"}).$$

The second equation is valid on the condition that all molecules of a substance are put into an activated state that is higher in energy by the same value ε , without otherwise altering them or their environment (type of solvent, temperature, pressure, concentrations, field strengths, etc.; N_A AVOGADRO constant).

Example: Freezing of a molecular vibration: We take a diatomic gas B and consider all gas particles, being in the same state of vibration with the vibrational quantum number ν , as molecules of a substance $B(\nu)$, and the entire gas as a mixture of these substances [1]. Since the different substances $B(\nu)$ are not distinguishable chemically, we assign to them the same standard potential μ_0 . The different energies in the different states of vibration ν are taken into account by a corresponding term. For sake of simplicity we regard the vibration as harmonic:

$$\mu_0(\nu) = \mu_0(0) + N_A h \nu \cdot \nu.$$

Changes of the state of vibration caused by collisions between the particles appear as reactions of the following type:



All these reactions will be in equilibrium within a short period of time. The chemical potential μ becomes identical for all substances, $\mu = \mu(\nu) = \mu(0)$, which means, if we take the mass action formula into consideration for $\mu(\nu)$ and $\mu(0)$:

$$\mu = \mu_0(0) + N_A h \nu \cdot \nu + RT \ln \frac{c(\nu)}{c_0} = \mu_0(0) + RT \ln \frac{c(0)}{c_0}. \quad (1)$$

By resolving the equation for $c(v)$ we obtain $c(v) = c(0) q^v$ with $q = e^{-hv/(kT)} < 1$. By summing up all $c(v)$ we derive for the total concentration c of gas B:

$$c = \sum_{v=0}^{\infty} c(0) \cdot q^v = c(0) \cdot \frac{1}{1-q} = \frac{c(0)}{1 - e^{-hv/(kT)}}.$$

$[1 - e^{-hv/(kT)}]^{-1}$ is the partition function for a linear harmonic vibrator. For the fraction $x(0) = c(0)/c$ of the molecules B(0) in the ground state we find (Fig. 1):

$$x(0) = 1 - e^{-hv/(kT)}. \quad (2)$$

If we reversely introduce $c(0) = c \cdot x(0)$ into equation (1) we obtain, in addition to the two terms $\mu_0(0)$ and $RT \ln(c/c_0)$, one term that describes the contribution $\mu_{\text{vib}}(T)$ of the molecular vibration to the chemical potential of B:

$$\mu_{\text{vib}}(T) = RT \ln(1 - e^{-hv/(kT)}).$$

By taking the derivative once or twice with respect to T , we may derive a relation for the contribution of the molecular vibration to the molar entropy $S_{\text{vib}} = -d\mu_{\text{vib}}/dT$, or to the molar heat capacity $C_{\text{vib}} = -T(d^2\mu_{\text{vib}}/dT^2)$, respectively (Fig. 2).

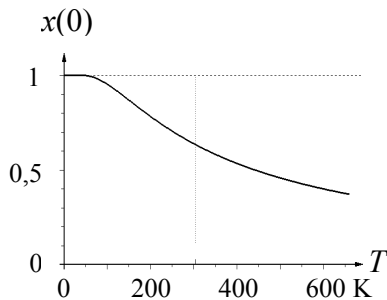


Figure 1: Freezing of a molecular vibration. The curve shows for I_2 vapour the fraction $x(0)$ of the number of molecules in the ground state of vibration ($v = 0$) related to the total number of I_2 molecules. For temperatures below 50 K practically all molecules are in the ground state.

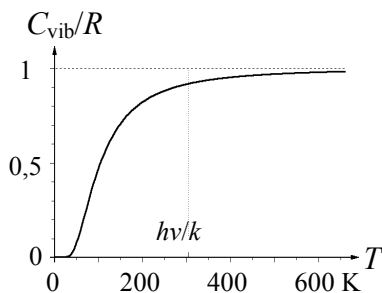


Figure 2: Freezing of a molecular vibration. Contribution C_{vib} of the molecular vibration to the molar heat capacity of I_2 vapour.

[1] To regard substances as equilibrium mixtures as above has a long tradition (see for instance A. EINSTEIN, Verhandlungen der Deutschen Physikalischen Gesellschaft **12** (1914) 820).