Ex4220: Cheimchal equilibrium: H2[3D]==2H[2D]

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The problem:

An H_2 molecule (mass $2\mathsf{m}_H$) decomposes into H atoms when it is absorbed upon a certain metallic surface. The H_2 and H have an energy gain ε_2 and ε_1 per atom respectively, related to each state. The binding of the H atoms is not to particular sites on the surface: the H atoms are free to move on the surface. Consider the H_2 and H as an ideal gas, and express the surface density of the H atoms as a function of the H_2 pressure.

The solution:

When the H_2 and H come to equilibrium (that is the system's free energy is minimized) their chemical potential are equal to zero. We'll start by finding the partition function.

$$Z_{1H_2} = \int \frac{d^3xd^3p}{(2\pi)^3} e^{-\beta(\frac{p^2}{2(2m)}+\varepsilon_2)} = e^{-\beta\varepsilon_2} V \left(\frac{m}{\beta\pi}\right)^{\frac{3}{2}} = e^{-\beta\varepsilon_2} \frac{2^{\frac{3}{2}}V}{\lambda_T^3} \tag{1}$$

$$Z_{1H} = \int \frac{d^2xd^2p}{(2\pi)^2} e^{-\beta(\frac{p^2}{2m}+\varepsilon_1)} = e^{-\beta\varepsilon_1} A \frac{m}{2\beta\pi} = e^{-\beta\varepsilon_1} \frac{A}{\lambda_T^2} \tag{2}$$

Now let's assume there are N H_2 molecules to begin with. With the definition of a macroscopic reaction coordinate n (See lecture notes: [5.3] The law of mass action) we know that in equilibrium there are $N-n$ H_2 molecules and $2n$ H atoms. Recalling both H_2 and H are ideal gasses we obtain:

$$Z_{H_2} = \frac{1}{(N-n)!} Z_{1H_2}^{N-n} = \frac{e^{-\beta\varepsilon_2(N-n)}}{(N-n)!} \left(V \left(\frac{m}{\beta\pi}\right)^{\frac{3}{2}} \right)^{N-n} \tag{3}$$

$$Z_H = \frac{1}{(2n)!} Z_{1H}^{2n} = \frac{e^{-\beta\varepsilon_1(2n)}}{(2n)!} \left(A \frac{m}{2\beta\pi} \right)^{2n} \tag{4}$$

$$F_{H_2} = -\frac{1}{\beta} ln(Z_{H_2}) = -\frac{1}{\beta} \left[-\beta\varepsilon_2(N-n) - (N-n)ln(N-n) + (N-n) + (N-n)ln(V \left(\frac{m}{\beta\pi}\right)^{\frac{3}{2}}) \right] \tag{5}$$

$$F_H = -\frac{1}{\beta} ln(Z_H) = -\frac{1}{\beta} \left[-\beta\varepsilon_1(2n) - 2nln(2n) + 2n + 2nln(A \frac{m}{2\beta\pi}) \right] \tag{6}$$

Note that Stirling's approximation $ln(N!) \approx Nln(N) - N$ was used in (5) and (6). We would like to first find the H_2 pressure, Then we'll equilibrate the chemical potential to find our desired solution.

$$P = -\frac{\partial F_{H_2}}{\partial V} = \frac{N-n}{\beta V} \tag{7}$$

$$\mu_{H_2} + \mu_H = 0 \tag{8}$$

$$\frac{\partial F_{H_2}}{\partial n} + \frac{\partial F_H}{\partial n} = 0 \tag{9}$$

$$-2ln(\frac{2n}{A}) - 2\beta\varepsilon_1 + 2ln(\frac{m}{2\pi\beta}) + ln(\frac{N-n}{V\beta}) + ln(\beta) + \beta\varepsilon_2 - \frac{3}{2}ln(\frac{m}{\pi\beta}) = 0 \tag{10}$$

Denoting the density of the H atoms:

$$\mathcal{N} = \frac{2n}{A} \tag{11}$$

Finally the density $\mathcal{N}$ of the H atoms is:

$$\mathcal{N}(P) = \frac{e^{-\frac{\beta}{2}(2\varepsilon_1 - \varepsilon_2)}}{2^{\frac{3}{4}}}\sqrt{\frac{\beta P}{\lambda_T}} \tag{12}$$