

CHEMICAL POTENTIAL OF AN IDEAL GAS

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The chemical potential is defined in terms of the entropy as

$$\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad (1)$$

This definition leads to a general thermodynamic identity

$$dU = TdS - PdV + \mu dN \quad (2)$$

We can get another formula for μ from this:

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} \quad (3)$$

We can apply these formulas to get the chemical potential of an ideal gas from the Sackur-Tetrode equation

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (4)$$

Schroeder applies 1 to this equation and gets the chemical potential as

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad (5)$$

Now consider a volume of gas a distance z above the Earth's surface. In this case, the energy of the gas is composed of both the kinetic energy of the moving molecules and the potential energy of the molecules, the latter of which is mgz per molecule. In order to find the chemical potential of this volume of gas, we need to modify 4 to write U in terms of the potential and kinetic energy.

To see how to do this, we need to review the derivation of the multiplicity of an ideal gas (Schroeder's equation 2.40). This derivation relied on arguments from quantum mechanics that gave the number of position and momentum states that are possible in a volume of gas. The energy U that

appeared in this derivation is entirely kinetic energy. Merely raising the volume of gas a distance above the Earth's surface doesn't change the number of possible states that gas can occupy; it merely shifts the total energy by a fixed amount $Nmgz$. Thus the U in 4 should really be written as U_K , the kinetic energy:

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U_K}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (6)$$

However, the U being held constant in 1 is the *total* energy, which is

$$U = U_K + Nmgz = \frac{3}{2}NkT + Nmgz \quad (7)$$

so to write 4 in terms of this constant energy and the potential energy, we have

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m (U - Nmgz)}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (8)$$

$$= Nk \left[\ln \left(V \left(\frac{4\pi m (U - Nmgz)}{3h} \right)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right] \quad (9)$$

$$= Nk \left[\ln \left(\alpha (U - Nmgz)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right] \quad (10)$$

where

$$\alpha \equiv V \left(\frac{4\pi m}{3h} \right)^{3/2} \quad (11)$$

We can now find the chemical potential by taking the derivative 1:

$$\begin{aligned} \mu &= -kT \left[\ln \left(\alpha (U - Nmgz)^{3/2} \right) - \ln N^{5/2} + \frac{5}{2} \right] - \\ &NkT \left[\frac{\alpha^{3/2} (U - Nmgz)^{1/2} (-mgz)}{\alpha (U - Nmgz)^{3/2}} - \frac{1}{N^{5/2}} \left(\frac{5}{2} N^{3/2} \right) \right] \end{aligned} \quad (12)$$

$$= -kT \left[\ln \left(\alpha (U - Nmgz)^{3/2} \right) - \ln N^{5/2} \right] + NkT \left[\frac{3mgz}{2(U - Nmgz)} \right] \quad (13)$$

We can now substitute α back in and use 7 to get

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + \frac{3}{2} NkT mgz \quad (14)$$

$$= -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + mgz \quad (15)$$

Thus the chemical potential is changed by exactly the potential energy of a single molecule.

Now suppose that we have two samples of the same ideal gas with equal volumes and temperatures, but with one at height z and the other at the Earth's surface so $z = 0$. If the two volumes are in diffusive equilibrium, then their chemical potentials are equal, so we have

$$\mu(z) = \mu(0) \quad (16)$$

$$-kT \ln \left[\frac{V}{N(z)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] + mgz = -kT \ln \left[\frac{V}{N(0)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] \quad (17)$$

Dividing both sides by $-kT$ and exponentiating, we get

$$\frac{V}{N(z)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-mgz/kT} = \frac{V}{N(0)} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \quad (18)$$

$$N(z) = N(0) e^{-mgz/kT} \quad (19)$$

Since the volumes and temperatures are equal, from the ideal gas law $PV = NkT$ this equation implies the same relation applies for the pressure as a function of height

$$P(z) = P(0) e^{-mgz/kT} \quad (20)$$

which is the barometric equation we obtained earlier.

COMMENTS

Remark 1. Victoria Jenne Oct 19, 2017 1:22 PM

Your logic is wrong here. The book defines U as internal energy so you can't add potential energy to kinetic energy without previously using a quantum mechanics proof to alter the multiplicity which would entail altering the volume variable. Because we are obviously not changing the internal energy of the system your proof is not valid, even if you did get the correct answer.

Best Wishes, Vicky

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If I understand what you're saying, I don't think there's a problem. The derivation of the Sackur-Tetrode equation given by Schroeder in section 2.5 counts the number of states available to an ideal gas by using the quantum uncertainty principle, and assumes that the gas is contained in a volume in free space (that is, no gravitational field). This leads to Schroeder's equation 2.40 which is in turn used to derive equation 2.49. The energy U in this derivation is entirely kinetic, since it's obtained from the 'volume' in momentum space. If we apply a gravitational field by placing the gas a distance z above the Earth's surface, we don't change the number of states available to the gas; all we do is shift their total energy by an amount mgz per molecule. Thus the derivation of the Sackur-Tetrode equation would still be valid, except that the kinetic energy in the formula would now be $U_K = U_{\text{total}} - Nmgz$.