

CHEMICAL POTENTIAL - APPLICATION TO THE EINSTEIN SOLID

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Thermodynamic systems can be in equilibrium in various ways: thermal equilibrium results from systems being able to exchange energy, resulting in them being at the same temperature and mechanical equilibrium results from being able to exchange volume, resulting in the pressures being equal. The final type of equilibrium is diffusive equilibrium, when systems can exchange actual matter (numbers of particles) with each other. Now the entropy is taken to be a function of energy U , volume V and particle number N and using the same logic as in deriving temperature and pressure from derivatives of entropy, we find that at diffusive equilibrium between two systems A and B with a constant total particle number $N = N_A + N_B$, the condition that entropy achieve its maximum value results in

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad (1)$$

This condition is used to define the *chemical potential* μ as

$$\mu \equiv -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad (2)$$

If the two systems are also in thermal equilibrium, the temperatures are equal, so at equilibrium

$$\mu_A = \mu_B \quad (3)$$

If the systems are not in equilibrium, then the tendency is for the overall entropy of the combined system to increase as it tends towards equilibrium. If $\frac{\partial S_A}{\partial N_A} > \frac{\partial S_B}{\partial N_B}$, then an increase in N_A results in a greater increase in entropy than an increase in N_B , so the diffusion will tend to transfer particles from B to A . From the definition of μ , a larger $\frac{\partial S}{\partial N}$ means a *lower* value of μ (due to the minus sign), so diffusion tends to transfer particles from the system with a higher chemical potential to the system with a lower chemical potential.

If a system is allowed to vary U , V and N , the overall change in entropy is the sum of the contributions from all three processes, so the generalized form of the thermodynamic identity is

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN \quad (4)$$

or, in its more usual form

$$\boxed{dU = TdS - PdV + \mu dN} \quad (5)$$

Example 1. Consider a very small Einstein solid containing $N = 3$ oscillators and $q = 3$ energy quanta. Although true derivatives aren't valid in such a small system, we can get an idea of how chemical potential works by considering what happens if we add another oscillator to the system in such a way that S and V don't change. The entropy before the addition is

$$S = k \ln \Omega \quad (6)$$

$$= k \ln \binom{3+3-1}{3} \quad (7)$$

$$= k \ln 10 \quad (8)$$

If we change N to 4, then to keep S constant, we need to decrease q . This example is contrived so that we *can* actually do this and get the same value for S , since with $N = 4$ and $q = 2$, we find $S = k \ln 10$. Thus in this case $\Delta U = -\epsilon$ where ϵ is the energy of a single quantum and so the chemical potential is (approximately)

$$\mu = \frac{\Delta U}{\Delta N} = \frac{-\epsilon}{1} = -\epsilon \quad (9)$$

Now suppose we started with $N = 3$ and $q = 4$, and then try to add another oscillator while keeping S constant. The entropy before the addition is

$$S = k \ln \binom{3+4-1}{4} = k \ln 15 \quad (10)$$

Reducing q to 3 after increasing N to 4 results in

$$S = k \ln \binom{4+3-1}{3} = k \ln 20 \quad (11)$$

so we're still not down to the original entropy. However, if we reduce q to 2, we get

$$S = k \ln \binom{4+2-1}{2} = k \ln 10 \quad (12)$$

so now we've dropped below the original entropy. To keep S constant, we'd need to remove somewhere around 1.5 quanta, so $\mu < -\epsilon$ and the chemical potential is lower (more negative) than in the first case.

Example 2. Still with an Einstein solid, but now at the other extreme where both q and N are large numbers. In this case, the multiplicity is approximately

$$\Omega \approx \sqrt{\frac{N}{2\pi q(q+N)}} \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \quad (13)$$

$$\approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \quad (14)$$

where we've dropped the square root as it is merely 'large' compared to the other two factors being 'very large'.

The entropy is therefore

$$S = k \ln \Omega \quad (15)$$

$$\approx (q+N) \ln(q+N) - q \ln q - N \ln N \quad (16)$$

Using 2, this gives a chemical potential of

$$\mu = -kT [\ln(q+N) + 1 - \ln N - 1] \quad (17)$$

$$= -kT \ln \frac{q+N}{N} \quad (18)$$

For $N \gg q$, this reduces to

$$\mu \rightarrow -kT \ln \left(1 + \frac{q}{N}\right) \approx -kT \frac{q}{N} \quad (19)$$

At the other extreme, $N \ll q$ and

$$\mu \rightarrow -kT \ln \left(\frac{q}{N}\right) \rightarrow -\infty \quad (20)$$

In the $N \gg q$ case, there are many more oscillators than energy quanta to put in them, so adding an extra oscillator won't make much difference to the multiplicity. Think of a simple case where you've got lots of bins and only one ball to put in them. In that case, adding an extra bin creates only one extra possible state. Thus we'd expect $\partial S / \partial N$ to be fairly small in this case.

In the $N \ll q$ case, there are many more quanta than oscillators to put them in, so adding an extra oscillator creates many more possible microstates, since we can place any number of quanta from 0 right up to q in the new oscillator. Thus the multiplicity, and hence the entropy, increases more rapidly in this case.

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