

GIBBS FREE ENERGY AND CHEMICAL POTENTIAL

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.22.

From the thermodynamic potential for the Gibbs free energy

$$(1) \quad dG = -S dT + V dP + \mu dN$$

we get a relation for the chemical potential

$$(2) \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

Notice that the two quantities T and P that are held constant in the derivative as both are intensive, so they don't depend on the total size of the system. As a result, the derivative must be the same no matter what the total size of the system is, or in other words, the plot of G versus N must be a straight line with slope μ .

The other formula for μ derived from the Helmholtz free energy is

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

This time, however, one of the quantities (V) that is held constant is *extensive*, so if we add more particles to a system at constant temperature and volume, the pressure must increase. Thus the local nature of the system changes in the sense that its intensive quantities change. The result is that we can't conclude that μ is constant in this case.

Returning to the Gibbs energy, we can integrate to get

$$(4) \quad G = N\mu + K$$

for some parameter K that doesn't depend on N . In practice, it is only differences in G and μ that matter, so we can take $K = 0$.

For an ideal gas, we can take the derivative of this equation to get

$$(5) \quad \left(\frac{\partial \mu}{\partial P} \right)_{T,N} = \frac{1}{N} \left(\frac{\partial G}{\partial P} \right)_{T,N} = \frac{V}{N} = \frac{kT}{P}$$

where the second equality follows from 1.

Integrating the first and last quantities with respect to P from some reference pressure usually written as P° (and usually taken to be 1 bar, or atmospheric pressure), we have

$$(6) \quad \mu(T, P) = \mu^\circ(T) + kT \ln \frac{P}{P^\circ}$$

where

$$(7) \quad \mu^\circ(T) \equiv \mu(T, P^\circ)$$

We can compare this to the earlier formula for the chemical potential of an ideal gas:

$$(8) \quad \mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]$$

From the ideal gas law

$$(9) \quad \frac{V}{N} = \frac{kT}{P}$$

and defining

$$(10) \quad a \equiv \frac{2\pi m}{h^2}$$

we have from 8

$$(11) \quad \mu = -kT \ln \left[a^{3/2} \frac{(kT)^{5/2}}{P} \right]$$

$$(12) \quad = kT \left[\ln P - \ln \left((kT)^{5/2} a^{3/2} \right) \right]$$

This has the same form as 6 if

$$(13) \quad -kT \ln \left((kT)^{5/2} a^{3/2} \right) = \mu^\circ(T) - kT \ln P^\circ$$

$$(14) \quad \mu^\circ(T) = kT \ln \frac{P^\circ}{(kT)^{5/2} a^{3/2}}$$

$$(15) \quad = kT \ln \left(\frac{P^\circ}{kT} \left(\frac{h^2}{2\pi m kT} \right)^{3/2} \right)$$

$$(16) \quad = -kT \ln \left(\frac{kT}{P^\circ} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right)$$

If we use 9 this reduces to 8 for an ideal gas at the reference pressure P° , so the two equations for μ are consistent.

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