

MAXWELL RELATIONS FROM THERMODYNAMIC IDENTITIES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.12.

The various partial derivatives that can be obtained from the four thermodynamic identities can be used to derive yet more partial derivatives known as the *Maxwell relations* (although Maxwell's main claim to fame is, of course, his unification of electricity and magnetism and subsequent prediction of electromagnetic radiation, he also made important contributions to thermal and statistical physics).

Starting with the original thermodynamic identity:

$$dU = T dS - P dV + \mu dN \quad (1)$$

we have

$$\frac{\partial U}{\partial S} = T \quad (2)$$

$$\frac{\partial U}{\partial V} = -P \quad (3)$$

[To save writing, all partial derivatives implicitly assume that only the variable with which the derivative is being taken varies, with the other 2 variables appearing in the differential in 1 being held constant. Thus $\frac{\partial U}{\partial S}$ assumes V and N are constant. The molecule number N is always constant in what follows.]

Using the fact that mixed second-order partial derivatives do not depend on the order in which the two derivatives are taken (for continuous, differentiable functions, which represents pretty well all functions of physical interest), we can take second derivatives of these equations to get

$$\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) = \left(\frac{\partial T}{\partial V} \right)_S = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right) = - \left(\frac{\partial P}{\partial S} \right)_V \quad (4)$$

In taking the second derivative, we assume that the variable in the first derivative is held constant, which is indicated by the subscripts. This gives us the first Maxwell relation:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (5)$$

From the enthalpy identity:

$$dH = T dS + V dP + \mu dN \quad (6)$$

we get

$$\frac{\partial H}{\partial S} = T \quad (7)$$

$$\frac{\partial H}{\partial P} = V \quad (8)$$

Taking second derivatives gives

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (9)$$

From the Helmholtz free energy:

$$dF = -S dT - P dV + \mu dN \quad (10)$$

we get

$$\frac{\partial F}{\partial T} = -S \quad (11)$$

$$\frac{\partial F}{\partial V} = -P \quad (12)$$

Taking second derivatives gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (13)$$

Finally, from the Gibbs free energy:

$$dG = -S dT + V dP + \mu dN \quad (14)$$

we get

$$\frac{\partial G}{\partial T} = -S \quad (15)$$

$$\frac{\partial G}{\partial P} = V \quad (16)$$

Taking second derivatives gives

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (17)$$

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