Answer on Question #81426 – Physics / Molecular Physics | Thermodynamics

Maxwell's relations are a set of equations in thermodynamics which are derivable from the symmetry of second derivatives and from the definitions of the thermodynamic potentials.

The structure of Maxwell relations is a statement of equality among the second derivatives for continuous functions. It follows directly from the fact that the order of differentiation of an analytic function of two variables is irrelevant.

If we view the first law of thermodynamics,

dU = TdS – PdV

as a statement about differential forms, and take the exterior derivative of this equation, we get

0 = dTdS – dPdV

since d(dU) = 0. This leads to the fundamental identity

dPdV = dTdS.

The physical meaning of this identity can be seen by noting that the two sides are the equivalent ways of writing the work done in an infinitesimal Carnot cycle. An equivalent way of writing the identity is

$$\frac{\partial(T,S)}{\partial(P,V)} = 1$$

The Maxwell relations now follow directly. For example,

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

In thermodynamics, the internal energy of a system is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields.

Internal energy changes in an ideal gas may be described solely by changes in its kinetic energy. Kinetic energy is simply the internal energy of the perfect gas and depends entirely on its pressure, volume and thermodynamic temperature.

The internal energy of an ideal gas is proportional to its mass (number of moles) n and to its temperature T

U = cnT ,

where c is the heat capacity (at constant volume) of the gas. The internal energy may be written as a function of the three extensive properties S, V, n (entropy, volume, mass) in the following way

$$U(S,V,n) = \text{const}\cdot e^{\frac{S}{cn}} V^{\frac{-R}{c}} n^{\frac{R+c}{c}} ,$$

where const is an arbitrary positive constant and where R is the universal gas constant. It is easily seen that U is a linearly homogeneous function of the three variables (that is, it is extensive in these variables), and that it is weakly convex. Knowing temperature and pressure to be the derivatives $T = \frac{\partial U}{\partial S}$ , $P = \frac{\partial U}{\partial V}$ , the ideal gas law immediately follows.

This means that U depends only on T for any ideal gas depending on only two variables. If you let it also depend on N then of course U now depends on U = U(T,N).