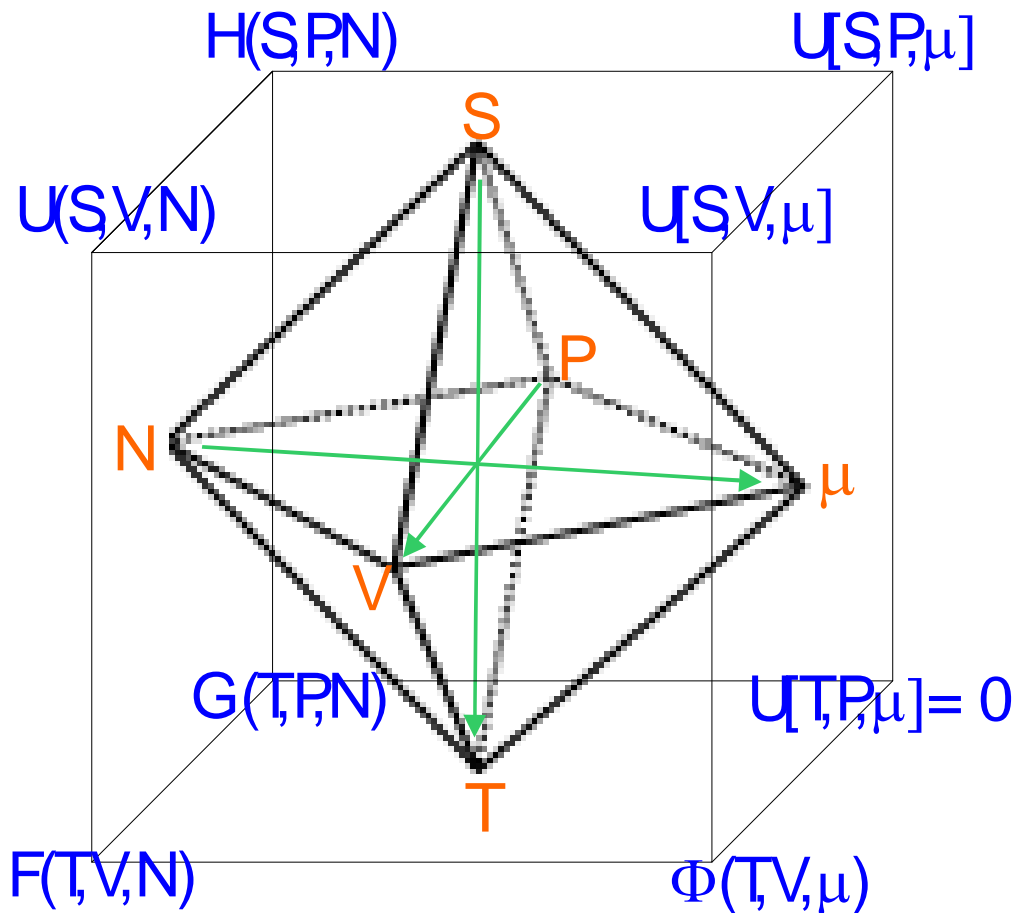


MAGIC THERMODYNAMIC CUBE AND OCTAHEDRON

GARY S. COLLINS

This generalization of the thermodynamic square, e.g. see Callen, allows for potentials that are functions of three thermodynamic variables. In the figure, variables are in orange and potentials in blue. Cube faces represent the variables and cube vertices the potentials. Each potential is at the vertex formed by the faces of its three natural variables. Thus, the internal energy $U(S,V,N)$ is at the vertex of faces S , V and N , and similarly for the enthalpy H , Helmholtz potential F and Gibbs potential G . One can alternatively think of the potentials as “belonging” to the triangular face of the octahedron surrounded by its natural variables; e.g. $U(S,V,N)$ belongs to the triangle SVN . Potentials that are functions of a given variable are found on the four corners of the face marked by the variable. For example, U , H , F and G are functions of N , and the grand potential Φ and three remaining potentials (which have no special names) are functions of μ . The potential $U[T,P,\mu]$ is identically zero. A Legendre transformation between variables moves one along a cube edge from one potential to another. Maxwell relations can be obtained using the inscribed octahedron. Related derivatives are along parallel edges on opposite sides of the octahedron. The green arrows help to determine signs of the relations.

For example, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, $\left(\frac{\partial P}{\partial N}\right)_V = -\left(\frac{\partial \mu}{\partial V}\right)_N$, and $\left(\frac{\partial \mu}{\partial T}\right)_N = -\left(\frac{\partial S}{\partial N}\right)_T$



Thermodynamic Octahedron
(Magic Octahedron)
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