Energies, Thermodynamic Identities, Maxwell Relations, and the Magic Square

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Thermodynamic identity for energy

$$dU = TdS - PdV(+\mu dN + \ldots)$$

Additional energies

$H = U + PV$ (Enthalpy)

$A = U - TS$ (Helmholtz free energy)

$G = U + PV - TS$ (Gibbs free energy)

Additional thermodynamic identities

$$dH = TdS + VdP(+\mu dN + \ldots)$$

$$dA = -SdT - PdV(+\mu dN + \ldots).$$

$$dG = -SdT + VdP(+\mu dN + \ldots).$$

Natural variables

$U \Rightarrow S$ & V (& N & ...)

$H \Rightarrow S$ & P (& N & ...)

$A \Rightarrow T$ & V (& N & ...)

$G \Rightarrow T$ & P (& N & ...)

Conjugate variables

S & T, P & V, (μ & N, ...)

Partial derivative relations

$$\left(\frac{\partial U}{\partial S}\right)_{V,N,\ldots} = T, \quad \left(\frac{\partial U}{\partial V}\right)_{S,N,\ldots} = -P, \ \ldots$$

$$\left(\frac{\partial H}{\partial S}\right)_{P,N,\ldots} = T, \quad \left(\frac{\partial H}{\partial P}\right)_{S,N,\ldots} = V, \ \ldots$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,N,\ldots} = -S, \quad \left(\frac{\partial A}{\partial V}\right)_{T,N,\ldots} = -P, \ \ldots$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N,\ldots} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T,N,\ldots} = V, \ \ldots$$

Maxwell relations

(obtained by equating reordered second derivatives of each energy with respect to its natural variables)

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

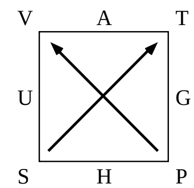
$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

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

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

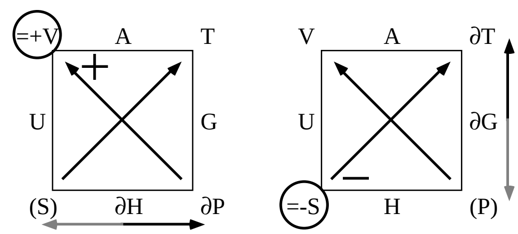
Magic Square VAT, UG, SHP (“Vat Ugh Ship”)

Notice that 1) each *side* has an *energy*, 2) each *energy* is flanked by its two most important *natural variables*, 3) *conjugate variables* occupy opposite ends of each *diagonal*, 4) crossed arrows point upward *toward* V and T and *away* from S and P.



Partial derivatives from the Magic Square

Starting at any energy, read *toward* one of the natural variables “Partial of – wrt –” and *away from* the other “at constant –” and look *across* for the result and its sign (as indicated by the arrow head) “is —.” For instance:



1) “Partial of H wrt P at constant S is $+V$”

2) “Partial of G wrt T at constant P is $-S$”

Thermodynamic identities from the Magic Square

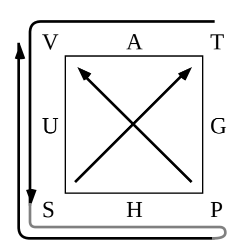
Intimately related to the partial derivative relations. For any energy read toward both of its natural variables and across for the conjugate variables and signs. For instance,

1) “dH is $+V$ times dP plus $+T$ times dS”

2) “dG is $-S$ times dT plus $+V$ times dP”

Maxwell Relations from the Magic Square

Using only corners, start at any corner and read clockwise *or* counterclockwise “Partial of — wrt — at constant —”. Proceed in the same direction to the next corner and then *reverse* direction to obtain the other side of the equation. Insert a minus sign if the arrows do *not* point toward or away from *both* starting points. For example:



“Partial of T wrt V at constant S and partial of P wrt S at constant V are *opposites*.” (Since T has an arrowhead and P doesn’t.)