Maxwell Relations: A Wealth of Partial Derivatives

Comment On Notation In most textbooks the internal energy is indicated by the symbol U and the symbol E is reserved for the exact energy of a system. Thus E may fluctuate and the internal energy is its mean value, $U = < E >$. Of course, the essence of thermodynamics is that the fluctuations of E about its mean are small and that the macroscopic properties of the system are dominated by its average U. In some texts, however (such as Reif), the symbol E is used for the internal energy. In most of my notes and lectures I have reserved U for the internal energy. In the development presented here I have chosen to use E for the internal energy for two reasons. First, it is then consistent with a treatment of the same topic in Reif. Second, it gives a pleasing form to a mnemonic device which is helpful in generating partial derivatives.

The Internal Energy For a hydrostatic system the combined first and second laws of thermodynamics give

$$dE = TdS - PdV$$

If one considers E to be a function of S and V (its "natural' variables), then one can expand it as an exact differential.

$$dE(S,V) = \underbrace{\left(\frac{\partial E}{\partial S}\right)_V}_{T} dS + \underbrace{\left(\frac{\partial E}{\partial V}\right)_S}_{-P} dV$$

Since this is an exact differential

$$\frac{\partial}{\partial V}\left(\left(\frac{\partial E}{\partial S}\right)_V\right)_S = \frac{\partial}{\partial S}\left(\left(\frac{\partial E}{\partial V}\right)_S\right)_V$$

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

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

This is useful information about derivatives of primary thermodynamic variables.

The same technique, applied to other systems, gives similar information.

$$dE(S, L) = TdS + \mathcal{F}dL \Rightarrow \left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial \mathcal{F}}{\partial S}\right)_L$$

$$dE(S, M) = TdS + HdM \Rightarrow \left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

et cetera

Reflect for a moment about how these derivative relations came about. Recall that for any state function $f(x, y)$ of two independent variables x and y

$$df = \underbrace{\left(\frac{\partial f}{\partial x}\right)_y}_{A(x,y)} dx + \underbrace{\left(\frac{\partial f}{\partial y}\right)_x}_{B(x,y)} dy.$$

The amazing mathematical feature of the combined first and second law is that when E is expressed in terms of the particular pair of variables S and V (reverting again to the hydrostatic system as an example), the coefficients of the differentials are simply the thermodynamic variables conjugate to S and V. That is why one refers to S and V as the "natural" variables for E. Note that if one actually had $E(S, V)$ and took the appropriate derivatives one would find T and P in terms of S and V, $T(S, V)$ and $P(S, V)$, perhaps not the most practical form in which to express these quantities. None the less, the differential form of the combined first and second law is exact no matter what variables are used to express T and P.

The technique used above for generating relations between the partial derivatives is so useful that one wonders if there are other related state functions to which it can be applied. There are, but the state functions must each have the feature that its total differential in terms of a pair of independent variables has, as coefficients, the other thermodynamic variables. There are three additional functions with the units of energy that have this property. These functions, together with the internal energy, are referred to as "Thermodynamic Potentials" and have interesting physical interpretations which will be studied later. For the moment we will concentrate on their utility in generating derivative relationships.

Helmholtz Free Energy $\quad F \equiv E - TS$

$$dF \;=\; d(E - TS)$$

$$dF \;=\; TdS - PdV - TdS - SdT$$

$$\;=\; -SdT - PdV$$

$$F \;=\; F(T,V) \qquad T\&V \text{ natural variables}$$

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

Enthalpy $\quad H \equiv E + PV$

$$dH \;=\; d(E + PV)$$

$$dH \;=\; TdS - PdV + PdV + VdP$$

$$\;=\; TdS + VdP$$

$$H \;=\; H(S,P) \qquad S\&P \text{ natural variables}$$

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

Gibbs Free Energy $\qquad G \equiv E + PV - TS$

$$
\begin{aligned}
dG &= d(E + PV - TS) \\[2mm]
dG &= TdS - PdV + PdV + VdP - TdS - SdT \\[2mm]
&= -SdT + VdP \\[2mm]
G &= G(T, P) \qquad T\&P \text{ natural variables} \\[2mm]
\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}
$$

Mnemonic Device

$$
\begin{array}{ccc}
E & X & F \\[4mm]
S & & \text{-T} \\[4mm]
H & \text{-\underline{X}} & G
\end{array}
$$

The figure above is constructed for a combined first and second law having the work term written in generic fashion.

$$dE = TdS + Xdx$$

The four thermodynamic potentials are displayed at the corners of a square, proceeding clockwise in alphabetic order. The side of the square between two thermodynamic potentials displays the differential of the natural variable which is common to the potentials, along with the sign of the associated term in the differential of the potential. Thus each thermodynamic potential is bracketed by its natural variables. Note that thermodynamically conjugate variables appear on opposite sides of the square with different signs.

A Maxwell relation is generated by stepping around the four sides of the square in order (in either direction) then turning around and taking two steps backward. The thermodynamic variables encountered in this trip are placed in the six positions in the two partial derivatives in the Maxwell relation. The signs are accumulated on the appropriate sides of the equality.
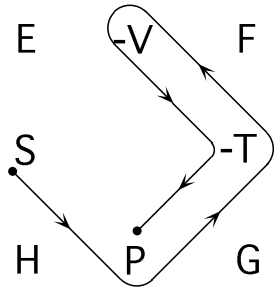
For a simple hydrostatic system

$$(-1)\left(\frac{\partial S}{\partial P}\right)_T = (-1)(-1)\left(\frac{\partial V}{\partial T}\right)_P$$
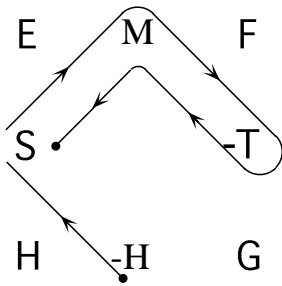
For a simple magnetic system

$$(-1)\left(\frac{\partial H}{\partial S}\right)_M = (-1)\left(\frac{\partial T}{\partial M}\right)_S$$