Example Problem 10.1 For a system that can only do electric work derive the four Maxwell Relations from the different potentials and sketch the corresponding mnemonic diagram.

Solution 10.1 The correct form for the differential of the internal energy per unit volume is given below where T is the temperature, s is the entropy per unit volume, $\vec{D}$ is the electric displacement vector and $\vec{E}$ is the applied electric field.

$$du = Tds + \vec{E} \cdot d\vec{D}$$

The Maxwell relation resulting from the equality of the mixed second derivatives of this state function (perfect differential) is:

$$\left(\frac{\partial T}{\partial \vec{D}}\right)_s = \left(\frac{\partial \vec{E}}{\partial s}\right)_{\vec{D}}$$

Legendre transforms to change the variables of the potential to create the enthalpy density, h, the Helmholtz free energy density, f and the Gibbs free energy density, g are shown in sequence along with the resulting Maxwell relation.

The enthalpy density:

$$h = u - \vec{E}\vec{D}$$
$$dh = Tds - \vec{D} \cdot d\vec{E}$$
$$-\left(\frac{\partial T}{\partial \vec{E}}\right)_s = \left(\frac{\partial \vec{D}}{\partial s}\right)_T$$
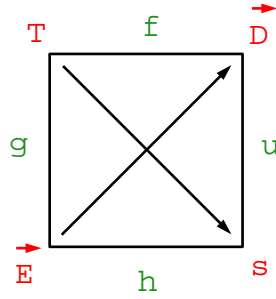
The Helmholtz free energy density:

$$f = u - Ts$$
$$df = -sdT + \vec{E} \cdot d\vec{D}$$
$$-\left(\frac{\partial s}{\partial \vec{D}}\right)_T = \left(\frac{\partial \vec{E}}{\partial T}\right)_{\vec{D}}$$

The Gibbs free energy density:

$$g = u - Ts - \vec{E}\vec{D}$$
$$dg = -sdT - \vec{D} \cdot d\vec{E}$$
$$-\left(\frac{\partial s}{\partial \vec{E}}\right)_T = \left(\frac{\partial \vec{D}}{\partial T}\right)_{\vec{E}}$$

The mnemonic diagram is below. Each potential (green) is flanked by its natural variables in red. The arrows indicate the sign for each Maxwell relation.

Example Problem 10.2
Reduce $\left(\frac{\partial H}{\partial V}\right)_{T,N}$ in terms of C_p, α, κ_T, T and P.

Solution 10.2
Start with the expression for the enthalpy for a system that can do chemical and mechanical work.

$$dH = TdS + VdP + \mu dN$$

Taking the derivative with respect to volume at constant T and N gives:

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

From the Maxwell relations from the Helmholtz free energy we have:

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

Substitution gives:

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

$$\left(\frac{\partial H}{\partial V}\right)_{T,N} = -T\left(\frac{\partial V}{\partial T}\right)_{P,N} \Big/ \left(\frac{\partial V}{\partial P}\right)_{T,N} + V\left(\frac{\partial P}{\partial V}\right)_{T,N}$$

Recognizing the definitions of the thermal expansion coefficient, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, and the isothermal compressibility, $\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, the expression reduces to the following.

$$\left(\frac{\partial H}{\partial V}\right)_{T,N} = \frac{T\alpha - 1}{\kappa_T}$$