MSE-204 Thermodynamics for Materials Science

L2. Part 2 | Auxiliary Functions & Their Meaning

Fundamental Equations & Natural Variables | Maxwell's Relations

Vaso Tileli | MXD 237

Summary: Fundamental Equations of State for Open Systems

The basic equations are:

$$dU = TdS - pdV + \sum_i \mu_i \, dn_i \quad + \ldots$$

$$dH = TdS + Vdp + \sum_i \mu_i \, dn_i \quad + \ldots$$

$$dA = -SdT - pdV + \sum_i \mu_i \, dn_i \quad + \ldots$$

$$dG = -SdT + Vdp + \sum_i \mu_i \, dn_i \quad + \ldots$$

pressure work + chemical work

From these, the following equations can be extracted:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} = \left(\frac{\partial H}{\partial S}\right)_{p,n_i}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} = \left(\frac{\partial H}{\partial p}\right)_{S,n_i}$$

Change of Characteristic Variables

One can change the characteristic variables of U, H, A, and G, according to what fits best the experiment. Below, we will change the characteristic variables of internal energy from $U=U(S, V, n_i)$ to variables that we can measure easier $U=U(T, V, n_i)$. We will do the transformation in a closed system.

$$dU = TdS - pdV$$

$U = U(S, V, n_i)$ $\quad dn_i = 0 \quad U = U(S, V) \longrightarrow U = U(T, V)$

$S = S(T, V) \quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$dU = T\left(\frac{\partial S}{\partial T}\right)_V \underline{dT} + \left(T\left(\frac{\partial S}{\partial V}\right)_T - p\right) \underline{dV} \quad U = U(T, V)$

$C_v = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$ $\quad\Big|\quad$ $C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$

MATHEMATICAL RELATIONS BETWEEN THE VARIOUS FUNCTIONS OF STATE: MAXWELL'S RELATIONS

An additional number of useful identities, know as Maxwell's relations, can be obtained by applying a theorem of the calculus concerning exact differentials (Euler's reciprocal relation). Maxwell's relations are relationships between partial derivatives.

$f = f(x, y)$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

For example, let consider the internal energy: $U = U(S, V, n_i)$

$$\left(\frac{\partial}{\partial S}\underbrace{\left(\frac{\partial U}{\partial V}\right)_{S,n_i}}_{-P}\right)_{V,n_i} = \left(\frac{\partial}{\partial V}\underbrace{\left(\frac{\partial U}{\partial S}\right)_{V,n_i}}_{T}\right)_{S,n_i}$$

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

one of Maxwell's relations

SUMMARY: IMPORTANT MAXWELL'S RELATIONS

$$\left(\frac{\partial T}{\partial V}\right)_{S,n_i} = -\left(\frac{\partial p}{\partial S}\right)_{V,n_i}$$

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

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

$$-\left(\frac{\partial S}{\partial p}\right)_{T,n_i} = \left(\frac{\partial V}{\partial T}\right)_{p,n_i}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,n_i,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,n_i,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,V,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{S,n_i,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{S,p,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial S}\right)_{V,n_i,n_j} = \left(\frac{\partial T}{\partial n_i}\right)_{V,S,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,n_i,n_j} = -\left(\frac{\partial p}{\partial n_i}\right)_{V,S,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{V,S,n_{k\neq j}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{V,S,n_{k\neq i}}$$

Method For Choice of Maxwell's Relations

Suppose you want to understand how the entropies of materials change as you squeeze them: $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$

First, identify what independent (or characteristic) variables are needed. p, T, n_i (denominator + constants)

Second, find the natural function of these variables. $G(T, p, n_i)$

Third, express the total deferential of the natural function. $dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i$

Fourth, based on Euler's reciprocal relation, set equal the two cross derivatives you want.

$$\left(\frac{\partial}{\partial p}\underbrace{\left(\frac{\partial G}{\partial T}\right)_{p,n_i}}_{=-S}\right)_{T,n_i} = \left(\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial G}{\partial p}\right)_{T,n_i}}_{=V}\right)_{p,n_i} \Rightarrow -\left(\frac{\partial S}{\partial p}\right)_{T,n_i} = \left(\frac{\partial V}{\partial T}\right)_{p,n_i}$$

The Maxwell's relation gives you a quantity you cannot measure $\left(\frac{\partial S}{\partial p}\right)_{T,n_i}$ from a quantity that is easy to measure $\left(\frac{\partial V}{\partial T}\right)_{p,n_i}$

EXAMPLE: INTERNAL ENERGY (& ENTHALPY) OF IDEAL GAS

Earlier, we expressed the internal energy of a closed system using V and T as the characteristic variables:

$$dU = \boxed{\left\{-p + T\left(\frac{\partial S}{\partial V}\right)_T\right\}} dV + \boxed{T\left(\frac{\partial S}{\partial T}\right)_V} dT \quad \leftarrow \quad U = U(V, T)$$

$$dU = \boxed{\left(\frac{\partial U}{\partial V}\right)_T} dV + \boxed{\left(\frac{\partial U}{\partial T}\right)_V} dT$$

Through Maxwell's relations we know that:

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

For the ideal gas

$$pV = nRT \Rightarrow p = \frac{nRT}{V}$$

Therefore, for an ideal gas the variation of internal energy with respect to volume is:

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial S}{\partial V}\right)_T = -p + T\left(\frac{\partial p}{\partial T}\right)_V = -p + p = 0$$

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The internal energy of the ideal gas dU=0 [redacted] does not change when the volume changes

$$\left(\frac{\partial H}{\partial p}\right)_T = 0$$

The enthalpy of the ideal gas dH=0 [redacted] does not change when p changes

OR Enthalpy of the ideal gas is independent of the pressure