1 Simple Applications of macroscopic thermodynamics

1.1 General relationship of thermodynamics

Fundamental thermodynamic relation for a quasi-static process:

$$dS = \frac{dQ}{T}$$

where

$$dQ = dE + dW = dE + pdV$$

The only external parameter of change is V

$$\implies dE = TdS - pdV$$

This specifies certain relationship between T, S, p, V i.e. S & V are independent variables

$$E = E(S, V)$$

So we have a pure mathematical relationship

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V} dS + \left(\frac{\partial E}{\partial V}\right)_{S} dV$$

where

$$\begin{cases} T = \left(\frac{\partial E}{\partial S}\right)_V \\ -p = \left(\frac{\partial E}{\partial V}\right)_S \end{cases}$$

which we already know! Because dE is an exact differential

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

this is known as the first Maxwell relation (wiki).

How about S, P?

From our favorite starting point

$$dE = TdS - pdV$$

we need to change $dV \to dp$ so from chain rule

$$d(pV) = pdV + Vdp \implies pdV = d(pV) - Vdp$$

so

$$dE = TdS - d(pV) + Vdp$$

or

$$d(E + pV) = TdS + Vdp$$

lets call this new parameter H = E + pV the **enthalpy** i.e.

$$H = H(S, p)$$

So

$$\begin{cases} T = \left(\frac{\partial H}{\partial S}\right)_p \\ V = \left(\frac{\partial H}{\partial p}\right)_S \end{cases}$$

where dH is an exact differential

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

or the second Maxwell relation!

Worksheet We can derive the Helmholtz free energy F = F(T, V) by starting with

$$d(TS) = TdS + SdT \implies TdS = d(TS) - SdT$$

so

$$dE = d(TS) - SdT - pdV$$

$$d(E - TS) = -SdT - pdV$$

1. Thus the Hemholtz free energy $F \equiv E - TS$ so

$$\begin{split} dF &= dE - (TdS + SdT) \\ &= TdS - pdV - Tds - SdT \\ &= -SdT - pdV \end{split}$$

2. So F = F(T, V) the we know that

$$\begin{cases} -S = \left(\frac{\partial F}{\partial T}\right)_V \\ -p = \left(\frac{\partial F}{\partial V}\right)_T \end{cases}$$

and dF is an exact differential

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

Finally for independent parameters T, p:

$$dE = TdS - pdV$$

we need to change $dV \to dp$ so from chain rule

$$d(pV) = pdV + Vdp \implies pdV = d(pV) - Vdp$$

so also using TdS = d(TS) - SdT

$$dE = (d(TS) - SdT) - (d(pV) - Vdp)$$

$$d(E - TS + pV) = -SdT + VdP$$

where G = E - TS + pV is the Gibbs free energy G = G(T, p)

$$\begin{cases} -S = \left(\frac{\partial G}{\partial T}\right)_p \\ V = \left(\frac{\partial G}{\partial p}\right)_T \end{cases}$$

and dG is an exact differential

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