

1 Simple Applications of macroscopic thermodynamics

1.1 General relationship of thermodynamics

Fundamental thermodynamic relation for a *quasi-static process*:

$$dS = \frac{\delta Q}{T}$$

where

$$\delta Q = dE + \delta W = dE + p dV$$

The only external parameter of change is V

$$\implies dE = T dS - p dV$$

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

$$dE = T dS - p dV$$

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

$$d(pV) = p dV + V dp \implies p dV = d(pV) - V dp$$

so

$$dE = T dS - d(pV) + V dp$$

or

$$d(E + pV) = T dS + V dp$$

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!

