Classical Thermodynamics and Statistics

Thermodynamic Potentials

Internal Energy $E(S,V)$

Enthalpy or Total Heat $H(S,P) = E(S,V) + PV$
$(= G(T,P) + TS)$

Free Energy $F(T,V) = E(S,V) - TS$

Free Enthalpy or Gibbs Function $G(T,P) = E(S,V) - TS + PV$
$(= F(T,V) + PV)$

Internal Energy

(a) $E(S, V)$: We have from the second law of thermodynamics

$$dE = TdS - PdV$$

and

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

and hence the *first Maxwell relation*:

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

Enthalpy or Total Heat

(b) $H(S,P)$: We obtain from the definition of H:

$$dH(S,P) = dE + PdV + VdP = TdS + VdP,$$

and (recall also that $H(S,P) = E(S,V) + PV$)

$$\therefore \qquad \left(\frac{\partial H}{\partial P}\right)_S = V, \qquad \left(\frac{\partial H}{\partial S}\right)_P = \left(\frac{\partial E}{\partial S}\right)_P = T,$$

and hence the *second Maxwell relation*:

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

Free Energy

(c) $F(T,P)$: We obtain from the definition of F:

$$dF(T,V) = dE - TdS - SdT = -SdT - PdV,$$

and

$$\therefore \qquad \left(\frac{\partial F}{\partial T}\right)_V = -S, \qquad \left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T = -P,$$

and hence the *third Maxwell relation*:

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

Free Enthalpy or Gibbs Function

(d) $G(T, P)$: We obtain from the definition of G:

$$dG(T, P) = dE - TdS - SdT + PdV + VdP = VdP - SdT,$$

and

$$\therefore \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S = \left(\frac{\partial F}{\partial T}\right)_V, \qquad \left(\frac{\partial G}{\partial P}\right)_T = V,$$

and hence the *fourth Maxwell relation*:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.$$

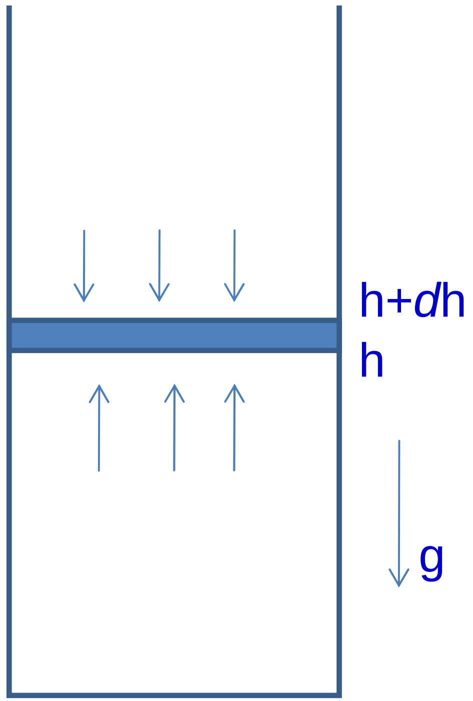
The Boltzmann Law

$$n = n_0 \exp(-E/kT)$$

Maxwell Velocity Distribution

$$f(v)dv = C \exp(-mv^2/2kT)\, dv$$

The exponential atmosphere



$dP = P_{h+dh} - P_h = -nmg\,dh$

$P = nkT$

$T = \text{Const.}$

$\therefore dP = kT\,dn = -nmg\,dh$

$dn/n = -nmg\,dh/kT$

$\Rightarrow n = n_0 \exp(-mgh/kT)$