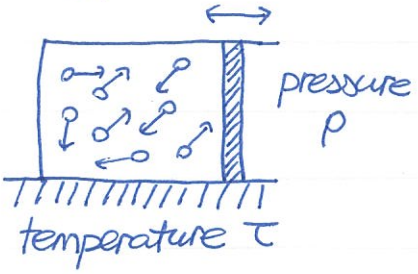
HH0028 Gibbs Free Energy

When a system is placed at constant temperature τ and pressure p, it is useful to introduce the Gibbs free energy G,

$$\boxed{G = U - \tau\sigma + pV}$$

$G = G(\tau, p, N)$ important!



We first show that G is a minimum for a system in equilibrium at constant τ and p.

$$dG = dU - \tau d\sigma - \cancelto{0}{\sigma d\tau} + p dV + \cancelto{0}{V dp}$$

thermodynamic identity

$$dU = \tau d\sigma - p dV + \mu dN$$

Thus, $dG = \mu dN$. But the system is not connected with a particle reservoir, $dN = 0 \longrightarrow \boxed{dG = 0}$ ← system in equilibrium

Here we see G is an extremum (turns out to be minimum) for a system in thermal equilibrium.

① Legendre transformation: $V \leftrightarrow p$

The relation between $F = F(\tau, V, N)$ and $G = G(\tau, p, N)$ is just the Legendre transformation between V and p.

$$\boxed{G = F + pV} \quad \text{with} \quad p = -\left(\frac{\partial F}{\partial V}\right)_{\tau,N} \quad \text{and} \quad V = \left(\frac{\partial G}{\partial p}\right)_{\tau,N}$$

It is helpful to work out all partial derivatives.

$$dG = \left(\frac{\partial G}{\partial \tau}\right)_{p,N} d\tau + \left(\frac{\partial G}{\partial p}\right)_{\tau,N} dp + \left(\frac{\partial G}{\partial N}\right)_{\tau,p} dN$$

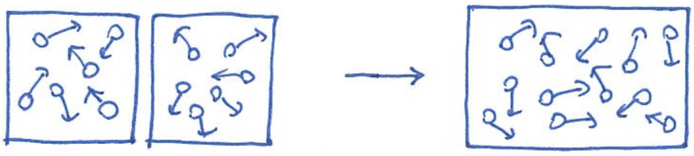
$\left(\frac{\partial F}{\partial \tau}\right)_{V,N} = -\sigma$ just volume V $\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \mu$

$$\longrightarrow \boxed{dG = -\sigma d\tau + V dp + \mu dN}$$

can be derived from $G = U - \tau\sigma + pV$ as well!

⊘ extensive v.s. intensive

Thermodynamic quantities like τ, P, μ, do not change when two identical systems are put together. ⟶ intensive. For those whose values double, they are called extensive.



$$\tau, P, \mu \longrightarrow \tau, P, \mu$$ ← intensive

$$\sigma, V, N \longrightarrow 2\sigma, 2V, 2N$$ ← extensive

Consider a system with only one species. The Gibbs free energy is extensive and can be written as

$$\boxed{G(\tau,P,N) = N\cdot\varphi(\tau,P)} \longrightarrow \left(\frac{\partial G}{\partial N}\right)_{\tau,P} = \varphi(\tau,P) \longrightarrow \boxed{\mu = \varphi(\tau,P)}$$

We thus arrive at a simple-looking expression for G,

$$\boxed{G = \mu N \quad \text{or} \quad G(\tau,P,N) = N\cdot\mu(\tau,P)}$$ ← surprisingly simple !!

The magic works because the natural variables of G are all intensive except N. Take the Helmholtz free energy as an example,

$$F(\tau,V,N) = N\,\varphi\left(\tau,\frac{N}{V}\right)$$ ← φ is intensive

$$\left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \mu \quad \text{but} \quad \left(\frac{\partial F}{\partial N}\right)_{\tau,V} = \varphi\left(\tau,\frac{N}{V}\right) + N\cdot\left(\frac{\partial \varphi}{\partial N}\right)_{\tau,V} \neq \varphi\ !$$

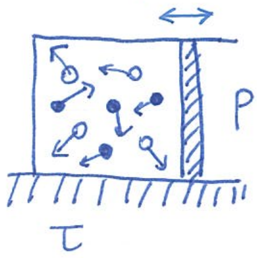
Therefore, no such simple expression for F ⍨ The difference is clear when looking at the ideal gas.

$$\underbrace{F = N\tau\left[\log\left(\frac{N}{Vn_Q}\right) - 1\right]}, \quad G = F + pV \overset{pV = N\tau}{=} N\tau\log\left(\frac{N}{Vn_Q}\right)$$

Expressed in its natural variables, $\boxed{G = N\tau\log(P/\tau n_Q)}$

Since we already know the chemical potential is $\mu = \tau\log(P/\tau n_Q)$ ⟶ $G = N\mu$ verified!

⊘ Many species of particles.



For more than one species, the Gibbs free energy is generalized to

$$\boxed{G = \sum_j N_j \mu_j}$$

and its total differential is

$$\longrightarrow \boxed{dG = \sum_j \mu_j \, dN_j - \sigma d\tau + V dp}$$

Let's apply it to equilibrium in chemical reactions.

$$\underbrace{H_2}_{A_1} + \underbrace{Cl_2}_{A_2} \rightleftarrows \underbrace{2HCl}_{A_3} \longrightarrow \nu_1 A_1 + \nu_2 A_2 + \nu_3 A_3 = 0$$

where $\nu_1 = 1$, $\nu_2 = 1$ and $\nu_3 = -2$

The chemical reaction can be represented as $\boxed{\sum_j \nu_j A_j = 0}$

Suppose the reaction takes place at constant τ and p (thus $d\tau = 0$ & $dp = 0$),

$$dG = \sum_j \mu_j \, dN_j - \sigma \overset{0}{\cancel{d\tau}} + V \overset{0}{\cancel{dp}} \longrightarrow \boxed{dG = \sum_j \mu_j \, dN_j}$$

Equilibrium requires $dG = 0$, implying the chemical potentials satisfy the constraint, $\sum_j \mu_j \, dN_j = 0$. But $dN_j = \nu_j \, dN$.

$$\longrightarrow \boxed{\sum_j \nu_j \mu_j = 0}$$

← equilibrium condition for reactions at constant τ & p

Suppose the particles are described as ideal gas,

$$\mu_j = \tau \log (n_j / c_j) \quad \text{where} \quad c_j = n_{Q_j} Z_j(\text{int})$$

The equilibrium condition can be written as

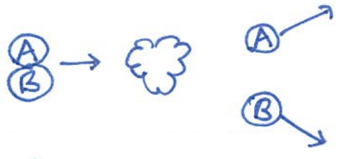
$$\sum_j \nu_j \log n_j = \sum_j \nu_j \log c_j \longrightarrow \log \prod_j n_j^{\nu_j} = \log \prod_j c_j^{\nu_j}$$

The law of mass action emerges:

$$\boxed{\prod_j n_j^{\nu_j} = K(\tau)} \longrightarrow K(\tau) = \prod_j c_j^{\nu_j} = \prod_j \left[n_{Q_j} Z_j(\text{int}) \right]^{\nu_j}$$

⓪ Kinetic model of mass action.

collision-induced combination



decomposition

Consider the chemical reaction

$$A+B \rightleftarrows AB.$$

One can write down the equations for rates of change according to the kinetic model as shown on the left.

$$\boxed{\begin{aligned} \frac{dn_{AB}}{dt} &= Cn_An_B - Dn_{AB} \\ \frac{dn_A}{dt} = \frac{dn_B}{dt} &= Dn_{AB} - Cn_An_B \end{aligned}}$$

When reaching equilibrium, the rates of change should be zero, $\frac{dn_{AB}}{dt}=0$, $\frac{dn_A}{dt}=0=\frac{dn_B}{dt}$. Therefore, $Cn_An_B - Dn_{AB}=0$

$$\rightarrow \boxed{\frac{n_A \cdot n_B}{n_{AB}} = \frac{D}{C}}$$ the same as $n_A^1 \cdot n_B^1 n_{AB}^{-1} = K(\tau)$

The equality is obtained by the so-called "the principle of detailed balance": the direct and the reversed rates cancel when approaching equilibrium.

Happy

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