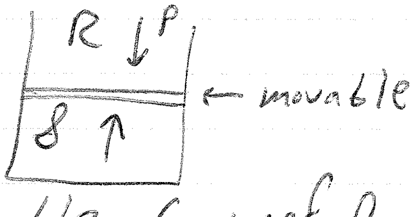
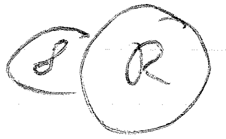
Gibbs free energy

We have considered systems in thermal or diffusive contact with reservoir. In many applications, we should consider mechanical contact as well. That is, in equilibrium the system is at the same pressure as the reservoir — i.e. the system is "open to the atmosphere" and remains at atmospheric pressure. This means that some of the work done by the system is not available for useful purposes — it is needed to maintain the pressure equilibrium.



Recall our discussion of thermal contact and Helmholtz free energy. Work done is



$$\bar{d}W = dU - \bar{d}Q = dU - \tau\, d\sigma$$

(this is work done on the system)

In an isothermal process, $\tau = \text{const}$

$$\bar{d}W = d(U - \tau\sigma) = dF$$

$F = U - \tau\sigma$ is the Helmholtz free energy, whose change reflects the amount of work done on/by system at constant temperature.

But... suppose both pressure and temperature are controlled and held fixed, but not volume (this is "mechanical contact." The "mechanical work" done on system is $\bar{d}W_{mech} = -p\,dV$

The work that is available for other purposes

"Available work" $\bar{d}W' = \bar{d}W - \bar{d}W_{mech}$

$= \bar{d}W + p\,dV$

If temp = constant and pressure = constant, then

$$\bar{d}W' = d(F + pV) \equiv dG$$

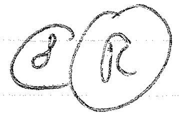
$G = F + pV = U - \tau\sigma + pV$ is the "Gibbs free energy"

"Free energy" keeps track of the energy of the system that we can <u>use</u> (after heat transfer with reservoir, and work on reservoir are taken into account)

<u>Most probable configuration:</u>

Gibbs free energy is what system minimizes in its most probable configuration, when in contact with R at specified τ and p

Recall our earlier discussion of thermal contact. Most probable configuration minimizes



$$\sigma_s + \sigma_R$$

conservation of energy $\Rightarrow dU_s = -dU_R$

therefore

$$d(\sigma_s + \sigma_R) = \left(\frac{1}{\tau_s} - \frac{1}{\tau_R}\right) dU_s = 0 \text{ in equili.}$$

$\Rightarrow \hat{\tau}_s = \hat{\tau}_R$

or... if $\tau = \tau_R$ = constant, in equilibrium $d(U - \tau\sigma) = 0$, where U, σ are system quantities

That is $F = U - \tau\sigma$ is minimized, and evaluating it at the minimum gives a function of τ: $F(\tau)$

We are finding where $e^{-F/\tau} = e^{-U/\tau} e^{\sigma}$ has a peak

e^{σ} is the system's entropy

$e^{-U/\tau}$ is the reservoir's entropy

For a large system, it is overwhelmingly probable that $e^{-F/\tau}$ is close to the peak

For a system in thermal <u>and</u> <u>mechanical</u> contact with reservoir, we use the same idea. Now

$$dV_S = -dV_R \quad \text{("conservation of volume")}$$

and $p = -\left(\frac{\partial F}{\partial V}\right)_\tau$, so

$$d(F_S + F_R) = -(p_S - p_R)\, dV_S = 0$$

To minimize free energy of system + reservoir, we have mechanical equilibrium $p_S = p_R$

Equivalently, most probable configuration is found by minimizing $F + pV = G$ of <u>system</u> at specified τ and p.

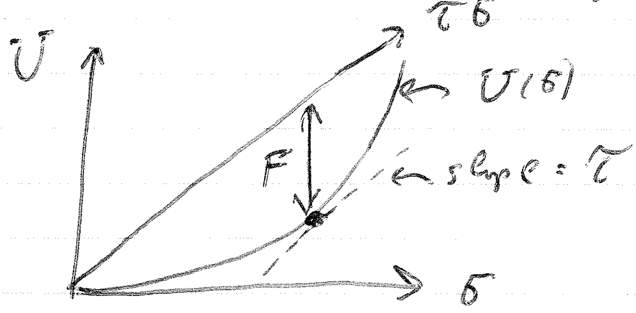
When this quantity is minimized, we have a function $G = G(\tau, p)$ of the temperature and pressure

Legendre Transform

Mathematically, the procedure we use for changing the dependent variable of a function is called a "Legendre Transform"

$$U(\sigma,V) \rightarrow F(\tau,V) \rightarrow G(\tau,p)$$

U is a function of σ, but we can't control σ, rather the variable we can control is $\tau = \frac{dU}{d\sigma}$, the slope of the function $U(\sigma)$



we assume $\frac{dU}{d\sigma}$ is monotonic (we say $U(\sigma)$ is convex)

We obtain a function of τ by evaluating $U - \tau\sigma$ at its minimum

$$F(\tau) = (U - \tau\sigma)_{\text{stat},\sigma}$$

the stationary point is unique, because of convexity

Then – how does F change as we change τ

$$dF = d(U - \tau\sigma) = dU - \tau d\sigma - \sigma d\tau$$

To change the slope, we need to change σ a little, but to first order $dU = \tau d\sigma$, so

$$dF = -\sigma d\tau \Rightarrow \left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma$$

And the Gibbs free energy G is obtained similarly from F

$$G(\tau,p) = F(\tau,V) + pV\Big|_{\substack{\text{stat in}\\ V}}$$

and $dG = dF + p\,dV + V\,dp$
(with τ fixed) $= V\,dp \Rightarrow \left(\frac{\partial G}{\partial p}\right)_\tau = V$

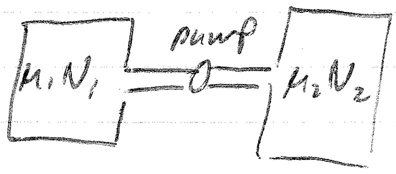
and if we vary both τ and p

$$dG = -\sigma\, d\tau + V\,dp : \quad \text{"another Thermodynamic identity"}$$
$$(+\mu\, dN)$$

"Chemical Work"

when we say G keeps track of systems "nonmechanical work" what do we mean?

An example is chemical work: Two systems, with different chemical potentials

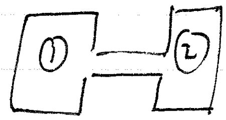


Just as we need to do work to pump heat against a Temperature gradient (in operation of a refrigerator) we need to do work to pump particles against a chemical potential gradient. The work required is

$$W = (\mu_2 - \mu_1)\Delta N$$ (if there is no heat flow and no change in volume)

For example, recall classical ideal gas (this illustrates chemical work, not Gibbs free energy – i.e. this is not a process at constant pressure):

For the classical ideal gas $\mu = \tau \log(n/n_Q)$



Then when ΔN molecules are moved from ① to ②

$$W = (\mu_2 - \mu_1)\Delta N = \tau \Delta N \log(n_2/n_1)$$

This is the same as the amount of work required to compress ΔN gas molecules from concentration n_1 to n_2

$$dW = -p\,dV = -N\tau \frac{dV}{V} \Rightarrow W = N\tau \log V_1/V_2$$
$$= N\tau \log(n_2/n_1)$$

Gibbs free energy and Chemical Potential

Recall the distinction between intensive and extensive quantities: if we scale the system up, intensive quantities are independent of N, and extensive quantities scale linearly with N.

σ, U, V, N are extensive; so are G and F
τ, p, μ are intensive

If we divide an extensive quantity by N, it becomes intensive

$U(\sigma, V, N) = N u(\sigma/N, V/N)$ - u = energy per particle
$F(\tau, V, N) = N f(\tau, V/N)$ - f = free energy per particle
$G(\tau, p, N) = N g(\tau, p)$ - g = Gibbs free energy per particle

Note: since g is a function of intensive τ and p, it has no dependence on N

Recall that $dG = -\sigma\, d\tau + V\,dp + \mu\, dN$ $\quad (G = U - \sigma\tau + pV)$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{\tau, p} = g(\tau, p) \Rightarrow G = N\mu(\tau, p)$$

The chemical potential μ, expressed as a function of τ and p, is the Gibbs free energy per particle (It is obvious really – G is the usable energy at fixed τ and p; so that N is the only thing that we can vary.)

If there are many species, then there is a chemical potential for each one

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{\tau, p, \text{other species}}$$

If we scale out N_1

$$G(N_1, N_2, \text{—}, \tau, p) = N_1\, g\left(N_2/N_1, N_3/N_1, \text{--}\ \tau, p\right)$$

Hence G is "homogeneous of degree one"

$$G(\lambda N_1, \lambda N_2, \text{--}) = \lambda\, G(N_1, N_2, \text{—})$$

If we differentiate with respect to λ

$$\frac{d}{d\lambda}[\quad] = G = \sum_i N_i \frac{\partial G}{\partial N_i} = \sum_i N_i \mu_i$$

Note, though, that here the μ_i's can be functions of the relative concentrations N_j/N_k, as well as of τ, p

Gibbs free energy in chemistry

Many chemical reactions take place in the lab at constant temperature and pressure. For these G is useful.

Example: $H_2 + Cl_2 \leftrightarrow 2HCl$

Write it in the form

$$(1)\, H_2 + (1)\, Cl_2 + (-2)\, HCl = 0$$

In general, we write the reaction in the form
$\sum \nu_i A_i = 0$ where A_i's are species
ν_i's are quantities
above $\nu_1 = \nu_2 = 1$; $\nu_3 = -2$

Strictly speaking, we defined μ, and argued $\mu_{sys} = \mu_{res}$ for most probable configuration, assuming that N was a conserved quantity (the system's loss was the reservoir's gain). The reaction relaxes the conservation law, but not completely. A constraint $dN_i \propto \nu_i$ remains in effect

In the most probable configuration, the N_i's are adjusted by the reaction to maximize entropy of the universe, which at fixed τ and p means minimizing G:

$$dG = \sum_i \mu_i \, dN_i = 0$$

and from the constraint we conclude $\boxed{\sum \mu_i \nu_i = 0}$
condition for chemical equilibrium

Example: Suppose all species are ideal gases at fixed τ and p
Before we discuss it, consider:

Internal Partition Function of an Ideal Gas

Consider the Gibbs sum for a single orbital of an ideal gas (Chapter 6)

$$\mathfrak{z} = \sum_{n=0}^{\infty} \lambda^n e^{-n\varepsilon/\tau}$$

But for the classical regime, we ignore the (rare) double occupancy and sum over $n = 0, 1$

$$z \cong 1 + \lambda e^{-\varepsilon/\tau}$$

However the gas molecule might have internal degrees of freedom as well:

vibration
rotation
binding energy

The point of "binding energy" is that the reaction might be "exothermic" or "endothermic" and we need to use a consistent zero of energy. The Boltzman factor will favor the configuration that minimizes the amount of "internal" energy locked in the gas.

Anyway, in the classical case, we'll have

$$z \cong 1 + \lambda e^{-\varepsilon/\tau} \sum_{int} e^{-\varepsilon_{int}/\tau}$$

$$= 1 + \lambda Z_{int} e^{-\varepsilon/\tau}$$

So, in effect, the "internal partition function" of the gas gets absorbed into λ - larger Z_{int} mean larger effective λ, and hence fewer particles

This gives the distribution function

$$f(\varepsilon) = \frac{\lambda_{eff} e^{-\varepsilon/\tau}}{1 + \lambda_{eff} e^{-\varepsilon/\tau}}, \quad \lambda_{eff} = \lambda Z_{int}$$

$$\cong \lambda_{eff} e^{-\varepsilon/\tau} \text{ in the classical regime}$$

Summing over orbitals (as in Chap 3 and 6) gives

$$N = \lambda_{eff} n_Q V = \lambda Z_{int} n_Q V$$

Therefore $f = e^{+\mu/\tau} = \frac{n}{n_Q Z_{int}} \Rightarrow \boxed{\mu = \tau \log\left(\frac{n}{n_Q Z_{int}}\right)}$

We can factorize

$$Z_{int} = \sum_{int} e^{-\epsilon_{int}/\tau} = e^{-E_0/\tau} Z_{vib} Z_{rot}$$

E.g. a diatomic molecule has one vibrational mode

$$Z_{vib} = \sum_n e^{-\hbar\omega n/\tau} = \frac{1}{1-e^{-\hbar\omega/\tau}} \approx \begin{cases} 1 & \tau \ll \hbar\omega \\ \tau/\hbar\omega & \tau \gg \hbar\omega \end{cases}$$

Okay, now that we have

$$\mu = \tau(\log n - \log c)$$

$$c = n_Q Z_{int}$$

Our condition for equilibrium

$$\sum \mu_i \nu_i = 0 = \sum \nu_i (\log n_i - \log c_i)$$

depends on species through Z_{int}

Taking exp of both sides

$$\prod_i n_i^{\nu_i} = \prod c_i^{\nu_i} = K(\tau)$$

this is a function of temp, but not of the concentrations

$$\boxed{\begin{aligned} &\text{And} \quad \sum \nu_i A_i = 0 \\ &\Rightarrow \quad \prod_i n_i^{\nu_i} = K(\tau) \end{aligned}}$$

is called the "Law of Mass Action"

It describes how the concentrations adjusts when we add more of one of the reactants. And it is more general than the "ideal gas" setting in which we have derived it

- the formula $\mu = \tau \log n + n\text{-independent}$ applies also to solutes in solution

- It applies to a solute interacting with a solvent, or with a solid, where μ of solvent (or solid) does not dependent on how much solvent or solid is present.

Example: $H + H \longleftrightarrow H_2$

or $(-2)H + (1)H_2 = 0$

then law of mass action is

$$\frac{[H_2]}{[H]^2} = K(\tau)$$

where $[A]$ denotes concentration of A

Let's recall $K(\tau) = \prod c_i^{\nu_i}$ $\qquad c = n_Q Z_{int}$

$$= \frac{(n_Q Z_{int})_{H_2}}{(n_Q Z_{int})_H^2} \sim 2^{3/2} \frac{(Z_{int})_{H_2}}{(n_Q)_H (Z_{int})_H^2}$$

[Since $n_Q = \left(\frac{m\tau}{2\pi\hbar^2}\right)^{3/2} \propto m^{3/2}$

and $m_{H_2} \sim 2m_H$, we have $\frac{(n_Q)_{H_2}}{(n_Q)_H} \sim 2^{3/2}$]

Since H is a monatomic gas, we have $(Z_{vib})_H (Z_{rot})_H = 1$

But we have to be careful about the zero of energy. Let E_{BE} be the binding energy - i.e. the energy released in $H + H \rightarrow H_2$. then

$$K(\tau) \sim 2^{3/2} e^{E_{BE}/\tau} \frac{1}{(n_Q)_H} (Z_{vib} Z_{rot})_{H_2}$$

$\uparrow$ predominates at low τ, favoring H_2

or $$\frac{[H_2]}{[H]} = Z^{3/2} e^{E_{BE}/\tau} (Z_{vib} Z_{rot})_{H_2} \frac{[H]}{(n_Q)_H}$$

At low concentration, H will be favored, to maximize entropy.

Let C denote the total (conserved) number of H atoms (per unit volume) in a closed box

$$[H] + 2[H_2] = C$$

Now use $[H_2] = K[H]^2 \Rightarrow$

$$K[H]^2 + \tfrac{1}{2}[H] - \tfrac{1}{2}C = 0$$

$$\Rightarrow [H] = \frac{1}{2K}\left[-\tfrac{1}{2} \pm \sqrt{\tfrac{1}{4} + 2KC}\right]$$

$$= \frac{1}{4K}\left[\sqrt{1+8KC} - 1\right]$$

In the limit of low density, $KC \to 0$, we have

$$\sqrt{1+8KC} \sim 1 + 4KC \text{ and}$$

$$[H] \simeq C$$

there is no molecular Hydrogen when the concentration is low

And $$\frac{[H_2]}{[H]} = K[H] \simeq KC \ll 1$$