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" at a constant 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

\[ dW = dU - dQ = dU - TdS \]

In an isothermal process, \( T \) is constant:

\[ dW = d(U - TS) = dF \]

\( F = U - TS \) is the Helmholtz free energy, whose change reflects the amount of work done on/by the 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

\[ dW = -p\,dT \]

The work not is available for other purposes.
"Available work" $dW = dW - dW_{\text{mech}}$

$= dW + pdV$

Temp = constant and

If pressure = constant, then

$dW' = d(F + pV) = dG$

$G = F + pV = U - TS + pV$ is the "Gibbs free energy"

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

Most probable configuration:

Gibbs free energy is what system minimizes in its most probable configuration when in contact with $\mathcal{R}$ at specified $T$ and $p$

Recall our earlier discussion of thermal contact. Most probable configuration minimizes $G_s + G_R$

$\delta U = -\delta U_R$

Therefore

$d(G_s + G_R) = \left( \frac{1}{T_s} - \frac{1}{T_R} \right) dU_R = 0$ unqual.

$\Rightarrow \delta G = \delta G_R$

or... if $T = T_R$ constant, in equilibrium

$d(U - TS) = 0$, where $U, S$ and $T$ 

system quantities
that is: \( F = U - T \delta \) is minimized, and evaluating it at the minimum gives a function of \( \tau \): \( F(\tau) \).

We are finding where \( e^{-F/\tau} \) is large.

\( e^{-U/\tau} \) is the reservoir's entropy.

\( e^{-F/\tau} \) is the system's entropy.

For large systems, it is overwhelmingly probable that \( e^{-F/\tau} \) is close to the peak.

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

\[ dV = -dV_F \quad \text{(conservation of volume)} \]

and

\[ \rho = \left( \frac{\partial F}{\partial V} \right)_\tau, \quad \text{so} \]

\[ d(F_F + F_R) = -(p_2 - p_R) dV_F = 0 \]

To minimize free energy of system + reservoir, we have mechanical equilibrium, \( p_2 = p_R \).

Equivalently, most probable configuration is found by minimizing \( F + p V = G \) of system at specified \( \tau \) and \( \rho \).

When this quantity is minimized, we have a function \( G = G(\tau, \rho) \) of temperature and pressure.
Legendre Transform

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

$$U(\beta, V) \rightarrow F(\beta, V) \rightarrow G(\beta, \rho)$$

$U$ as a function of $\beta$, but we can’t control $\beta$; rather, the variable we can control is $\beta = \frac{d\rho}{d\beta}$, the slope of the function $U(\beta)$.

We assume $\frac{d\rho}{d\beta}$ is monotonic (we say $U(\beta)$ is convex).

We obtain a function of $\beta$ by evaluating $U - \beta \rho$ at its minimum.

$$F(\beta) = (U - \beta \rho)_{\text{stat}}$$

Then - how does $F$ change as we change $\beta$?

$$dF = d(U - \beta \rho) = dU - \beta d\rho - \rho d\beta$$

To change the slope, we need to change $\beta$ a little, but to first order, $dU = \beta d\rho$, so

$$dF = -\rho d\beta \Rightarrow \left(\frac{\partial F}{\partial \beta}\right)_{\rho} = -\rho$$

And the Gibbs free energy $G$ is obtained similarly from $F$. 
\[ G(T, p) = F(T, V) + \rho V \]

and

\[ dG = dF + \rho dV + V d\rho \]

\((\text{with } V \text{ fixed})\) \quad \Rightarrow \quad V d\rho \Rightarrow \left( \frac{\partial G}{\partial \rho} \right)_V = V

and if we vary both \( T \) and \( \rho \)

\[ d\mathcal{F} = -S dT + V d\rho : \quad \text{another \ 'thermodynamic identity'}\]

"Chemical Work"

when we say \& keeps track of systems as "non-mechanical work" what do we mean?

An example as chemical work:

Two systems, with different chemical potentials.

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

\[ W = (\mu_2 - \mu_1) AN \]

If there is no heat flow and no change in volume.

For example, recall chemical ideal gas (this illustrates chemical work, not Gibbs free energy — i.e. it is not a process at constant pressure).
For the classical ideal gas \( m = r \log(\frac{V}{N_0}) \)

Then when \( AN \) molecules are moved from 1 to 2:

\[
W = (\mu_2 - \mu_1)AN = rAN \log(\frac{N_2}{N_1})
\]

This is the same as the amount of work required to compress \( AN \) gas molecules from concentration \( N_1 \) to \( N_2 \):

\[
dW = -pdV = -N_2 \frac{dV}{V} \Rightarrow W = NT \log \frac{N_2}{N_1} = N r \log \left( \frac{N_2}{N_1} \right)
\]

**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 \( N \).

\( \sigma, U, V, N \) are extensive; so are \( G \) and \( F \)

\( \tau, \rho, \mu \) are intensive

If we divide an extensive quantity by \( N \), it becomes intensive:

\[
U(\sigma, V, N) = Nu \left( \frac{\sigma}{N}, \frac{V}{N} \right) \quad \text{u = energy per particle}
\]

\[
F(\tau, V, N) = Nf \left( \frac{\tau}{N}, \frac{V}{N} \right) \quad \text{f = free energy per particle}
\]

\[
G(\tau, \rho, N) = Ng \left( \frac{\tau}{N}, \frac{\rho}{N} \right) \quad \text{g = Gibbs free energy per particle}
\]

Note: since \( g \) is a function of intensive \( \tau \) and \( \rho \), it has no dependence on \( N \).

Recall the total Gibbs free energy:

\[
G = U - \sigma \tau + \rho V + mN \quad (G = U - \sigma \tau + \rho V)
\]

\[
\mu = \left( \frac{\partial G}{\partial N} \right)_{\tau, \rho} = g(\tau, \rho) \Rightarrow G = N\mu(\tau, \rho)
\]
The chemical potential $\mu_i$ expressed as a function of $T$ and $p$, as the Gibbs free energy per particle (it is obvious, really—G is the usable energy at fixed $T$ and $p$; so $kT/N$ is the only thing that we can vary.)

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

$$\mu_i = \frac{\partial G}{\partial N_i} |_{T, p, \text{other species}}$$

If we scale out $N_i$,

$$G(N_1, N_2, \ldots, T, p) = \sum N_i \mu_i$$

Hence, $G$ is homogeneous degree one:

$$G(\lambda N_1, \lambda N_2, \ldots) = \lambda G(N_1, N_2, \ldots)$$

If we differentiate with respect to $\lambda$,

$$\frac{d}{d\lambda} G = \sum \frac{\partial G}{\partial N_i} N_i = \sum \mu_i N_i$$

Note, though, that here the $\mu_i$'s can be functions of the relative concentrations $N_i/N_k$, as well as $T$, $p$.

Gibbs free energy in chemistry

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

Example: $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$

Write it in the form:

$$(1) \text{H}_2 + (1) \text{Cl}_2 + (2) \text{HCl} = 0$$
In general, we write the reaction in the form
\[ \Sigma V_i A_i = 0 \] where \( A_i \) are species, \( V_i \) are quantities above \( V_1 = V_2 = 1; V_3 = -2 \).

Strictly speaking, we defined \( m \) and argued that \( m \) is the most probable configuration, assuming that \( \Sigma n_i \) was a conserved quantity (the system's loss was the reservoir's gain). The reaction relaxes the conserved \( \Sigma n_i \), but not completely. A constraint \( \Sigma n_i \) remains in effect.

In the most probable configuration, the \( n_i \) is adjusted by the reaction to maximize entropy \( G \), the universe, which at fixed \( T \) and \( p \) means maximizing \( G \):
\[ \Delta G = \Sigma \mu_i dN_i = 0 \]
and from the constraint we conclude \[ \Sigma \mu_i V_i = 0 \] (condition for chemical equilibrium).

Example: Suppose all species are ideal gases at fixed \( T \) and \( p \). Before we discuss, consider:

**Internal Partition Function of an Ideal Gas**

Consider the Gibbs sum for a single orbital of an ideal gas (Chapter 9):
\[ Z = \sum_{n=0}^{\infty} e^{-n \beta \varepsilon / k} \]
But for the closed shell regime, we ignore the (not double occupancy and sum over \( n = 0 \))
\[ y = 1 + 1e^{-3/2} \]

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 Boltzmann factor will favor the configuration that minimizes the amount of "internal" energy locked in the gas.

Anyway, in the classical case, we'll have
\[ y = 1 + 1e^{-3/2} \sum_{\text{int}} e^{-E_{\text{int}}/\beta} \]
\[ = 1 + Z_{\text{int}} e^{-3/2} \]

So, in effect, the "internal partition function" of the gas gets absorbed into \( Z \) - longer \( Z_{\text{int}} \) means longer effective \( T \), and hence fewer particles.

This gives the distribution function
\[ f(\varepsilon) = \frac{\text{left } e^{-\varepsilon/\beta}}{1 + \text{left } e^{-3/2}} \quad \text{left } = 1/2 \text{mpr} \]
\[ \equiv \text{left } e^{-\varepsilon/2} \quad \text{in the classical regime} \]

Summing over orbitals (as in Chap. 3 and 6) gives
\[ N = \text{left } N_0 V = 1/2 \text{mp} \text m_0 \text V \]
Therefore \( t = e^{\frac{E_0}{RT}} \cdot \frac{n}{n_0 Z_{int}} \Rightarrow \mu = T \log (\frac{n}{n_0 Z_{int}}) \)

We can restate
\[ Z_{int} = \sum e^{-E_i/RT} = e^{E_0/RT} Z_{vib} Z_{rot} \]

E.g. a diatomic molecule has one vibrational mode
\[ Z_{vib} = \sum e^{-k_i/RT} = \frac{1}{1 - e^{-k_i/RT}} \]
\[ \sum 1 \leq 2 \leq k_t \leq l \]
\[ \sum \frac{1}{2} \leq k_t \leq \pi \]

Okay, now that we have
\[ \mu = T(\log n - \log c) \]
\[ c = n_0 Z_{int} \]

Our condition for equilibrium
\[ \sum \mu_i V_i = 0 = \sum V_i (\log n_i - \log c_i) \]

Taking exp of both sides
\[ \prod n_i^{V_i} = \prod c_i^{V_i} = K(T) \]

\[ \Rightarrow \sum V_i A_i = 0 \]
\[ \prod n_i^{V_i} = K(T) \]

As called the Law of Mass Action.

It describes how the concentrations of a reaction are affected by the amount of reactants, and it is more general than the "ideal gas" setting in which we have derived it.
The formula \( \mu = T \log N + \mu \) is independent applies also to solutes in solution.

It applies to a solute interacting with a solvent or with a solid, where \( \mu \) of solvent (instead) does not depend on how much solvent or solid is present.

Example: \( H + H \rightarrow H_2 \) or \( (-2) H + (1) H_2 = 0 \)

then law of mass action is

\[
\frac{[H_2]}{[H]^2} = K(T) \quad \text{where } [A] \text{ denotes concentration of } A
\]

Let's recall \( K(T) = \prod C_i V_i \)

\[
C = \frac{N_O Z \text{inta}}{3V}
\]

\[
= \frac{(n_O Z \text{inta}) H_2}{(n_O Z \text{inta})^2 H} \sim Z \frac{Z \text{inta} H_2}{(n_O Z \text{inta})^2 H}
\]

\[
\text{since } n_O = \left( \frac{m_T}{2 \pi \epsilon_0} \right)^{\frac{3}{2}} \quad 1 \quad \text{and } M_{H_2} \sim 2 M_H, \text{ we have } \frac{(n_O) H_2}{(n_O) H} \sim Z^{3/2}
\]

Since \( H \) has a molecular gas, we have \( \frac{(V, b)}{V} H = 1 \)

but we have to be careful about the zero energy. Let \( E_b \) be the binding energy - i.e. the energy released in \( H + H \rightarrow H_2 \). Then

\[
K(T) \sim Z^{3/2} e^{E_b/2T} \frac{1}{(n_O) H} \left( Z \frac{Z \text{inta} H_2}{(n_O) H} \right)
\]

\[ \downarrow \text{approximately low } T, \text{ forming } H_2 \]
\[
\frac{[H_2]}{[H]} = 2^{3/2} e^{\Delta G_E/T} (Z_\text{unf})^2 \frac{[H]}{[H_2]}
\]

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.

\( [H_2] + 2[H] = C \)

Now use \( [H_2] = K C [H]^2 \) \( \Rightarrow \)

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

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

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

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

\[
\sqrt{1+8KC} \approx 1 + 4KC \text{ and}
\]

\[
[H] \approx C \]

Here is no molecular hydrogen when the concentration is low.

And \( \frac{[H_2]}{[H]} = K C [H] \approx KC \ll 1 \)