

June 17, 1980

Clausius \leq and thermo potentials 838-840
vapor pressure of solid 847-864
equilibrium for ideal gas reactions 865

835

Briefly review the criteria for a heat reservoir (also called a thermostat). It is a system with a large number of energy levels distributed "quasi-continuously" so that one can speak of the density of energy levels $\sigma(E)dE$.

One has two requirements: The reservoir is supposed to have a total energy E_0 . It gets connected to a small system whose energy levels are small. The first requirement is that

$$\frac{\sigma(E_0 + \Delta E)}{\sigma(E_0)} = e^{\beta_0 \Delta E}$$

is a good approximation for ΔE an energy level of the small system. Thus

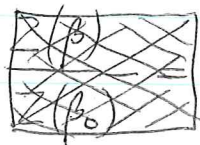
$$\left. \frac{d \log \sigma}{dE} \right|_{E_0} = \beta_0$$

and we want $\log \sigma(E)$ to be linear to a good approximation around $E = E_0$.

The second requirement is that the actual behavior of the reservoir at energy E_0 should be very close to its thermal behavior. This means that in the partition function

$$Z(\beta_0) = \int e^{-\beta_0 E} \sigma(E) dE$$

the measure should peak near $E = E_0$ so that a steepest descent calculation is good:



$$-\beta_0 E + \log \sigma = -\beta_0 E_0 + \log \sigma(E_0) + \frac{1}{2} \left. \frac{d^2 \log \sigma(E)}{dE^2} \right|_{E_0} (E - E_0)^2 + \dots$$

$$\frac{Z(\beta)}{Z(\beta_0)} = \frac{\int e^{-\Delta \beta E} e^{-\beta_0 E + \log \sigma} dE}{\int e^{-\beta_0 E + \log \sigma} dE} \doteq e^{-(\Delta \beta) E_0} \frac{\int e^{-\Delta \beta (E - E_0) - \frac{1}{2} (E - E_0)^2} dE}{\int e^{-\frac{1}{2} a (E - E_0)^2} dE}$$

$$\frac{Z(\beta)}{Z(\beta_0)} = e^{-(\Delta\beta)E_0 + \frac{1}{2}\tilde{a}(\Delta\beta)^2}$$

Now the steepest descent calculation is apt to be accurate when a is large. But this would mean that $\log \sigma(E)$ is not very linear near E_0 . So the two requirements are slightly inconsistent, so it appears.

Consider for example N copies of the same system with partition fn.

$$Z(\beta) = \int e^{-\beta E} \sigma(E) dE.$$

Then $Z_N(\beta) = Z(\beta)^N = \int e^{-\beta E} \sigma_N(E) dE$

is the partition function for the ensemble (Notice: the thermal behavior of the ensemble is always easy to compute.)

Let's compute σ_N by steepest descent around $E_0 = N\varepsilon_0$
 where $\varepsilon_0 = -\frac{\partial}{\partial \beta} \log Z(\beta) \Big|_{\beta_0}$. $\sigma_N(E) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} e^{\beta E} Z(\beta)^N d\beta$

$$\frac{\sigma_N(E)}{\sigma_N(N\varepsilon_0)} = \frac{\int e^{\beta(E - N\varepsilon_0) + (\beta\varepsilon_0 + \log Z)^N} d\beta}{\int e^{(\beta\varepsilon_0 + \log Z)^N} d\beta}$$

$$\beta\varepsilon_0 + \log Z = \beta_0\varepsilon_0 + \log Z(\beta_0) + \underbrace{\frac{1}{2} \frac{d^2}{d\beta^2} \log Z(\beta) \Big|_{\beta_0}}_{\tilde{a}} (\beta - \beta_0)^2 + \dots$$

$$\frac{\sigma_N(E)}{\sigma_N(N\varepsilon_0)} = \frac{\int e^{\beta_0(E - N\varepsilon_0) + (\beta - \beta_0)(E - N\varepsilon_0) + \frac{N}{2}\tilde{a}(\beta - \beta_0)^2} d\beta}{\int e^{\frac{N\tilde{a}}{2}(\beta - \beta_0)^2} d\beta} = e^{\beta_0(E - N\varepsilon_0) - \frac{1}{2N\tilde{a}}(E - N\varepsilon_0)^2}$$

Thus
$$\frac{\sigma_N(E)}{\sigma_N(N\varepsilon_0)} \approx e^{\beta_0 \Delta E - \frac{1}{2N\tilde{a}}(\Delta E)^2}$$

where $\Delta E = E - N\varepsilon_0$ and $\tilde{a} = \left. \frac{d^2}{d\beta^2} \log Z(\beta) \right|_{\beta_0}$

Therefore one sees that ~~the~~ for large N , the quadratic part ~~becomes~~ becomes negligible (for $\log \sigma_N(E)$). On the other hand ~~if~~ if one looks at the partition function

$$Z_N(\beta_0) = Z(\beta_0)^N = \int e^{-\beta_0 E} \sigma_N(E) dE$$

and asks about the relative distribution of measure, one should write

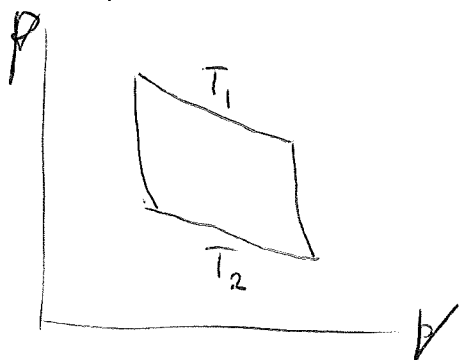
$$\int e^{-\beta_0 E} \sigma_N(E) dE = N \int e^{-\beta_0 N\varepsilon} \sigma_N(N\varepsilon) d\varepsilon$$

and notice that

$$\frac{e^{-\beta_0 N\varepsilon} \sigma_N(N\varepsilon)}{e^{-\beta_0 N\varepsilon_0} \sigma_N(N\varepsilon_0)} \approx e^{-\frac{1}{2N\tilde{a}}(N(\varepsilon - \varepsilon_0))^2}$$

so one does get the required concentration of the measure $e^{-\beta_0 E} \sigma_N(E) dE$ near $E = N\varepsilon_0$.

Let's go over thermo. potentials. Consider a heat engine executing a Carnot cycle between the temperatures T_1 and T_2 .



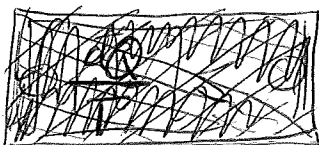
$$\text{efficiency} = \frac{\text{work done}}{\text{heat in}} = \frac{Q_1 - Q_2}{Q_1}$$

The 2nd law + Kelvin definition of temperature says $\frac{Q_1 - Q_2}{Q_1} \leq \frac{T_1 - T_2}{T_1}$

hence $1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$, $\frac{T_2}{T_1} \leq \frac{Q_2}{Q_1}$

or $\frac{Q_1}{T_1} \leq \frac{Q_2}{T_2}$ (can remember by looking at the case $T_1 > T_2$, $Q_1 = Q_2$)

For a general cycle, one breaks it up into little Carnot cycles to get the inequality of Clausius:



$$\oint \frac{dQ}{T} \leq 0$$

with equality for a reversible engine. (dQ is not the differential of a function; it is also not the differential $dU + pdV$ for irreversible changes. If I use $dQ = dU + pdV$, then the above integral is zero.)

The entropy S satisfies $dS = \frac{dU + pdV}{T}$ and hence for a reversible change from A to B we have

$$\int_A^B \frac{dQ}{T} = S_B - S_A$$

and in general Clausius inequality gives

$$\int_A^B \frac{dQ}{T} \leq S_B - S_A$$

↑
along any change
from A to B

Consider constant temperature changes

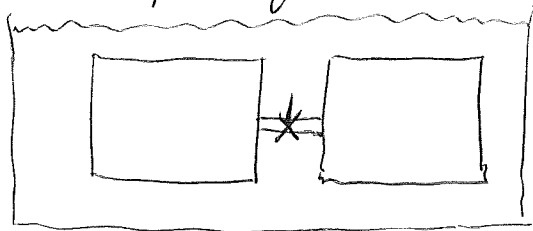
$$\int_A^B dQ \leq TS_B - TS_A$$

heat put
into engine

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839

Example of an irreversible change: Joule experiment



Initially the gas is on one side with pressure p , volume V , temp. T and $pV = nRT$

The stopcock is opened and it is found that the temperature stays the same. Of course $p \mapsto p/2$ because $V \mapsto 2V$.

The process is irreversible because suppose we allowed the expansion to go slowly against a piston from V to $2V$. Then work is done so heat has to be added. In Joule expansion no work is done and no heat is added.

Let's compute the Clausius inequality in this case

$$S_B - S_A = \int \frac{dQ}{T} = \int \frac{pdV}{T} = \int nR \frac{dV}{V} = nR \log\left(\frac{V_B}{V_A}\right)$$

↑
for
slow
expansion

Thus the entropy increase is $nR \log\left(\frac{V_B}{V_A}\right)$ but the work done is 0.

Return to isothermal change where

$$\int_A^B dq \leq TS_B - TS_A$$

heat in = $U_B - U_A$ + work done. Therefore

$$\text{work done from A to B} \leq F_A - F_B \quad F = U - TS$$

If ~~we~~ we have a change at constant pressure and temperature, then

$$\text{work done} = p(V_B - V_A)$$

and so we get the inequality

$$\phi_A \geq \phi_B \quad \text{where } \phi = U - TS + pV$$

for a change at ~~constant~~ constant temperature and pressure.

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841

To see if I can get the Sackur-Tetrode formula ~~from~~ from the vapor pressure of a crystalline solid. Assume the solid occupies 0 volume and that it satisfies Einstein's model in that all the modes have the same frequency. Let n_s be the number of solid molecules. For a single oscillator

$$Z = \frac{e^{-\beta \frac{1}{2} \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \quad U = \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \approx \frac{1}{\beta} = kT$$

$$F = -\frac{1}{\beta} \log Z = \frac{1}{2} \hbar \omega + \frac{1}{\beta} \log(1 - e^{-\beta \hbar \omega})$$

Thus

$$F_s = 3n_s \left(\frac{1}{2} \hbar \omega + kT \log(1 - e^{-\frac{\hbar \omega}{kT}}) \right)$$

and since the ~~volume~~ volume is zero

$$\phi_s = F_s + pV = F_s$$

Next look at the gas which is assumed to be ideal. monatomic

Thus

$$U = \frac{3}{2} NkT \quad pV = NkT \quad H = U + pV = \frac{5}{2} NkT$$

$$TdS = dU + pdV = \frac{3}{2} Nk dT + d(pV) - Vdp$$

$$dS = \frac{5}{2} Nk \frac{dT}{T} - Nk \frac{dp}{p}$$

$$S = Nk \log(T^{5/2}/p) + S_0(N)$$

$$\phi_g = H - TS = \frac{5}{2} NkT - NkT \log(T^{5/2}/p) - TS_0(N)$$

At equilibrium with n_s solid molecules and n_g gas molecules we have $\phi_s = \phi_g$ or

$$3n_s \left(\frac{1}{2} \hbar \omega + kT \log(1 - e^{-\frac{\hbar \omega}{kT}}) \right) = \frac{5}{2} n_g kT - n_g kT \log(T^{5/2}/p) - TS_0(n_g)$$

If you are given p, T and the total number of molecules, then this equation tells you how many gas + solid molecules there are, provided $S_0(n)$ is known. Now I want there to be a p, T at which the solid + gas can interchange freely, which means that this equation should hold for all n_s, n_g with $n_s + n_g = N$ constant. This seems to be impossible for this model. In effect $S_0(n_g)$ has to be linear in n_g and

$$-TS_0(0) = 3N \left(\frac{1}{2} \hbar \omega + kT \log \left(1 - e^{-\frac{\hbar \omega}{kT}} \right) \right)$$

depends on N .

So if we want a model which will exhibit vapor and gas in equilibrium we have to do something else. The basic problem is ~~whether~~ whether it is possible to have an equation $\phi_s = \phi_g$ for all n_s, n_g with $n_s + n_g = N$.

$$\phi_s = \underbrace{n_s}_{N-n_g} \cdot \tilde{\phi}_s = n_g \tilde{\phi}_g$$

This relation can hold only if $\tilde{\phi}_s = \tilde{\phi}_g = 0$. ?

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843

Yesterday I ran into difficulty with a solid + vapor in equilibrium. Possibly the difficulty is due to treating the number of molecules in the wrong way. One has to treat N "macroscopically" maybe, which means you form a grand ensemble and choose μ appropriately. So I should go over chemical potential.

Recall the basic formulas

$$dU = TdS - pdV$$

$$dF = -SdT - pdV$$

$$d\phi = -SdT + Vdp$$

$$F = U - TS$$

$$\phi = U - TS + pV$$

which hold provided the number of molecules of different types remains fixed. Suppose more generally we have different constituents, types of molecules, in our system and that the numbers n_i of these can change. Then one defines the chemical potential μ_i by

$$d\phi = -SdT + Vdp + \sum \mu_i dn_i$$

i.e.
$$\mu_i = \left(\frac{\partial \phi}{\partial n_i} \right)_{T, p}$$

It follows that

$$dF = -SdT - pdV + \sum \mu_i dn_i$$

or
$$\mu_i = \left(\frac{\partial F}{\partial n_i} \right)_{T, V}$$

I need to get some feeling for this notion of chemical potential. Suppose we have a gas made up of N ~~particles~~ ^{particles} in a box of volume V . Suppose the ~~particles~~ particles repel each other. Then adding an

extra particle increases the energy, ~~and~~ and μ should be a positive quantity, so that lowering energy means fewer particles.

Make this quantitative: suppose the N particle gas described by partition function $Z(T, V, N)$. Think of the system running through all the different energy states with the appropriate frequency. Then the internal or average energy is the appropriate average

$$U = \langle E_x \rangle = -\left(\frac{\partial \log Z}{\partial \beta}\right)_{V, N}$$

~~Now~~ Now μ is going to be like p in that you figure out how the energy changes without changing the probability distribution. One computes $\frac{\partial E}{\partial N}$ for each occurring state and then averages. Thus

$$\begin{aligned} \mu &= \left\langle \frac{\partial E}{\partial N} \right\rangle = -\frac{1}{\beta} \frac{\partial}{\partial N} \log Z(T, V, N) \\ &= \left(\frac{\partial F}{\partial N}\right)_{T, V} \end{aligned}$$

(Check out the formulas: $F = -\frac{1}{\beta} \log Z = -kT \log Z(T, V, N)$)

$$\begin{aligned} U &= -\frac{\partial}{\partial \beta} \log Z & P &= \frac{1}{\beta} \frac{\partial}{\partial V} \log Z = -\frac{\partial F}{\partial V} \\ \mu &= \frac{\partial F}{\partial N} \end{aligned}$$

$$\begin{aligned} -\frac{\partial F}{\partial T} &= \frac{\partial}{\partial T} (kT \log Z) = k \log Z + kT \underbrace{\left(\frac{\partial}{\partial \beta} \log Z\right)}_{-U} \underbrace{\frac{\partial}{\partial T} (\beta)}_{-\frac{1}{kT^2}} \\ &= k(\log Z + U\beta) = S \end{aligned}$$

so $dF = -SdT - pdV + \mu dN$

Also $du = d(F+TS) = TdS - pdV + \mu dN$

$$\text{so } dQ = dU + pdV - \mu dN$$

$$\text{or } dU = dQ - pdV + \mu dN$$

so that each ^{new} particle ^{adds} extra energy μ .

The above is for fixed N and is not yet "macroscopic." so one forms the grand partition fun

$$Z_G(T, V, \mu) = \sum_N Z(T, V, \mu) e^{(\beta\mu)N}$$

which is a kind of Laplace transform with respect N .

Assume ~~_____~~ this has a dominant term at N , then

$$\frac{\partial}{\partial N} (\log Z(N) + \beta\mu N) = \frac{\partial}{\partial N} \log Z + \beta\mu = 0$$

$$\text{or } \mu = + \frac{\partial}{\partial N} \left(- \frac{\log Z(T, V, N)}{\beta} \right) = \frac{\partial F}{\partial N}$$

so that μ is indeed the chemical potential at N . ~~_____~~

Approximating by dominant term gives

$$Z_G \approx Z(N) e^{(\beta\mu)N}$$

$$- \frac{\log Z_G}{\beta} \approx - \frac{\log Z(N)}{\beta} - \mu N$$

so that if ~~_____~~ $\Omega(T, V, \mu) = - \frac{1}{\beta} \log Z_G(T, V, \mu)$ is the thermodynamic potential, then

$$\Omega = F - \mu N = F - N \frac{\partial F}{\partial N}$$

is the Legendre transform of $F(T, V, N)$ wrt N .

New viewpoint: Let us start by being given $\sigma(E, V, N)$ = number of states with energy E , volume V ,

and N particles. Following Boltzmann we define

$$(*) \quad S(E, V, N) = k \log \sigma(E, V, N)$$

which immediately presents S as a function of E, V, N which are its natural variables. Then T, p, μ can be defined by the fundamental relation

$$Tds = dE + pdV - \mu dN$$

The above^(*) is only reasonable "macroscopically". One normally Laplace transforms with respect to E or with respect to E, N .

$$Z(T, V, N) = \sum_E e^{-\frac{E}{kT}} \sigma(E, V, N)$$

$$Z_G(T, V, \mu) = \sum_{N, E} e^{\beta \mu N} e^{-\beta E} \sigma(E, V, N)$$

Assume $Z(T, V, N) = \sum_E e^{-\beta E} \sigma(E, V, N)$

has a ~~dominant~~ term when $\frac{\partial \log \sigma}{\partial E} = \beta$. Then

$$\log(Z) \approx -\beta E + \log \sigma$$

~~is~~ is the Legendre transform of $-\log \sigma(E, V, N)$ wrt E . Thus we have

$$-\frac{\partial \log Z}{\partial \beta} = E$$

$$\text{and } S = k(\beta E + \log Z) = k \log \sigma$$

The Laplace transform method, i.e. using S

~~defined~~ defined in terms of Z is somehow always correct even when $(*)$ isn't.

Question: Why isn't Laplace transform wrt V used?

June 22, 1980 (40 years old)

847

vapor pressure of a crystal: N atoms total, n in gas and $N-n$ in solid. The problem is to compute the probability of n gas atoms. One has the partition fn.

$$\sum_n \sum_{\substack{\text{states } \alpha \\ \text{with } n \text{ gas} \\ \text{atoms}}} e^{-\beta E_\alpha}$$

and p_n is proportional to $\sum_{\substack{\text{states } \alpha \\ \text{with } n \\ \text{gas molecules.}}} e^{-\beta E_\alpha}$

The picture used by Stern (I guess - see Fermi or Tolman books) is to assume that there is only one possible state for the solid having a given number of atoms, and that it has zero energy. Then there are two ways of getting the partition function.

1) distinguishable atoms. The N atoms have to be divided into solid + gas. This gives combinatorial factor:

$$\binom{N}{n} \underbrace{(N-n)!}_{\text{different ways to assemble the unique solid state with } (N-n) \text{ atoms.}} = \frac{N!}{n!}$$

Supposing the gas molecules have potential energy w relative to the solid, and mass m , the 1-gas molecule partition fn. is

$$Z_1 = \int_{\text{in } V} e^{-\beta \left(\frac{p^2}{2m} + w \right)} \frac{d^3 q d^3 p}{h^3} = e^{-\beta w} V \beta^{-3/2} \left(\frac{m 2\pi}{h^2} \right)^{3/2}$$

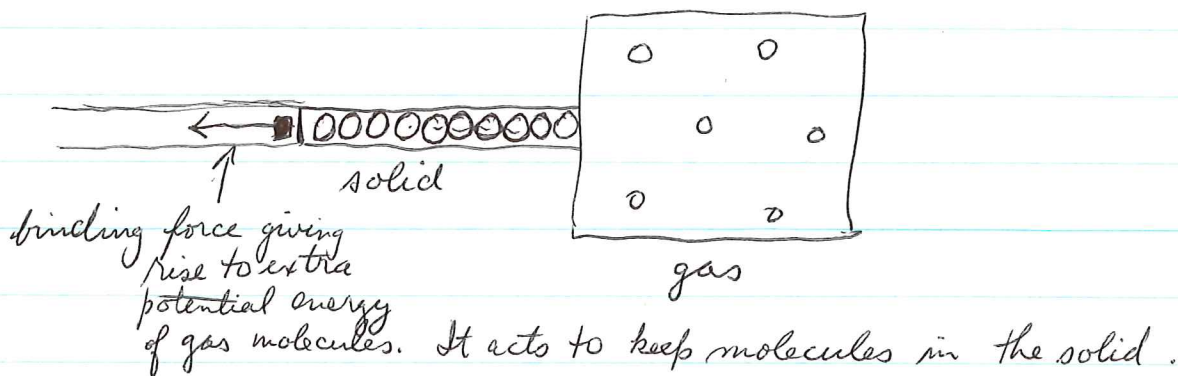
The grand partition function is then

$$Z_G = \sum_{n \leq N} \frac{N!}{n!} \left(e^{-\beta w} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right)^n$$

2) indistinguishable atoms. In this case the combinatorial factor is missing, but $(Z_1)^n$ has to be replaced by $Z_1^n/n!$ for the gas atoms. However, still one is assuming only one solid configuration. Then

$$Z_G = \sum_{n \leq N} \frac{1}{n!} \left(e^{-\beta w} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right)^n$$

Here is a good picture of the way the system looks



Note: The above model simply gives the grand partition function for an ideal gas with chemical potential $\mu = -w$.

So now we can compute the expected value of n by maximizing probability:

$$P_n \sim \frac{1}{n!} Z_1^n$$

$$\log P_n = n \left[e^{-\beta w} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right] - (n \log n - n) + \text{const}$$

$$0 = \frac{d}{dn} \log P_n = e^{-\beta w} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} - \log n$$

$$n = e^{-\frac{w}{kT}} V \left(\frac{2\pi m kT}{h^2} \right)^{3/2}$$

Alternatively we can use the partition function Z_G directly to get the expected value of n :

$$n = -\frac{1}{\beta} \frac{\partial}{\partial \omega} \log Z_G = -\frac{1}{\beta} \frac{\partial}{\partial \omega} \left(e^{-\beta \omega} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right)$$

to get the same formula. (This is exact only as $N \rightarrow \infty$).
 since $Z_G = \sum_{n \leq N}$


For an ideal gas we have $n = pV\beta$ so

$$pV\beta = e^{-\beta \omega} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2}$$

$$p = e^{-\beta \omega} \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2}$$

or
$$p = e^{-\frac{\omega}{kT}} (kT)^{5/2} \left(\frac{2\pi m}{h^2} \right)^{3/2}$$

formula for the vapor pressure.

This could be obtained more simply  from

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z_G \quad \blacksquare$$

Note: When the method of maximum probability is applied to

$$Z_G = \sum_{n=0}^{\infty} \frac{1}{n!} (e^{\beta \mu} Z_1)^n = e^{(e^{\beta \mu} Z_1)}$$

one gets

$$\log p_n = n \log (e^{\beta \mu} Z_1) - \log (n!) - \log (Z_G)$$

$$0 = \frac{d}{dn} \log p_n = \log (e^{\beta \mu} Z_1) - \log n$$

$$\text{or } n = e^{\beta \mu} Z_1$$

This is the same if one puts $n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G$. Thus we have an example where maximum probability is exact.

Next problem to examine is where there is a fixed number N of atoms. Here we have to pay attention to the fact that the partition function is summed for $0 \leq n \leq N$. If we use the maximum probability method then we don't see this cutoff until $n = N$. Assuming N is large the dominant term method ought to be pretty accurate.

Example: Consider $e^n = \sum_{k=0}^{\infty} \frac{n^k}{k!}$ where n is large. The dominant term occurs when

$$\frac{d}{dk} (k \log n - k!) = \log n - \log k = 0 \quad k = n$$

Approximating the sum by its dominant term yields

$$e^n \approx \frac{n^n}{n!} \quad \text{or} \quad n! \approx n^n e^{-n},$$

which is OK by Stirling's formula.

So let's consider the partition function for the crystal-vapor system with N atoms:

$$Z = \sum_{n=0}^N \frac{1}{n!} \left(e^{-\beta w} V \beta^{-3/2} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right)^n$$

\propto

Let's use the dominant term method to compute the equation of state. T, V are the independent variables.

The dominant term in the above series was computed above and gave

$$n = V \beta^{-3/2} e^{-\beta w} \propto$$

provided $n \leq N$; otherwise the dominant term is $n = N$. Let's fix the temperature and begin to increase V . Then the number of gas atoms increases linearly with V until the solid is completely evaporated.

What is the pressure when $n \leq N$. In general

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z$$

It is clear that $\frac{\partial}{\partial V}$ takes V^n to nV^{n-1} so that when one has the dominant term at n :

$$p = \frac{1}{\beta} n \frac{1}{V} \quad \text{or} \quad pV = nkT$$

which is the ideal gas law. From another viewpoint if the dominant term occurs for $n \leq N$, then

$$Z \sim e^{-\beta w} V \beta^{-3/2} \alpha \Rightarrow p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z = \frac{1}{\beta} e^{-\beta w} \beta^{-3/2} \alpha$$

which leads to the same result. Note

$$p = \frac{1}{\beta} \frac{n}{V} = e^{-\beta w} \beta^{-5/2} \alpha$$

is the equation for the vapor pressure in terms of T . This is constant as V goes from 0 to

$$V = N / \beta^{-3/2} e^{-\beta w} \alpha$$

As V increases beyond this point the dominant term in the partition function is the N -th, so

$$Z \approx \frac{1}{N!} (e^{-\beta w} V \beta^{-3/2} \alpha)^N$$

which is the partition function for N -molecules of an ideal monatomic gas, except for the factor $e^{-\beta w N}$ which contributes only a constant to the internal energy.

Question: Can one make the above approximations exact by making N "macroscopic"? Somehow let the parameters N, V go to infinity.

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852

Consider the frozen solid which has 1 state of zero energy having N atoms for each $N \geq 0$. Thus

$$Z(T, V, N) = 1 \quad \text{for all } N.$$

Review the grand formalism: One puts

$$Z_G(T, V, \mu) = \sum_{N \geq 0} (e^{\beta \mu})^N Z(T, V, N)$$

If one is in a good situation, where the dominant term method works, then

$$\log Z_G(\mu) = N(\beta \mu) + \log Z(N)$$

$$\text{where } N \text{ is such that } \beta \mu + \frac{\partial}{\partial N} \log Z(N) = 0$$

$$\text{or } \mu = -\frac{1}{\beta} \frac{\partial}{\partial N} \log Z(N) = \frac{\partial}{\partial N} \underbrace{\left(-\frac{\log Z(N)}{\beta} \right)}_{F(N)}$$

It follows that $\frac{1}{\beta} \log Z_G(\mu)$ is the Legendre transform of $\frac{\log Z(N)}{\beta}$ so that

$$\frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G(\mu) = N$$

In general one uses this formula relating μ and N when the dominant term method doesn't work.

For example with $Z(N) = 1$ for all N we have

$$Z_G(\mu) = \sum_{N \geq 0} (e^{\beta \mu})^N = \frac{1}{1 - e^{\beta \mu}}$$

and

$$N = \frac{-1}{\beta} \frac{\partial}{\partial \mu} \log(1 - e^{\beta \mu}) = \frac{e^{\beta \mu}}{1 - e^{\beta \mu}} = \frac{1}{e^{-\beta \mu} - 1}$$

Of course μ has to be < 0 in order that this have any meaning. There is no resistance to adding more particles to the solid, so that in order to get a finite number

of particles we have to provide them with energy to keep them away. Thus we see that the chemical potential of the solid is < 0 , in fact

$$\mu = \frac{1}{\beta} \log\left(\frac{N}{N+1}\right) \stackrel{\text{large } N}{\approx} \frac{-kT}{N}$$

Notice: For $T > 0$ the solid wants to grow bigger - that's what $\mu < 0$ means. However the larger N is, the less the tendency to grow is.

Next project is to compute the grand partition function for the solid + gas. We saw yesterday that if we had m solid molecules and n gas molecules, then the partition function is

$$Z(T, V, m, n) = \frac{(e^{-\beta \omega} Z_1(T, V))^n}{n!}$$

where $Z_1(T, V)$ is the partition fn. for a single gas molecule:

$$Z_1(T, V) = V \beta^{-3/2} \underbrace{\left(\frac{2\pi m}{h^2}\right)^{3/2}}_{\alpha}$$

~~So the grand partition function for this model is~~
 ~~$Z_0(T, V, \mu) = \sum_{m, n} \frac{1}{m! n!} (e^{-\beta \omega} Z_1)^n (Z_2)^m$~~

The partition function when N atoms are present is

$$\sum_{m+n=N} Z(T, V, m, n) = \sum_{n \leq N} \frac{1}{n!} (e^{-\beta \omega} Z_1)^n$$

Hence the grand partition function is

$$Z_G(T, V, \mu) = \sum_N e^{\beta\mu N} \sum_{m+n=N} \frac{(e^{-\beta\omega} Z_1)^n}{n!}$$

$$= \sum_{m,n} e^{\beta\mu(m+n)} \frac{(e^{-\beta\omega} Z_1)^n}{n!}$$

$$= \frac{1}{1-e^{\beta\mu}} e^{e^{\beta\mu} e^{-\beta\omega} Z_1}$$



$$Z_G = \frac{1}{1-e^{\beta\mu}} e^{(e^{\beta(\mu-\omega)} Z_1)}$$

$$\log Z_G = -\log(1-e^{\beta\mu}) + e^{\beta(\mu-\omega)} Z_1$$

$$\log Z_G = -\log(1-e^{\beta\mu}) + e^{\beta(\mu-\omega)} V \beta^{-3/2} \alpha$$

Then μ is to be determined so that

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{e^{\beta\mu}}{1-e^{\beta\mu}} + e^{\beta(\mu-\omega)} V \beta^{-3/2} \alpha$$

number of solid ~~atoms~~ atoms

$n =$ number of gas ~~atoms~~ atoms

Also

$$P = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z_G = \frac{1}{\beta} e^{\beta(\mu-\omega)} \beta^{-3/2} \alpha = \frac{n}{\beta V}$$

so the vapor behaves like ~~an~~ an ideal monatomic gas.

Suppose β, N fixed and we let n vary. We can

solve

$$N = \frac{1}{e^{\beta\mu} - 1} + n \quad \text{to get} \quad \mu = \frac{1}{\beta} \log \left(\frac{N-n}{N-n+1} \right)$$

for μ . Then we can determine V .

$$\approx -\frac{kT}{N-n}$$

We see that because of the μ dependence in

$$n = e^{\beta(\mu - w)} V \beta^{-3/2} \alpha$$

the volume V is not a linear function of n . Consequently from $p = \frac{n}{\beta V}$ one sees that the pressure is not really constant as we vaporize the solid.

It would be nice to be able to plot on a p, V diagram an isothermal ~~curves~~ curves. Let's rewrite our basic equations in terms of $z = e^{\beta\mu}$ and the constants $\beta, \gamma = e^{-\beta w} \beta^{-3/2} \alpha$.

Then

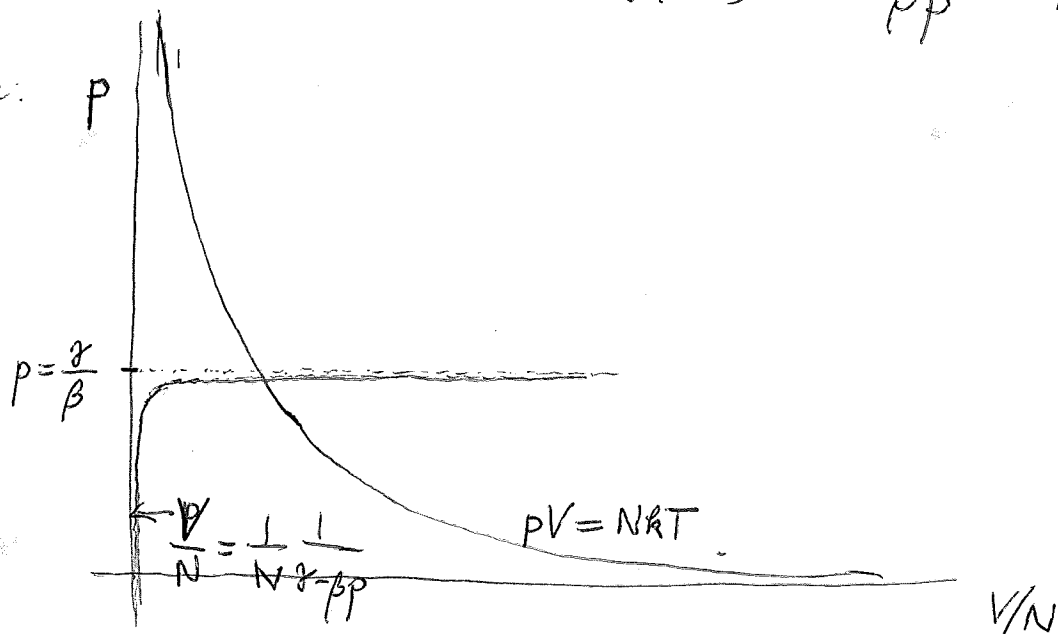
$$p = \frac{z}{\beta} \gamma \quad N = \frac{z}{1-z} + zV\gamma$$

These are parametric equations for the isothermal curve.

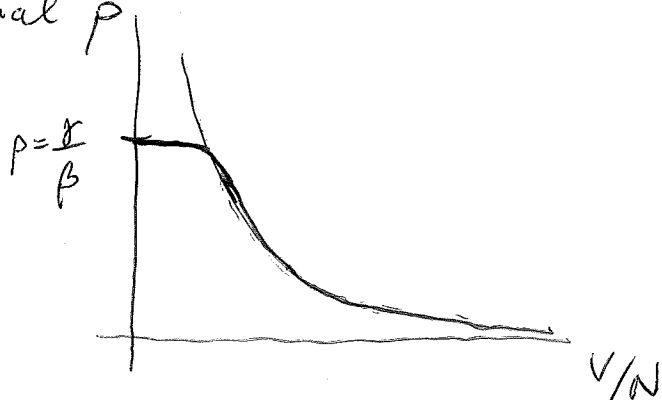
$$z = \frac{\beta}{\gamma} p \quad \gamma z \frac{V}{N} = 1 - \frac{1}{N} \frac{z}{1-z}$$

$$\frac{V}{N} = \frac{1}{\gamma z} - \frac{1}{N} \frac{1}{\gamma(1-z)} = \frac{1}{\beta p} - \frac{1}{N} \frac{1}{\gamma - \beta p}$$

Picture:



When these curves are put together one gets the isothermal p



and the larger N is the flatter the isothermal curve becomes at the beginning. As $N \rightarrow \infty$ one gets

$$p = \frac{\gamma}{\beta} = e^{-\beta u} \beta^{-5/2} \alpha = e^{-\frac{u}{kT} - \frac{5}{2} \ln \left(\frac{2\pi m}{h^2} \right)^{3/2}}$$

June 24, 1980

857

chemical potential approach. Ideal gas:

Method 1: $Z(T, V, N) = \frac{1}{n!} (V \beta^{-3/2} \alpha)^n$ $\alpha = \left(\frac{2\pi m}{h^2} \right)^{3/2}$

$$F = -\frac{1}{\beta} \log Z(N) = -\frac{1}{\beta} (n \log(V \beta^{-3/2} \alpha) - n \log n + n)$$

$$= -\frac{n}{\beta} \left(\log \left(\frac{V \beta^{-3/2} \alpha}{n} \right) + 1 \right)$$

$P = -\frac{\partial F}{\partial V} = \frac{n}{\beta} \frac{1}{V}$ as usual. $\therefore \frac{V}{n} = \frac{1}{\beta P}$

so $F = -\frac{n}{\beta} \left(\log \left(\frac{\beta^{-5/2} \alpha}{P} \right) + 1 \right)$

and so $\phi = F + pV = F + \frac{n}{\beta}$ or

$$\phi = -\frac{n}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{P} \right)$$

Gibbs potential
for ideal monatomic
gas

Recall $\begin{cases} dU = TdS - pdV + \mu dn \\ dF = -SdT - pdV + \mu dn \\ d\phi = -SdT + Vdp + \mu dn \end{cases}$

hence the chemical potential is given by

$$\mu = \left(\frac{\partial \phi}{\partial n} \right)_{T, P} = -\frac{1}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{P} \right)$$

Method 2: $Z_G(T, V, \mu) = \sum_n e^{\beta \mu n} Z(T, V, n)$. When the dominant term method works on this sum we have

$$\log Z_G(\mu) = \beta \mu n + \log Z(n) \quad \text{where}$$

n is such that $\mu = -\frac{1}{\beta} \frac{\partial}{\partial n} \log Z(n) = \left(\frac{\partial F}{\partial n} \right)_{T, V}$

June 25, 1980

858

Let's review the chemical potential approach to equilibrium between the solid and gas. First we need the chemical potential of the ideal gas.

Method 1 based upon $Z(T, V, n)$, the n -particle partition function:

$$Z(T, V, n) = \frac{1}{n!} (V \beta^{-3/2} \alpha)^n \quad \alpha = \frac{(2\pi m)^{3/2}}{h^3}$$

The free energy is

$$F = -\frac{1}{\beta} \log Z \quad \blacksquare$$

and one has

$$dF = -SdT - pdV + \mu dn.$$

Hence

$$\mu = \left(\frac{\partial F}{\partial n} \right)_{T, V} = \frac{\partial}{\partial n} \left(-\frac{1}{\beta} (n \log(V \beta^{-3/2} \alpha) - n \log n + n) \right)$$

$$= -\frac{1}{\beta} \log(V \beta^{-3/2} \alpha) + \frac{\log n}{\beta} \quad \blacksquare$$

$$\mu = -\frac{1}{\beta} \log \left(\frac{V \beta^{-3/2} \alpha}{n} \right) \quad \text{as a fn. of } T, V, n$$

Also

$$p = -\frac{\partial F}{\partial V} = \frac{n}{\beta} \frac{1}{V} \quad \text{or} \quad \frac{V}{n} = \frac{1}{\beta p}$$

so

$$\mu = -\frac{1}{\beta} \log \left(\beta^{-5/2} \alpha / p \right) \quad \text{as a fn. of } T, p, n.$$

If the gas atoms have extra potential energy w then

$$\mu = w - \frac{1}{\beta} \log(\beta^{-5/2} \alpha / p)$$

Notice also that if we form the Gibbs free energy

$$\phi = F + pV = -\frac{n}{\beta} \log \left(\frac{V \beta^{-3/2} \alpha}{n} \right) - \frac{n}{\beta} + \frac{n}{\beta}$$

$$\phi = -\frac{n}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{p} \right)$$

then $\mu = \left(\frac{\partial \phi}{\partial n} \right)_{T, p} = -\frac{1}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{p} \right)$ as it should be.

Method 2 based upon grand partition fn.

$$Z_G(T, V, \mu) = \sum_n e^{\beta \mu n} Z(T, V, n)$$

When ~~max~~ dominant term method works, we have

$\log Z_G \approx \beta \mu n + \log Z$ where $\beta \mu + \frac{\partial}{\partial n} \log Z = 0$
and hence we get the formula and $\frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = n$

$$F(T, V, n) = -\frac{1}{\beta} \log Z(T, V, n)$$

$$F(T, V, n) = -\frac{1}{\beta} \log Z_G(T, V, \mu) + \mu n$$

where $n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G(T, V, \mu)$

These formulas are used even when dominant term method doesn't work.

For ideal gas $Z_G(T, V, \mu) = e^{e^{\beta \mu} V \beta^{-3/2} \alpha}$

so

$$n = e^{\beta \mu} V \beta^{-3/2} \alpha$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z_G = e^{\beta \mu} \beta^{-5/2} \alpha = \frac{n}{V \beta}$$

and so

$$\mu = -\frac{1}{\beta} \log \left(\frac{V \beta^{-3/2} \alpha}{n} \right) = -\frac{1}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{p} \right)$$

Next consider the solid where $Z(T, V, n) = 1$ for all n . In this case we have to use the grand partition fn.

$$Z_G(T, V, \mu) = \sum_n e^{\beta \mu n} = \frac{1}{1 - e^{\beta \mu}}$$

Then

$$n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log \left(\frac{1}{1 - e^{\beta \mu}} \right) = \frac{e^{\beta \mu}}{1 - e^{\beta \mu}}$$

$$n = \frac{e^{\beta \mu}}{1 - e^{\beta \mu}} \quad e^{\beta \mu} = \frac{n}{n+1} \quad \mu = \frac{1}{\beta} \log \left(\frac{n}{n+1} \right)$$

Equilibrium between solid and vapor at constant T, V is achieved when the Helmholtz free energy

$$F_s + F_g \text{ is minimum}$$

Equilibrium at constant T, p is achieved ~~when~~ when the Gibbs free energy

$$\phi_s + \phi_g \text{ is minimum}$$

These must be minimized as n_s, n_g vary subject to $n_s + n_g = N$. Thus (when $dT = dp = 0$) at equilibrium

$$d(\phi_s + \phi_g) = \mu_s dn_s + \mu_g dn_g = 0$$

$$dN = dn_s + dn_g = 0$$

which means that

$$\mu_s = \mu_g \text{ determines } n_s, n_g$$

This is the same condition whether we work at constant T, V or constant T, p .

In the solid-vapor system

$$\mu_s = \frac{1}{\beta} \log \frac{n_s}{n_s + 1}$$

$$\mu_g = w - \frac{1}{\beta} \log \left(\frac{\beta^{-5/2} \alpha}{p} \right) = -\frac{1}{\beta} \log \left(\frac{e^{-\beta w} \beta^{-3/2} \alpha}{\beta p} \right) = \gamma$$

so

$$\mu_s = \mu_g \text{ means}$$

$$\frac{n_s + 1}{n_s} = 1 + \frac{1}{n_s} = \frac{\gamma}{\beta p}$$

$$n_s = \frac{1}{\gamma/\beta p - 1}$$

$$\boxed{n_s = \frac{\beta p}{\gamma - \beta p}}$$

equilibrium
condition

since

$$n_s = N - n_g = N - pV\beta \text{ we get}$$

$$N - pV\beta = \frac{\beta p}{\gamma - \beta p}$$

$$\frac{N}{\beta p} - V = \frac{1}{\gamma - \beta p}$$

or

$$\frac{V}{N} = \frac{1}{\beta p} - \frac{1}{N\gamma - \beta p}$$

which is the

equation of state derived before.

June 26, 1980

862

The goal is to understand solid \leftrightarrow vapor when the solid is described by the Einstein or Debye model. Take the Einstein model where

$$Z(T, V, n) = \left(\underbrace{\frac{e^{-\beta \frac{1}{2} h \omega}}{1 - e^{-\beta h \omega}}}_{Z_1} \right)^{3n}$$

Then $F = -\frac{1}{\beta} \log Z = -\frac{3n}{\beta} \log Z_1$

and $\mu = \frac{\partial F}{\partial n} = -\frac{3}{\beta} \log Z_1$ is independent of n .

But if we form

$$Z_G(T, V, \mu) = \sum_n e^{\beta \mu n} Z(T, V, n) = \frac{1}{1 - e^{\beta \mu} Z_1^3}$$

Then $n = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{e^{\beta \mu} Z_1^3}{1 - e^{\beta \mu} Z_1^3}$

$$e^{\beta \mu} Z_1^3 = \frac{n}{n+1}$$

$\therefore \mu = -\frac{3}{\beta} \log Z_1 + \frac{1}{\beta} \log \left(\frac{n}{n+1} \right)$ depends on n

However these two formulas agree in the limit as $n \rightarrow \infty$. In some sense the second formula is the more correct one.

Compare equilibrium condition $\mu_s = \mu_g$ with the use of the grand partition fn. for the system.

$$Z_G = \sum_{m, n} Z_s(T, V, m) Z_g(T, V, n) e^{\beta \mu (m+n)}$$

Clearly $Z_G = Z_G^s Z_G^g$. [REDACTED] The condition that N atoms total be present is

$$(*) \quad N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G^s + \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G^g$$

I've already seen how this leads to an equation of state. Now if one defines μ_s as a function of n_s via

$$n_s = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z_G^s(\mu_s)$$

and similarly defines μ_g as a function of n_g , then (*) is equivalent to

$$N = n_s + n_g \quad \text{and} \quad \mu_s = \mu_g.$$

So (*) and $\mu_s = \mu_g$ lead to the same equation of states.

Recall equation of equilibrium:

$$\mu_s = -\frac{3}{\beta} \log Z_1 + \frac{1}{\beta} \log \frac{n_s}{n_s+1} = \mu_g = -\frac{1}{\beta} \log(\gamma/p\beta)$$

where $\gamma = e^{-\beta\omega} \beta^{-3/2} \alpha$. Thus

$$1 + \frac{1}{n_s} = \frac{n_s+1}{n_s} = \frac{\gamma}{p\beta Z_1^3}$$

$$n_s = \frac{p\beta Z_1^3}{\gamma - p\beta Z_1^3} = N - n_g = N - pV\beta$$

$$\boxed{\frac{V}{N} = \frac{1}{p\beta} - \frac{1}{N} \frac{Z_1^3}{\gamma - p\beta Z_1^3}}$$

Same except that γ is replaced by γZ_1^{-3}

Note that the vapor pressure is given by

$$p = \frac{\gamma}{\beta} Z_1^{-3} = e^{-\beta w} \beta^{-5/2} \alpha Z_1^{-3}$$

where $Z_1 = \frac{e^{-\beta \frac{1}{2} h w}}{1 - e^{-\beta h w}}$.

Notice that this is what

we obtain if we use

$$\mu_s = -\frac{3}{\beta} \log Z_1 = \mu_g = -\frac{1}{\beta} \log \left(\frac{\gamma \alpha}{p \beta} \right)$$

↑
based on $Z(T, n)$

and so we see that μ_s as computed from $Z(T, n_s)$ is correct in the large n_s limit.

June 27, 1980

865

Equilibrium for ideal gas reactions. Suppose we have a container with T, V fixed in which there are three gas molecules of types A, B, C which can react according to the scheme



We want to determine the equilibrium concentrations. If there were no reaction, then our container would hold n_A, n_B, n_C molecules and the partition function would be

$$(1) \quad Z(T, V, n_A, n_B, n_C) = \frac{(z_1^A)^{n_A}}{n_A!} \frac{(z_1^B)^{n_B}}{n_B!} \frac{(z_1^C)^{n_C}}{n_C!}$$

where z_1^A is the partition function for a single A ~~molecule~~ ^{-molecule}:

$$z_1^A = V \beta^{-3/2} \alpha_A \quad \alpha_A = \frac{(2\pi m_A)^{3/2}}{h^3}$$

if A were monatomic (better - only ~~one~~ translational degrees of freedom). Actually, because of the interaction, ~~the~~ the numbers n_A, n_B, n_C can vary so that

$$n_A + n_C = \text{const} \quad \text{say } N_A$$

$$n_B + n_C = \text{const} \quad \text{say } N_B$$

and so the partition function is

$$(2) \quad Z(T, V, N_A, N_B) = \sum_{\substack{n_A + n_C = N_A \\ n_B + n_C = N_B}} Z(T, V, n_A, n_B, n_C)$$

also in going from C to $A + B$ some internal energy (represented by electronic energy = molecular orbitals) changes.

Thus in the 1-particle partition function there belongs a potential energy term $e^{-\beta \epsilon_0}$ where ϵ_0 is the ground state energy. This is a first approximation where we assume the higher molecular orbitals are not excited. Later one can add things like rotational, vibrational, and electronic energy to the 1-molecule partition functions.

Returning to (2) let's first determine the equilibrium condition by the dominant term method:

$$\frac{\partial}{\partial n_c} \log Z(T, V, n_A, n_B, n_C) = 0$$

where n_A, n_B are regarded as functions of n_C . What this amounts to is to take the free energy

$$F(T, V, n_A, n_B, n_C) = -\frac{1}{\beta} \log Z(T, V, n_A, n_B, n_C) \\ = F_A(T, V, n_A) + F_B(T, V, n_B) + F_C(T, V, n_C)$$

and then require dF to be zero while $dT=dV=0$ and $dn_A + dn_C = dn_B + dn_C = 0$. Thus

$$0 = dF = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C \\ = (-\mu_A - \mu_B + \mu_C) dn_C$$

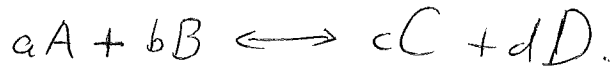
and so the equilibrium condition is

$$\mu_A + \mu_B = \mu_C$$

where

$$\mu_A = \left(\frac{\partial F_A}{\partial n_A} \right)_{T, V} \text{ etc.}$$

Next ~~consider~~ ^{consider} a reaction



Look at the vector (n_A, n_B, n_C, n_D) . This can change by a multiple of $(a, b, -c, -d)$ so that

$d(n_A, \dots, n_D)$ proportional to $(a, b, -c, -d)$.

Thus the equilibrium condition

$$0 = dF = \mu_A dn_A + \dots + \mu_D dn_D$$

becomes

$$\mu_A a + \mu_B b - \mu_C c - \mu_D d = 0$$

or

$$\boxed{a\mu_A + b\mu_B = c\mu_C + d\mu_D}$$

Return to $A + B \rightleftharpoons C$. Suppose

$$Z_1^A = V\beta^{-3/2} \alpha_A e^{-\beta\epsilon_A}$$

$$\alpha_A = \frac{(2\pi m_A)^{3/2}}{h^3}$$

Then

$$F(T, V, n_A) = -\frac{1}{\beta} \log \frac{(Z_1^A)^{n_A}}{n_A!}$$

$$= -\frac{n_A}{\beta} \left(\log(V\beta^{-3/2} \alpha_A e^{-\beta\epsilon_A}) - \log n_A + 1 \right)$$

$$\mu_A = -\frac{1}{\beta} \log \left(\frac{V\beta^{-3/2} \alpha_A e^{-\beta\epsilon_A}}{n_A} \right)$$

$$= \frac{1}{\beta} \log \left(\frac{n_A}{V} \frac{1}{\beta^{-3/2} \alpha_A e^{-\beta\epsilon_A}} \right)$$

So the condition $\mu_A + \mu_B = \mu_C$ becomes

$$\frac{\left(\frac{n_A}{V}\right)\left(\frac{n_B}{V}\right)}{\left(\frac{n_C}{V}\right)} = \frac{\alpha_A \alpha_B}{\alpha_C} \beta^{-3/2} e^{-\beta(\omega_A + \omega_B - \omega_C)}$$

Suppose we work at constant pressure + temperature.
Then we want to use

$$\mu_A = \frac{1}{\beta} \log\left(P_A \beta^{5/2} / \alpha_A e^{-\beta \omega_A}\right)$$

which leads to the formula

$$\boxed{\frac{P_A P_B}{P_C} = \beta^{-5/2} \frac{\alpha_A \alpha_B}{\alpha_C} e^{-\beta(\omega_A + \omega_B - \omega_C)}}$$

for equilibrium. Chemists like to write this as follows.
The free energy ~~is~~ for the A-gas is

$$\Phi_A = \frac{n_A}{\beta} \log\left(P_A \beta^{5/2} / \alpha_A e^{-\beta \omega_A}\right)$$

so μ_A is just the Gibbs free energy per molecule. At constant temperature T one has

$$\mu_A = \frac{1}{\beta} \log(P_A) + \text{const}$$

So that ~~if~~ if μ_A° = chemical potential at $p_A = 1$
we have

$$\mu_A - \mu_A^\circ = \frac{1}{\beta} \log(P_A)$$

Thus

$$\log\left(\frac{P_A P_B}{P_C}\right) = - \underbrace{\left(\mu_A^\circ + \mu_B^\circ - \mu_C^\circ\right)}_{\text{free energy change per molecule at the temp. } T \text{ from standard pressure}}$$

free energy change per molecule
at the temp. T from standard pressure)