

§13. Multispecies Systems13.1 Generalisation
to many species

Let us consider a situation now where our system contains ~~many~~ several different species of substances (particles). For example, it is a solution of some kind or a mixture of (reacting) chemicals, or plasma (containing various ^{species} ~~types~~ of ions + electrons + various neutral atoms, if it is partially ionised). Its thermodynamic state will be characterised by (average) # of each species, \bar{N}_i ^{↑ species index}.

We can again maximise entropy, now subject to all these \bar{N}_i being fixed. There will be a Lagrange multiplier for each, i.e., each species will have its own chemical potential μ_i .

The generalisation is obvious (Exercise!):

$$P_\alpha = e^{\beta(\Phi - E_\alpha + \sum_i \mu_i N_{i\alpha})}$$

where grand potential is

$$\Phi = U - TS - \sum_i \mu_i \bar{N}_i \quad (\text{cf. p.106})$$

From this, we can derive, as on pp.107-110,

$$d\Phi = -SdT - pdV - \sum_i \bar{N}_i d\mu_i$$

$$dU = TdS - pdV + \sum_i \mu_i d\bar{N}_i$$

$$dF = -SdT - pdV + \sum_i \mu_i d\bar{N}_i$$

$$dG = -SdT + VdP + \sum_i \mu_i d\bar{N}_i$$

and so $\mu_i = \left(\frac{\partial U}{\partial \bar{N}_i} \right)_{S, V, \bar{N}_{j \neq i}} = T \left(\frac{\partial S}{\partial \bar{N}_i} \right)_{U, V, \bar{N}_{j \neq i}} =$

$$= \left(\frac{\partial F}{\partial \bar{N}_i} \right)_{V, T, \bar{N}_{j \neq i}} = \left(\frac{\partial G}{\partial \bar{N}_i} \right)_{P, T, \bar{N}_{j \neq i}}$$

and again, because G is a homogeneous function of \bar{N}_i 's, we must have $G = \sum_i \mu_i \bar{N}_i \Rightarrow \Phi = -PV$

Exercise. Prove

$$\bar{N}_i = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu_i} \right)_{\beta, \mu_{j \neq i}}$$

$$U = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{\mu_1, \dots, \mu_m} + \sum_i \mu_i \bar{N}_i$$

Proof. $G = G(P, T, \bar{N}_1, \bar{N}_2, \dots) = U - TS + PV$

U, S and V are all extensive, so G must be extensive, i.e. if we change all particle quantities by a factor λ , G must change by λ . Since P and T are intensive, this gives

$$G(P, T, \lambda \bar{N}_1, \lambda \bar{N}_2, \dots) = \lambda G(P, T, \bar{N}_1, \bar{N}_2, \dots)$$

Differentiate wrt λ and then set $\lambda = 1$:

$$\sum_i \left(\frac{\partial G}{\partial \bar{N}_i} \right)_{P, T, \bar{N}_{j \neq i}} \cdot \bar{N}_i = G$$

"
 μ_i

$$\text{So } G = \sum_i \mu_i \bar{N}_i$$

Lecture 2

ended here.

Note that this means that the chemical potentials can only be functions of fractional concentrations of the species, i.e. ratios ~~of~~ \bar{N}_i/\bar{N}_j or,

equivalently, ~~of~~ $c_i = \frac{\bar{N}_i}{\bar{N}}$, $\bar{N} = \sum_i \bar{N}_i$.

[Indeed, $\mu_i = \left(\frac{\partial G}{\partial \bar{N}_i} \right)_{P, T, \bar{N}_j, j \neq i}$

So, if each \bar{N}_i is ^{scaled} ~~changed~~ $\bar{N}_i \rightarrow \lambda \bar{N}_i$, μ_i must stay the same. So,

$$\mu_i(P, T, \lambda \bar{N}_1, \lambda \bar{N}_2, \dots) = \mu_i(P, T, \bar{N}_1, \bar{N}_2, \dots). \quad (*)$$

which is only possible if it depends on their ratios only.]

~~Proof.~~ Proof.

~~Let~~ Let $\mu_i = \mu_i(P, T, c_1, c_2, \dots, c_{m-1}, \bar{N})$
 where m is the # of species, ~~and~~

$$\bar{N} = \sum_i \bar{N}_i \text{ and } c_i = \frac{\bar{N}_i}{\bar{N}}.$$

This is without loss of generality so far (just a different set of variables)

From (*), $\mu_i(P, T, c_1, \dots, c_{m-1}, \lambda \bar{N}) = \mu_i(P, T, c_1, \dots, c_{m-1}, \bar{N})$

Therefore, μ_i is independent of \bar{N} . q.e.d.

$$\boxed{\mu_i = \mu_i(P, T, c_1, c_2, \dots)}$$

Gibbs phase rule. ~~Derivation~~ [Digression]

In equilibrium, $\mu_i = \text{const}$ across the system for each species. Suppose that all these species (substances) can exist in several phases.

$m = \#$ of species

$r = \#$ of phases

Then $\mu_1^{(\text{phase 1})} = \mu_1^{(\text{phase 2})} = \dots = \mu_1^{(\text{phase } r)}$

$\mu_2^{(\text{phase 1})} = \mu_2^{(\text{phase 2})} = \dots = \mu_2^{(\text{phase } r)}$

⋮

$\mu_m^{(\text{phase 1})} = \mu_m^{(\text{phase 2})} = \dots = \mu_m^{(\text{phase } r)}$

Each $\mu_i^{(j)}$ is a function of P, T and $m-1$ concentrations $C_1^{(j)}, \dots, C_{m-1}^{(j)}$ within that phase j .

So, we have $m(r-1)$ equations for $2 + r(m-1)$ unknowns.

In order to have solutions, we must have

$$m(r-1) \leq 2 + r(m-1)$$

$$\boxed{r \leq m + 2} \quad \text{Gibbs' phase rule}$$

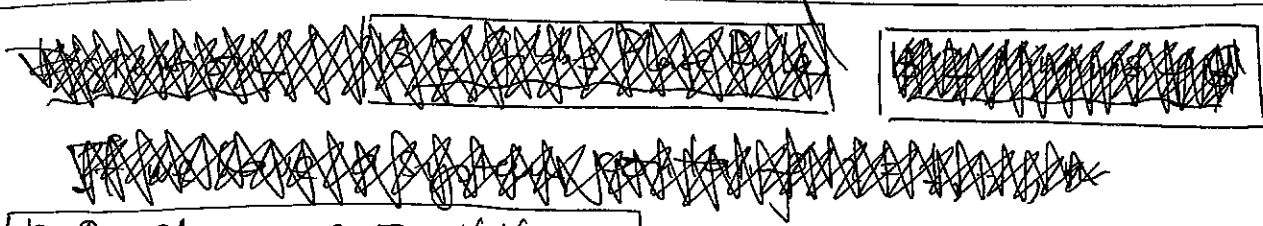
(System of m species can support no more than $m+2$ phases simultaneously in equilibrium.)

Eg. $m=1 \Rightarrow r \leq 3$ e.g. ~~gas, liquid, solid~~
gas, liquid, solid)

From the expression for μ_i in terms of S , we can prove (analogously to p. 108) that $\mu_i = \text{const}$ across a system in equilibrium for each species (Exercise)

→ Gibbs phase rule
 P + F + C = N + 1

But μ_i 's of different species do not have to be the same even if they are in contact. We will want to find out what relations they should satisfy.

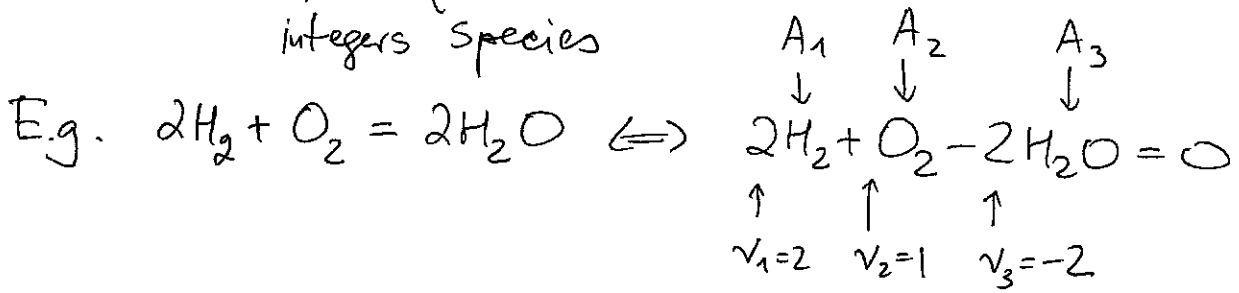


13.2 Chemical Equilibrium

Chemical reactions and analogous processes are expressed in the following form:

$$\sum_i \nu_i A_i = 0$$

$i \uparrow$ integers
 \uparrow species



$e^+ + e^- = \gamma$ pair production/annihilation

$p^+ + e^- = H$ ionisation/recombination of atomic hydrogen etc.

In general, the reaction can go both ways and in equilibrium, there will be some situation where concentration of each species assumes

Some value. How do we determine these equilibrium values?

Let us consider a system at fixed pressure and ^(set by the environment) temperature - the most common "laboratory" situation. How do we determine the equilibrium state of such an open system?

We already know the answer to this question from last term: we minimize its Gibbs function:

$$G = U - T_0 S + P_0 V \rightarrow \min$$

\uparrow fixed \uparrow fixed

(at const T, V , this becomes $F \rightarrow \min$; at const T, V, U , $S \rightarrow \min$)

Well, $G = G(P_0, T_0, \bar{N}_1, \bar{N}_2, \dots)$

$$dG = \sum_i \mu_i d\bar{N}_i = 0 \quad (\text{at const } P_0, T_0)$$

But $\sum_i \nu_i A_i = 0$ means that if \bar{N}_i changes by ν_i for some i , then \bar{N}_j change by ν_j for all $j \neq i$.

(i.e. $\frac{d\bar{N}_i}{d\bar{N}_1} = \frac{\nu_i}{\nu_1}$ for all i). Therefore

(for each reaction group on in the system)

$$\sum_i \nu_i \mu_i = 0$$

- equation of chemical equilibrium.

Note that this is effectively a constraint on the

~~fractional concentrations of the species because~~ fractional concentrations of

the species because $\mu_i = \mu_i(P_0, T_0, C_1, C_2, \dots)$ [see p112a]

Proof of $G \rightarrow \min$ prescription [review]

We have an open system in contact with surroundings, which set $P = P_0$ and $T = T_0$.

Suppose the system is initially not in equilibrium but does have $P = P_0$ and $T = T_0$.

As it equilibrates, ^{total} energy is conserved:

$$\Delta(U + U_0) = 0$$

and total entropy increases

$$\Delta(S + S_0) \geq 0$$

At const P_0, T_0 , we have $\Delta U_0 = T_0 \Delta S_0 - P_0 \Delta V_0$, so

$$\Delta U + T_0 \Delta S_0 + P_0 \Delta V_0 = 0$$

$$T_0 \Delta S_0 = -\Delta U - P_0 \Delta V$$

$$\text{and } T_0 \Delta S + T_0 \Delta S_0 \geq 0$$

$$\text{so } \Delta U - T_0 \Delta S + P_0 \Delta V \leq 0 \Leftrightarrow \Delta G \leq 0 \text{ q.e.d.}$$

Note that if $\Delta V = 0$ (system at const T_0, V_0),
because $T_0, P_0 = \text{const}$

$$\Delta U - T_0 \Delta S \leq 0 \Leftrightarrow \Delta F \leq 0$$

and if also $\Delta U = 0$ (isolated system),

$$-T_0 \Delta S \leq 0 \Leftrightarrow \Delta S \geq 0 \text{ as it should be.}$$

Note. In a system with ~~constant~~ fixed T_0 and V_0 , which is capable of creating and destroying particles (e.g. radiation)

$$F \rightarrow \min \Leftrightarrow \left(\frac{\partial F}{\partial N} \right)_{V, T} = 0 \Leftrightarrow \mu = 0$$

[see lectures on photon gas later on]

13.3 Chemical Equilibrium in a Mixture of Classical Ideal Gases

Our aim is to derive a useful relation between concentrations of various species from the eqn of chemical equilibrium $\sum_i \nu_i \mu_i = 0$.

For this, we need a specific expression for μ_i as a function of P, T, C_1, C_2, \dots

Again we consider our favorite case of a classical ideal gas. This is simply a generalization of the calculation of μ for a single-species system.

The grand partition function for a system of m species:

Ex.

$$\begin{aligned}
 \mathcal{Z} &= \sum_{\alpha} e^{-\beta E_{\alpha}} + \sum_i \beta \mu_i N_{i\alpha} = \text{sum of all energies} \\
 &= \sum_{N_1} \dots \sum_{N_m} e^{\beta \sum_i \mu_i N_i} \sum_{\{ \vec{p}_1^{(1)} \dots \vec{p}_{N_1}^{(1)} \dots \vec{p}_1^{(2)} \dots \vec{p}_{N_2}^{(2)} \dots \vec{p}_1^{(m)} \dots \vec{p}_{N_m}^{(m)} \}} e^{-\beta (E_{\vec{p}_1^{(1)}} + \dots + E_{\vec{p}_{N_m}^{(m)}})} \frac{1}{N_1! \dots N_m!} \\
 &= \sum_{N_1} \dots \sum_{N_m} e^{\beta \sum_i \mu_i N_i} \frac{[Z_1^{(1)}]^{N_1}}{N_1!} \dots \frac{[Z_1^{(m)}]^{N_m}}{N_m!} \\
 &= \sum_{N_1} \dots \sum_{N_m} \prod_i \frac{[Z_1^{(i)} e^{\beta \mu_i N_i}]^{N_i}}{N_i!} \\
 &= e^{\sum_i Z_1^{(i)} e^{\beta \mu_i}} = \prod_i \mathcal{Z}^{(i)}
 \end{aligned}$$

particles indistinguishable within each species, but distinguishable between species; quantum correlations neglected

We could have guessed this result: partition functions multiply because we have assumed that there is no interaction between different species (ideal gas). Thus, each species behaves like a separate subsystem, in equilibrium with the rest.

Note that this is not in general true for multicomponent systems — they interpenetrate, so can perfectly well be strongly interacting as have different collective energy levels from just sums of their components. So we are considering a rather simple special case.

OK, now

$$\bar{N}_i = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu_i} \right)_{\beta, \mu_{j \neq i}} = Z_1^{(i)} e^{\beta \mu_i} \Rightarrow \boxed{\mu_i = -k_B T \ln \frac{Z_1^{(i)}}{\bar{N}_i}}$$

Here $Z_1^{(i)} = \frac{V}{\lambda_{thi}^3}$, $\lambda_{thi} = \frac{1}{h} \sqrt{\frac{2\pi}{m_i k_B T}}$

as on p. 110c

So,

↑ mass of species i.

$$\mu_i = +k_B T \ln (n_i \lambda_{thi}^3) =$$

↑
 number density of species i
 $n_i = \bar{N}_i / V = c_i n$

$$= k_B T \ln (c_i n \lambda_{thi}^3) = k_B T \ln \left(c_i \frac{p \lambda_{thi}^3}{k_B T} \right),$$

where we used Dalton's law:

$$p = \sum_i p_i = \sum_i n_i k_B T = n k_B T$$

(can prove this directly by calculating $p = \left(\frac{\partial \Phi}{\partial V} \right)_{T, \mu}$ check!)

[Note. One has to be careful here. Since the partition functions multiply, ~~most~~ ^{some} extensive quantities just add: thus, you may check that

$$F(V, T, \bar{N}_1, \dots, \bar{N}_m) = \sum_i F_i(V, T, \bar{N}_i)$$

however,

$$\begin{aligned} G(P, T, \bar{N}_1, \dots, \bar{N}_m) &= \sum_i \mu_i \bar{N}_i = \sum_i G_i(P_i, T, \bar{N}_i) \\ &= \sum_i G_i(P, T, \bar{N}_i) + \underbrace{\sum_i k_B T \bar{N}_i \ln c_i}_{NB!} \end{aligned}$$

i.e. while F of the mixture is

just sum of F 's for each species at the same V and T , it is not true that G of the mixture is the sum of G 's for each species at the same P and T

— this is because they all share the same volume and temperature, but each has its own pressure.

Ex. Calculate entropy of mixing from this formalism (we have already discussed this when we encountered Gibbs paradox, see p. 87)

OK, now let's use $\sum_i \nu_i \mu_i = 0$ (chemical equilibrium)

$$k_B T \sum_i \nu_i \ln \left(c_i \frac{P \lambda_{thi}^3}{k_B T} \right) = 0$$

$$\sum_i \nu_i \ln c_i = - \sum_i \nu_i \ln \frac{P \lambda_{thi}^3}{k_B T}$$

Law of mass action

$$\left[\prod_i c_i^{\nu_i} = P^{-\sum_i \nu_i} \prod_i \left(\frac{k_B T}{\lambda_{thi}^3} \right)^{\nu_i} \equiv K(P, T) \right]$$

↑
↑

product of fractional concentrations
chemical equilibrium constant.

a known function of P, T and microphysics ($\nu_i \lambda_{thi}$)

Note that in fact, to make this universally useful, we should generalise just a bit. The formula

$$Z_1 = \frac{V}{\lambda_{th}^3}$$

was valid for single molecules whose

only energy levels were associated with translational motion. As we know, in general molecules can also rotate, vibrate and have other interesting internal energy levels. For example, if we wanted to use this formalism to describe the equilibrium state of ionisation/recombination in a partially ionised plasma, we must include the energy levels corresponding to the ground and excited states of electrons in atoms [cf. p. 110e - the case when energy levels in ext. field are added in a simpler way]

The generalisation is straightforward:

$$Z_1 = \frac{V}{\lambda_{th}^3} Z_{1\text{internal}}$$

↑ depends on T but not on V

$$Z_{1\text{internal}} = \sum_{\sigma} e^{-\beta \epsilon_{\sigma}^{(\text{internal})}}$$

↑ internal energy levels for particles

Thus, we must simply replace

$$\frac{V}{\lambda_{th}^3} \rightarrow \frac{V}{\lambda_{th}^3} Z_{1\text{internal}}$$

(NB: in none of the above formulae did we differentiate wrt T, on which $Z_{1\text{internal}}$ does depend, so ~~margin~~ this replacement is OK)

$$\prod_i C_i^{\nu_i} = P^{-\sum_i \nu_i} \prod_i \left[\frac{k_B T}{\lambda_{thi}^3} Z_{1\text{internal}}^{(i)} \right]^{\nu_i} \equiv K(P, T)$$

Note this formula also allows ^{to tell} us in which direction a chemical reaction will go if the system is not in equilibrium:

if $\prod_i C_i^{\nu_i} > K(P, T)$ it is direct (C_i 's of components with $\nu_i > 0$ go down, those with $\nu_i < 0$ up)

$\prod_i C_i^{\nu_i} < K(P, T)$ it is reverse.

OK, this is all the chemistry you need to know!

My point was that chemical potentials are quite useful. They will also be useful in the treatment of phase transitions.