

§15. Multispecies (Multicomponent) Systems

We now wish to consider systems containing several different components: species of molecules or particles, e.g.

- solutions
- mixtures of (reactive) chemicals
- plasmas (ions + electrons + also neutrals if partially ionized)
- pair plasmas (electrons + positrons + γ photons)

15.1 Generalisation of grand canonical ensemble to many species

Thermodynamic state of these systems is now characterised by the avg # of particles of each species, \bar{N}_s .

Again, we maximise S_G subject to all these \bar{N}_s being fixed - there is a Lagrange multiplier for each s , so each species has its own chemical potential μ_s .

Generalisation is obvious (exercise):

cf. eq. (4) p. 148 $P_\alpha = \frac{1}{\mathcal{Z}} e^{-\beta(E_\alpha - \sum_s \mu_s N_{s\alpha})}$ (1)

\uparrow # of particles of species s in microstate α

cf. eq. (5) p. 148 $\mathcal{Z} = \sum_\alpha e^{-\beta(E_\alpha - \sum_s \mu_s N_{s\alpha})}$ (2)

cf. eq. (6) p. 150 $U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} + \sum_s \mu_s \bar{N}_{s\alpha}$ (3)

cf. eq. (7) p. 150 $\bar{N}_s = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu_s}$ (4)

and

$$\Phi = -k_B T \ln \mathcal{Z} = U - TS - \sum_s \mu_s \bar{N}_s \quad (5)$$

cf. eq. (13) p. 151

The differentials:

$$\left. \begin{aligned} \text{cf. eq. (11) p. 151} \quad dU &= TdS - PdV + \sum_s \mu_s d\bar{N}_s \\ \text{cf. eq. (14) p. 151} \quad d\Phi &= -SdT - PdV - \sum_s \bar{N}_s d\mu_s \\ \text{cf. eq. (26) p. 157} \quad dF &= -SdT - PdV + \sum_s \mu_s d\bar{N}_s \\ \text{cf. eq. (28) p. 157} \quad dG &= -SdT + VdP + \sum_s \mu_s d\bar{N}_s \end{aligned} \right\} (6)$$

where

$$\begin{aligned} \mu_s &= \left(\frac{\partial U}{\partial \bar{N}_s} \right)_{S, V, \bar{N}_{s' \neq s}} = -T \left(\frac{\partial S}{\partial \bar{N}_s} \right)_{U, V, \bar{N}_{s' \neq s}} = && \text{cf. eqs. (12) p. 151, (27), (29) p. 157} \\ &= \left(\frac{\partial F}{\partial \bar{N}_s} \right)_{T, V, \bar{N}_{s' \neq s}} = \left(\frac{\partial G}{\partial \bar{N}_s} \right)_{T, P, \bar{N}_{s' \neq s}} && (7) \end{aligned}$$

Eq. (30) (p. 158), $G = \mu \bar{N}$, generalises to

$$\boxed{G = \sum_s \mu_s \bar{N}_s} \quad (8) \quad \Leftrightarrow \quad \Phi = -PV \quad \text{from (5)}$$

Same as eq. (32) p. 158.

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

U, S, V are all extensive, so G is extensive, viz.

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

Differentiate wrt λ and set $\lambda = 1$

$$\sum_s \underbrace{\left(\frac{\partial G}{\partial \bar{N}_s} \right)_{P, T, \bar{N}_{s' \neq s}}}_{\mu_s \text{ by (7)}} \cdot \bar{N}_s = G \Rightarrow \text{eq. (8) q.e.d.}$$

Since μ_s are intensive, they are functions only
 because of (7)

of fractional concentrations of ~~the~~ all the species,
 $c_s = \frac{\bar{N}_s}{\bar{N}}$, where $\bar{N} = \sum_s \bar{N}_s$

Indeed, under scaling

$$\bar{N}_s \rightarrow \lambda \bar{N}_s, \text{ or, equivalently, } \bar{N} \rightarrow \lambda \bar{N}, c_s \rightarrow c_s,$$

$$\mu_s = \frac{\partial G}{\partial \bar{N}_s} \rightarrow \mu_s \text{ because } G \rightarrow \lambda G.$$

$$\text{Thus, } \mu_s = \mu_s(P, T, c_1, c_2, \dots, c_{m-1}) \quad (9)$$

(independent of \bar{N})

\uparrow m is # of species.

L.12 ended here.

15.2 Particle Equilibrium

Argue exactly like in §14.3, we can prove that

$$\underline{\mu_s = \text{const across a system in equilibrium}}$$

for each species (Ex.)

NB: Chemical potentials of different species do not
 need to be equal even if they are in contact.

An immediate consequence of the above is the
 so-called Gibbs phase rule:

Consider a system of m species, which can be
 in Γ phases. Then, in equilibrium,

$$\forall s, \mu_s^{(\text{phase 1})} = \mu_s^{(\text{phase 2})} = \dots = \mu_s^{(\text{phase } \Gamma)} \quad (10)$$

$s = 1, \dots, m$

Now,

$$\mu_s^{(\text{phase } p)} = \text{function of } P, T, C_1^{(\text{phase } p)} \dots C_{m-1}^{(\text{phase } p)}$$

So, we have, in (10), $m(r-1)$ equations for $2 + r(m-1)$ unknowns

In order for this system to have solutions (not necessarily unique), we must have

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

$$\boxed{r \leq m+2} \quad (\text{ii}) \quad \text{Gibbs phase rule}$$

A system of m species can support no more than $m+2$ phases simultaneously in equilibrium

[e.g., $m=1 \Rightarrow r \leq 3$ gas, liquid, solid]

More on phase transitions in PART VI.

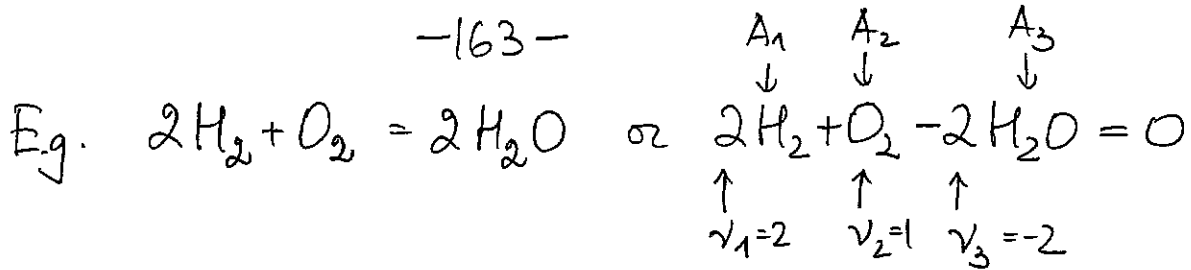
15.3 Chemical Equilibrium

Now let us work out how μ_s for different species are related to each other in equilibrium.

Obviously, they need be related at all only if these different species can transmute into each other (so the system can seek some optimal equilibrium situation) — i.e., if they are subject to chemical (or atomic) reactions. These are usually expressed in the form

$$\sum_s \nu_s A_s = 0 \quad (12)$$

\uparrow integer #s \uparrow species



$e^+ + e^- = \gamma$ ($\nu_1=1, \nu_2=1, \nu_3=-1$)

pair production/annihilation

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

In general, all these reactions can go both ways, until we have a stable soup where the concentration of each species has assumed its equilibrium value.

How do we find ~~these~~ these equilibrium values?

At const T, P (set by the environment - the most common laboratory situation), we have

$$dG = \sum_s \mu_s dN_s = 0 \tag{13}$$

(by the usual "availability" argument:

as the system equilibrates,

$$d(U + U_{env}) = 0 \text{ and } d(S + S_{env}) \geq 0$$

$$\Downarrow$$

$$dU = -dU_{env} = -(T_{env} dS_{env} - P_{env} dV_{env})$$

$$\Downarrow$$

$$T_{env} dS_{env} = -dU - P_{env} dV$$

\uparrow # of particles of the env. does not change
 $-dV$

$$0 \leq T_{env} (dS + dS_{env}) = T_{env} dS - dU - P_{env} dV = -dG$$

So $dG \leq 0 \Rightarrow$ equilibrium achieved for $G \rightarrow \min$)

But eq. (12) means that

$$d\bar{N}_1 : d\bar{N}_2 : \dots = \nu_1 : \nu_2 : \dots$$

and so, from (13),

$$\boxed{\sum_s \nu_s \mu_s = 0} \quad (14) \quad \text{equation of chemical equilibrium}$$

There is an eqn like this for each reaction the system is capable of. This gives a set of constraints on the fractional concentrations because

$$\mu_s = \mu_s(P, T, C_1, C_2, \dots) \quad (15)$$

\uparrow
 kept const.

classical

15.4 Chemical Equilibrium for a Mixture of Ideal gases

To apply eq. (14), we need explicit expressions (15) for μ_s , i.e. we need to solve eq. (4) (p.159):

$$C_s = \frac{k_B T}{N} \frac{\partial \ln Z}{\partial \mu_s} \Rightarrow \mu_s \quad (16)$$

Analogously to §14.4, the microstates of the mixture

$$\text{are } \alpha = (\alpha_1, \dots, \alpha_m, N_1, \dots, N_m)$$

with # of particle N_s → { microstates of each species # of particles for each species

energies of species 1...m for # of particles N_1, \dots, N_m

$$Z = \sum_{\alpha} e^{-\beta(E_{\alpha} - \sum_s \mu_s N_{s\alpha})} = \sum_{N_1} \dots \sum_{N_m} e^{\beta \sum_s \mu_s N_s} \sum_{\alpha_1} \dots \sum_{\alpha_m} e^{-\beta(E_{\alpha_1} + \dots + E_{\alpha_m})}$$

$$= \sum_{N_1} \dots \sum_{N_m} e^{\beta \sum_s \mu_s N_s} \prod_{s=1}^m \frac{Z_s^{N_s}}{N_s!} \leftarrow \text{single-particle partition functions of species } s$$

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$$= \sum_{N_1} \dots \sum_{N_m} \prod_{s=1}^m \frac{[z_{1s} e^{\beta \mu_s}]^{N_s}}{N_s!} =$$

$$= e^{\sum_{s=1}^m z_{1s} e^{\beta \mu_s}} = \prod_{s=1}^m Z_s \quad (17)$$

- obviously! this was just going to be the product of partition functions of all the species: indeed, this is an ideal gas, there are no interactions between particles and so each species behaves as a separate subsystem, in equilibrium with the rest (this is not true in general for multicomponent systems as they can interpenetrate, can be strongly interactive and have collective energy levels not simply equal to sums of the energy levels of the components)

From (16) and (17),

$$c_s \bar{N} = k_B T \frac{\partial}{\partial \mu_s} \sum_{s'} z_{1s'} e^{\beta \mu_{s'}} = z_{1s} e^{\beta \mu_s}$$

$$\Rightarrow \mu_s = -k_B T \ln \frac{z_{1s}}{c_s \bar{N}} \quad (18) \text{ cf. eq. (18) on p. 154}$$

But $z_{1s} = \frac{V}{\lambda_{ths}^3} \cdot z_{1s}^{(\text{internal})}$ $\lambda_{ths} = \frac{1}{h} \sqrt{\frac{2\pi}{m_s k_B T}}$

and so n_s density of s \uparrow mass of species s

$$\mu_s = k_B T \ln \left(\frac{c_s n \lambda_{ths}^3}{z_{1s}^{(\text{internal})}} \right) = k_B T \ln \left(\frac{c_s}{z_{1s}^{(\text{int})}} \frac{p \lambda_{ths}^3}{k_B T} \right) \quad (19)$$

[We have used Dalton's law

$$p = \sum_s p_s = \sum_s n_s k_B T = n k_B T$$

Ex. Prove this from $p = -\Phi/V$]

Finally, using eq. (14),

$$k_B T \sum_s \nu_s \ln \left(\frac{c_s P \lambda_{th,s}^3}{Z_{1s}^{(int)} k_B T} \right) = 0$$

$$\sum_s \nu_s \ln c_s = - \sum_s \nu_s \ln \left(\frac{P \lambda_{th,s}^3}{Z_{1s}^{(int)} k_B T} \right)$$

$$\prod_s c_s^{\nu_s} = P^{-\sum_s \nu_s} \prod_s \left[\frac{k_B T}{\lambda_{th,s}^3} Z_{1s}^{(int)} \right]^{\nu_s} \equiv K(P, T)$$

↑
 "The law of mass action". NB: $\sum_{s=1}^m c_s = 1$.
 f-u of T
 a known f-u of P, T and microphysics → "chemical equilibrium constant" (20)

This formula constrains concentrations in chemical equilibrium. It also allows one to determine in which direction the reaction will go from some initial non-equilibrium state:

if $\prod_s c_s^{\nu_s} > K(P, T)$, the reaction is direct

(i.e. c_s 's of the components with $\nu_s > 0$ will go down, those with $\nu_s < 0$ will go up)

if $\prod_s c_s^{\nu_s} < K(P, T)$ it is reverse (the opposite)

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 This is all the chemistry you need to know!
 (at least in this course)