

Recapitulation

We have considered the conditions of thermodynamic stability when a chemical species can be transferred between two phases: the chemical potential for that species must be uniform and the same among all phases that can absorb or desorb that species among themselves.

Conditions for Chemical Equilibrium and Stability

The equalities of the chemical potentials *are* necessary conditions for equilibrium between any two phases that can exchange a chemical species corresponding to each equality.

We also considered the conditions for stable equilibrium. These considerations showed that the slope of the chemical potential with respect to its conjugate number of species must be positive—this is equivalent to $\partial^2 G / \partial N_i^2 > 0$.

Independent Chemical Species

So far, it has been stated that in the sums implied by

$$dU = TdS - PdV + \vec{\mu}d\vec{N} \quad (1)$$

were written for only the *independent* chemical species. It must be clarified what is meant by chemical species, and we will do that for a case where there are dependent quantities.

Simple Case

We will do this with a straightforward example—which will yield a familiar result—which can be obviously generalized to any number of independent and dependent chemical species.

Suppose we have a system (like the Van't Hoff box) to which we can add and subtract H_2O .

It is possible that other substances, such as H and OH could form.

Thus, should the system to be composed of three substances. How many of these are independent? If only one independent species—why shouldn't any of the other species serve just as well?

We will ignore for the time being that the species may have an electronic charge—we will cover this later.

The answer lies in the fact that there are equations (or, constraints, if you like that word better) between the creation and destruction of the various substances, and these are given by the mass balance equations:



There must be mass balance that accounts for the fact that the disappearance of one species cannot take place without a cooperative change in another (the definition of dependence).

$$dN_{\text{H}_2\text{O}} = -dN_{\text{OH}} = -dN_{\text{H}} \quad (3)$$

Therefore, the condition for equilibrium can be written in terms of any one independent variables (here, we pick $N_{\text{H}_2\text{O}}$) by using the above two equations to eliminate two dependent quantities.

$$\begin{aligned} dU &= TdS - PdV + \mu_{\text{H}_2\text{O}}dN_{\text{H}_2\text{O}} + \mu_{\text{OH}}dN_{\text{OH}} + \mu_{\text{H}}dN_{\text{H}} \\ &= TdS - PdV + (\mu_{\text{H}_2\text{O}} - \mu_{\text{OH}} - \mu_{\text{H}})dN_{\text{H}_2\text{O}} \end{aligned} \quad (4)$$

Thus for a system of fixed volume and entropy, there is a linear relation for the dependent chemical species that specifies equilibrium.

This is the first of the familiar formulas from physical chemistry.

More General Case

Suppose that we have several reactions, for example:

$$\begin{array}{lll} \text{CO}_2 \rightleftharpoons \frac{1}{2}\text{O}_2 + \text{CO} & \text{Reaction } C \\ \text{H}_2\text{O} \rightleftharpoons \frac{1}{2}\text{O}_2 + \text{H}_2 & \text{Reaction } W \\ \text{H}_2 + \text{O}_2 \rightleftharpoons \text{H}_2\text{O}_2 & \text{Reaction } P \end{array}$$

Further suppose that initially the system is composed of

1 mole of carbon dioxide	2 mole of water
3 mole of H ₂	4 moles of O ₂

I find that the following system helps organize the quantification of such reactions (it is easily generalizable). We introduce a symbol (sometimes called the *extent* of reaction) ζ ; there will be a zeta for each of the independent reactions—call them ζ_C , ζ_W , ζ_P .

Reaction <i>C</i>				Reaction <i>W</i>					
Amount	Reactants		Products		Amount	Reactants		Products	
Species	CO ₂		O ₂	CO	Species	H ₂ O		O ₂	H ₂
Initial	1		0	0	Initial	2		0	0
Final	1 - ζ_C		$\zeta_C/2$	ζ_C	Final	2 - ζ_W		$\zeta_W/2$	ζ_W

Reaction <i>P</i>			
Amount	Reactants		Products
Species	H ₂	O ₂	H ₂ O ₂
Initial	3	4	0
Final	3 - ζ_P	4 - ζ_P	ζ_P

Notice that, in the above, we are considering each reaction independently: the amount created or destroyed by *each* reaction is tracked separately. However, the rate of appearance of a species in total is the sum of each reaction in which it appears. We use a superscript to keep track of each reaction.

$$\begin{aligned} dN_{\text{CO}_2} &= -d\zeta_C & dN_{\text{O}_2}^{\text{Rx}:C} &= \frac{d\zeta_C}{2} & dN_{\text{CO}} &= d\zeta_C \\ dN_{\text{H}_2\text{O}} &= -d\zeta_W & dN_{\text{O}_2}^{\text{Rx}:W} &= \frac{d\zeta_W}{2} & dN_{\text{H}_2}^{\text{Rx}:W} &= d\zeta_W \\ dN_{\text{H}_2}^{\text{Rx}:P} &= -d\zeta_P & dN_{\text{O}_2}^{\text{Rx}:P} &= -d\zeta_P & dN_{\text{H}_2\text{O}_2} &= d\zeta_P \end{aligned}$$

Therefore, for the species that appear in more than one of the reactions

$$\begin{aligned} dN_{\text{O}_2}^{\text{total}} &= \frac{d\zeta_C}{2} + \frac{d\zeta_W}{2} - d\zeta_P \\ dN_{\text{H}_2}^{\text{total}} &= d\zeta_W - d\zeta_P \end{aligned} \tag{5}$$

For those species that appear in only one reaction, there is only one $d\zeta$.

Therefore the differential expression for dU becomes:

$$dU = TdS - PdV + \mu_{\text{CO}_2}dN_{\text{CO}_2} + \mu_{\text{O}_2}dN_{\text{O}_2} + \mu_{\text{CO}}dN_{\text{CO}} + \mu_{\text{H}_2\text{O}}dN_{\text{H}_2\text{O}} + \mu_{\text{H}_2}dN_{\text{H}_2} + \mu_{\text{H}_2\text{O}_2}dN_{\text{H}_2\text{O}_2} \tag{6}$$

Collecting terms, one for each reaction,

$$dU = TdS - PdV + \left(\frac{1}{2}\mu_{\text{O}_2} + \mu_{\text{CO}} - \mu_{\text{CO}_2}\right)d\zeta_C + \left(\frac{1}{2}\mu_{\text{O}_2} + \frac{1}{2}\mu_{\text{H}_2} - \mu_{\text{H}_2\text{O}}\right)d\zeta_W + (\mu_{\text{H}_2\text{O}_2} - \mu_{\text{O}_2} - \mu_{\text{H}_2})d\zeta_P \quad (7)$$

From which we derive three independent equations for equilibrium:

$$\begin{aligned} 0 &= \frac{1}{2}\mu_{\text{O}_2} + \mu_{\text{CO}} - \mu_{\text{CO}_2} \\ 0 &= \frac{1}{2}\mu_{\text{O}_2} + \frac{1}{2}\mu_{\text{H}_2} - \mu_{\text{H}_2\text{O}} \\ 0 &= \mu_{\text{H}_2\text{O}_2} - \mu_{\text{O}_2} - \mu_{\text{H}_2} \end{aligned} \quad (8)$$

Thus, we conclude that *the number of independent species is equal to the total number of species extant in the model minus the number of independent mass balance equations.*

Even More General

For a general chemical reaction between several species such as $\nu_A A + \nu_B B \rightleftharpoons \nu_C C$ in terms of the stoichiometric coefficients ν_i , we can use the general method described in section 4.4 of Denbigh. There will be one such equation (i.e., Denbigh Eq 4.10: $\sum_{\text{products}} \nu_i \mu_i = \sum_{\text{reactants}} \nu_j \mu_j$) for each independent reaction.

The only thing missing is a relation between the $\vec{\mu}$ and the composition \vec{X} ($|\vec{X}| = 1$), which is either determined by experiment or an approximate model. With the functional form for the $\vec{\mu}(\vec{X})$, one can calculate the equilibrium composition \vec{X}^{eq} by using the equations of equilibrium.

Electrochemistry

While on the topic of chemical potentials and dependencies in the differential form dU , consider another relevant case:

Suppose that the species that is transmitted from “osmotic syringes” to the Van’t Hoff is charged; suppose that the charge is positive. Now, if we invoke the constraint that the phase must remain neutral (i.e., no net charge), then every mole of species transferred to the phase must be accompanied by a mole of electrons (or equivalent charge thereof).

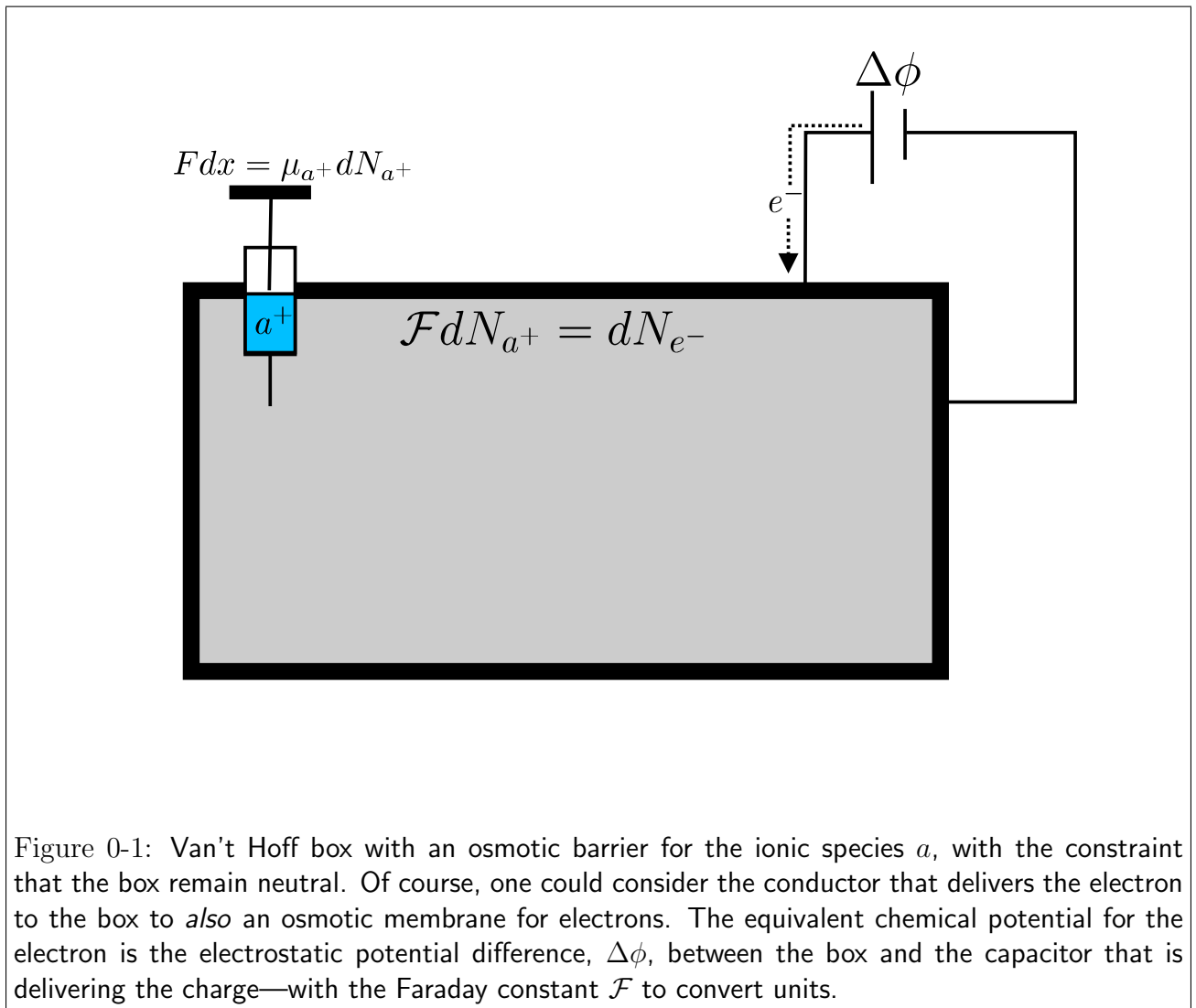


Figure 0-1: Van't Hoff box with an osmotic barrier for the ionic species a , with the constraint that the box remain neutral. Of course, one could consider the conductor that delivers the electron to the box to *also* an osmotic membrane for electrons. The equivalent chemical potential for the electron is the electrostatic potential difference, $\Delta\phi$, between the box and the capacitor that is delivering the charge—with the Faraday constant \mathcal{F} to convert units.

The Faraday constant, \mathcal{F} , relates how many coulombs are associated with a mole of electrons.

Furthermore, we must consider that the electrons transport to the phase may be at a potential ϕ^{res} that is different from ϕ^α .

Thus,

$$dU = TdS - PdV + \phi^{res}dq^{res} + \phi^\alpha dq^\alpha + \mu^{res}dN^{res} + \mu^\alpha dN^\alpha \quad (9)$$

using the relations, $dq^{res} = -dq^\alpha$, $dN^{res} = -dN^\alpha$, and $\mathcal{F}dN = dq$,

$$dU = TdS - PdV + [\mathcal{F}(\phi^{res} - \phi^\alpha) + \mu^{res} - \mu^\alpha]dN^{res} \quad (10)$$

The quantity in brackets defines the condition of electrochemical equilibrium—from which the electrochemical potential is derived.

Molar and Partial Molar Quantities

We often need to distinguish between the *amount of an extensive quantity per mole of all species* (for molar quantities) and the *rate at which an extensive quantity changes with the addition of a species*.

Total amounts of extensive quantities depend on the size of a system; they are not interesting for describing the properties of a material (just as mass is not useful for describing the properties of gold and lead: the relevant comparison is density). The molar volume of an ideal gas is about 22 liters per mole of gas species.

Partial molar quantities are used to define extensive variables per mole of each component indicate how a particular extensive quantity changes. For example, consider how the volume of a free-standing sponge change with the addition of water: the partial molar volume of water in the sponge is

$$V_{\text{H}_2\text{O}}^{\text{sponge}} = \left(\frac{\partial V^{\text{sponge}}}{\partial N_{\text{H}_2\text{O}}} \right)_{\text{all other variables}} \quad (11)$$

is clearly *not* simply related to the molar volume of pure water. (Note that, the superscript-subscript notation has the same convention as μ_i^j .)

Extra Information and Notes

Potentially interesting but currently unnecessary

Extensive quantities are homogeneous-degree-one functions of their extensive variables—triple each of the variables and the value of the function triples. Therefore, partial molar quantities must be homogeneous-degree-zero functions of their associated chemical species. In other words, the partial molar quantities are *material properties* and not system properties.

Molar Quantities

A molar quantity can be defined for each phase by dividing an extensive quantity, \mathcal{E} , by the total number of atoms in that phase:

$$\overline{\mathcal{E}}^\alpha (= \mathcal{E}^\alpha) \equiv \frac{\mathcal{E}^\alpha}{\sum_i N_i^\alpha} = \frac{\mathcal{E}^\alpha}{N_{\text{total}}^\alpha} = \frac{\mathcal{E}^\alpha}{|\vec{N}^\alpha|} \quad (12)$$

I like to use the “overbar” notation $\overline{\mathcal{E}}$; Denbigh uses a lower case letter, \mathcal{E} . $\overline{G}^\alpha = g^\alpha$, $\overline{S}^\alpha = s^\alpha$, and $\overline{V}^\alpha = v^\alpha$ are molar quantities for Gibb’s free energy, entropy, and volume. For example,

$$\overline{G}^\alpha = g^\alpha = \frac{G^\alpha}{\sum_i N_i^\alpha} \quad (13)$$

We could also define a molar quantity for an entire system by summing over all of the phases contained in the system; for example:

$$G = \sum_j G^j = \sum_j \sum_i N_i^j \overline{G}^j \quad (14)$$

dividing by $N_{\text{total}}^{\text{system}}$

$$\overline{G} = \frac{G}{\sum_i \sum_j N_i^j} = \frac{\sum_j \sum_i N_i^j \overline{G}^j}{\sum_i \sum_j N_i^j} = \sum_j f^j \overline{G}^j \quad (15)$$

where the phase fractions f^j

$$f^j \equiv \frac{\sum_i N_i^j}{\sum_i \sum_j N_i^j} \quad (16)$$

are the fractions of atoms in each phase.

If we divide the internal energy by the total number of atoms present in the system, we get the differential relation between the changes in the entire system.

$$\begin{aligned}\frac{dU}{\sum_i N_i} &= \frac{TdS - PdV + \sum_i \mu_i dN_i}{\sum_i N_i} \\ d\bar{U} &= Td\bar{S} - Pd\bar{V} + \sum_i \mu_i d\bar{N}_i \\ d\bar{U} &= Td\bar{S} - Pd\bar{V} + \sum_i \mu_i dX_i\end{aligned}\quad (17)$$

where a new symbol for the molar composition $X_i = N_i/N_{\text{total}} \equiv \bar{N}_i$ is introduced because it is used so often.

Important: *there is one less degree of freedom in the composition \vec{X} than the total numbers of atoms \vec{N} , because $|\vec{X}| = \sum_i X_i = 1$ and therefore $d\sum_i X_i = 0$ (i.e., we can solve for any one of the dX_k in terms of the other dX_i).*

These quantities could also be written per phase:

$$d\bar{U}^j = Td\bar{S}^j - Pd\bar{V}^j + \sum_i \mu_i dX_i^j \quad (18)$$

and these could be related to the total molar quantities through the phase fractions f^j defined above. Here, are all the principle thermodynamic differential energies in terms of molar quantities, written on a per-phase basis:

$U^\alpha = TS^\alpha - PV^\alpha + \vec{\mu} \cdot \vec{N}^\alpha$	$dU^\alpha = TdS^\alpha - PdV^\alpha + \vec{\mu} \cdot d\vec{N}^\alpha$
$\bar{U}^\alpha = T\bar{S}^\alpha - P\bar{V}^\alpha + \vec{\mu} \cdot \vec{X}^\alpha$	$d\bar{U}^\alpha = Td\bar{S}^\alpha - Pd\bar{V}^\alpha + \vec{\mu} \cdot d\vec{X}^\alpha$
$H^\alpha = U^\alpha + PV^\alpha$	$dH^\alpha = TdS^\alpha + V^\alpha dP + \vec{\mu} \cdot d\vec{N}^\alpha$
$\bar{H}^\alpha = \bar{U}^\alpha + P\bar{V}^\alpha$	$d\bar{H}^\alpha = Td\bar{S}^\alpha + \bar{V}^\alpha dP + \vec{\mu} \cdot d\vec{X}^\alpha$
$F^\alpha = U^\alpha - TS^\alpha$	$dF^\alpha = -S^\alpha dT - PdV^\alpha + \vec{\mu} \cdot d\vec{N}^\alpha$
$\bar{F}^\alpha = \bar{U}^\alpha - T\bar{S}^\alpha$	$d\bar{F}^\alpha = -\bar{S}^\alpha dT - Pd\bar{V}^\alpha + \vec{\mu} \cdot d\vec{X}^\alpha$
$G^\alpha = U^\alpha - TS^\alpha + PV^\alpha$	$dG^\alpha = -dS^\alpha dT + V^\alpha dP + \vec{\mu} \cdot d\vec{N}^\alpha$
$\bar{G}^\alpha = \bar{U}^\alpha - T\bar{S}^\alpha + P\bar{V}^\alpha$	$d\bar{G}^\alpha = -\bar{S}^\alpha dT + \bar{V}^\alpha dP + \vec{\mu} \cdot d\vec{X}^\alpha$

Partial Molar Quantities

Partial molar quantities are material properties relating the change of an extensive quantity with respect to the change of a chemical species. Here is the definition, written for phase j .

$$\mathcal{E}_i^j \equiv \left(\frac{\partial \mathcal{E}^j}{\partial N_i} \right)_{\text{all other quants.}} \quad (19)$$

Important: *Watch the notation difference between the molar quantity, $\bar{\mathcal{E}}_i^j$ of \mathbf{E}_i^j (which is a number density) and a partial molar quantity \mathcal{E}_i^j (which is an intrinsic property).*

For example, if all of the intrinsic properties are held fixed, then

$$d\mathcal{E}^\alpha = \sum_i \frac{\partial \mathcal{E}^\alpha}{\partial N_i} dN_i = \sum_i \mathcal{E}_i^\alpha dN_i \quad (20)$$

Because \mathcal{E} is homogeneous-degree-one in the \vec{N} , we can (Euler) integrate:

$$\mathcal{E}^\alpha = \sum_i \mathcal{E}_i^\alpha N_i \quad (21)$$

In particular for the Gibbs free energy,

$$\begin{aligned} \mu_i^\alpha &= \left(\frac{\partial G^\alpha}{\partial N_i} \right)_{P,T,\text{other } N_{j \neq i}} \\ G^\alpha &= \sum_i \mu_i^\alpha N_i^\alpha \\ \overline{G}^\alpha &= \sum_i \mu_i^\alpha X_i^\alpha \\ G &= \sum_i \mu_i N_i \\ \overline{G} &= \sum_i \mu_i X_i \end{aligned} \quad (22)$$

Comparing this to the last entry in the table, we have the Gibbs-Duhem relations:

$$\begin{aligned} 0 &= S^\alpha dT - V^\alpha dP + \sum_i N_i^\alpha d\mu_i^\alpha \\ 0 &= \overline{S}^\alpha dT - \overline{V}^\alpha dP + \sum_i X_i^\alpha d\mu_i^\alpha \end{aligned} \quad (23)$$

which can be conveniently written as follows

$$0 = \vec{\mathcal{E}} \cdot d\vec{\mathcal{I}} \quad (24)$$

We will discuss this equation's geometry and its application to the Gibbs phase rule in following lectures.