Recapitulation and Elucidation

Last time we introduced the chemical potential—sometimes is useful to think of μ_i^α as *just a different kind of work* related to a force to insert a particular type of chemical specie i. Larger μ_i^α corresponds to a larger force pushing back on the piston: the chemical species i tends to flow from regions of high chemical potential to low chemical potential. Gradients in chemical potential are the driving forces for diffusion.

Conditions for Chemical Equilibrium and Stability

The equalit*ies* of the chemical potential*s* *are* necessary condition*s* are necessary condition*s* for equilibrium between any two phases that can exchange a chemical species corresponding to to each equality.

The above paragraph is a mouthful of words that is succinctly written as C equations, $\mu_i^\alpha = \mu_i^\beta$.

Recall that there are three cases for a single mobile species, i, that can be transferred between α and β:

$(\mu_i^\alpha - \mu_i^\beta) > 0$ Then, dN_i^α will be negative, i will flow from α to β resulting in a total internal energy decrease at constant S and V (i.e., $dU < 0$)

$(\mu_i^\alpha - \mu_i^\beta) < 0$ Then, dN_i^α will be positive, i will flow to β from α resulting in a total internal energy decrease at constant S and V (i.e., $dU < 0$)

$\mu_i^\alpha = \mu_i^\beta$ Then, dN_i^α is unrestricted, but there is no benefit in going either way: this is equilibrium— and we can drop the super-script for phase at equilibrium for any i that can be exchanged.

Consider first of these statements more carefully, suppose α and β satisfy the first condition $\mu_i^\alpha(N_i^\alpha) > \mu_i^\beta(N_i^\beta)$. The specie i will flow from α and thereby decrease N_i^α and increase N_i^β— but, how will stability be attained? Because it is necessary for equilibrium that the $\mu_i^\beta(N_i^\beta)$ increase faster than $\mu_i^\alpha(N_i^\alpha)$ decreases (i.e., so that it can catch up).

There are two ways that a phase could gain or lose a specie and change the N_i contained in that phase:

1. The phase could transform to another phase—thus, any specie that is in α would find itself in β.

2. The specie could flow from one phase to the other, while keeping the phase fractions fixed.
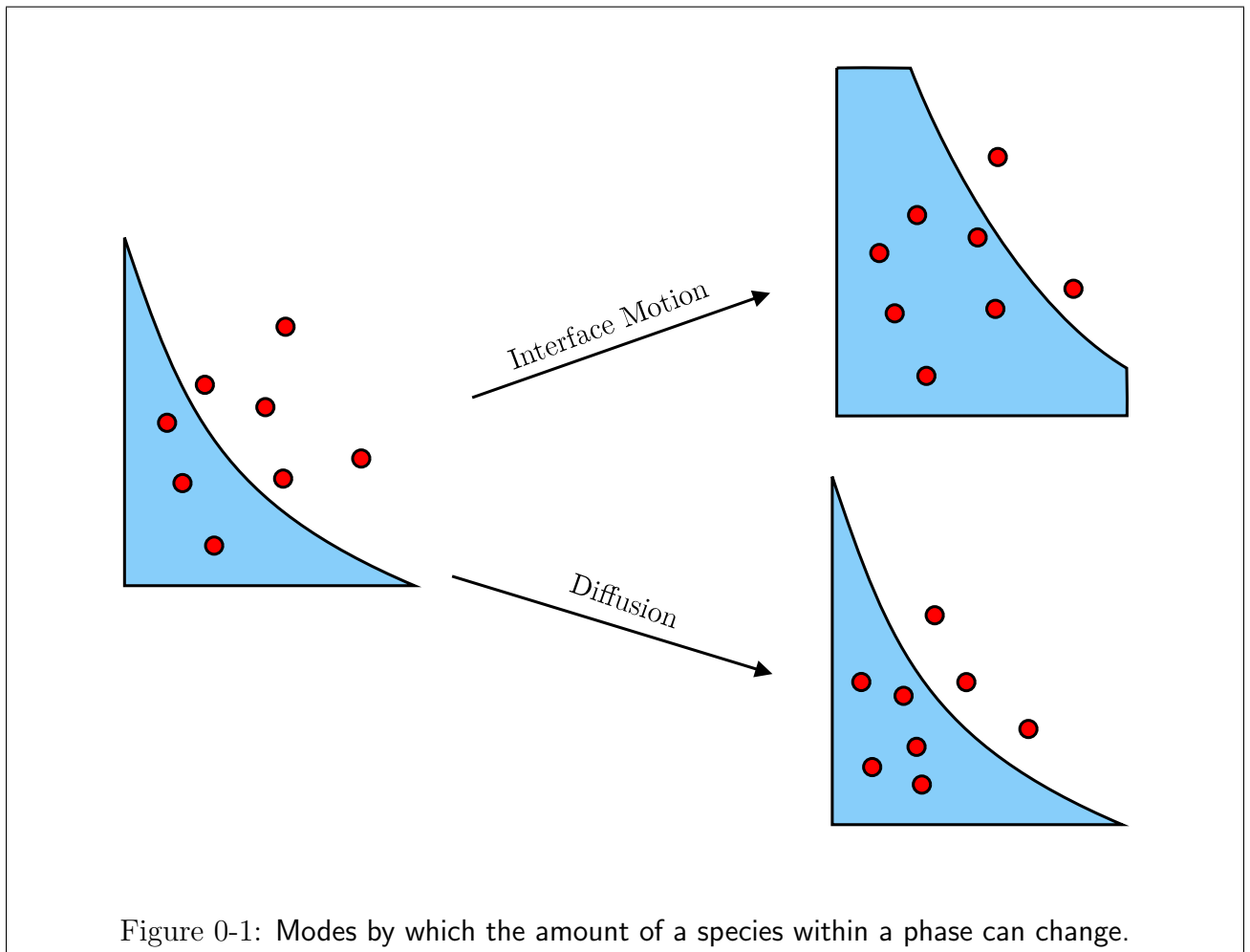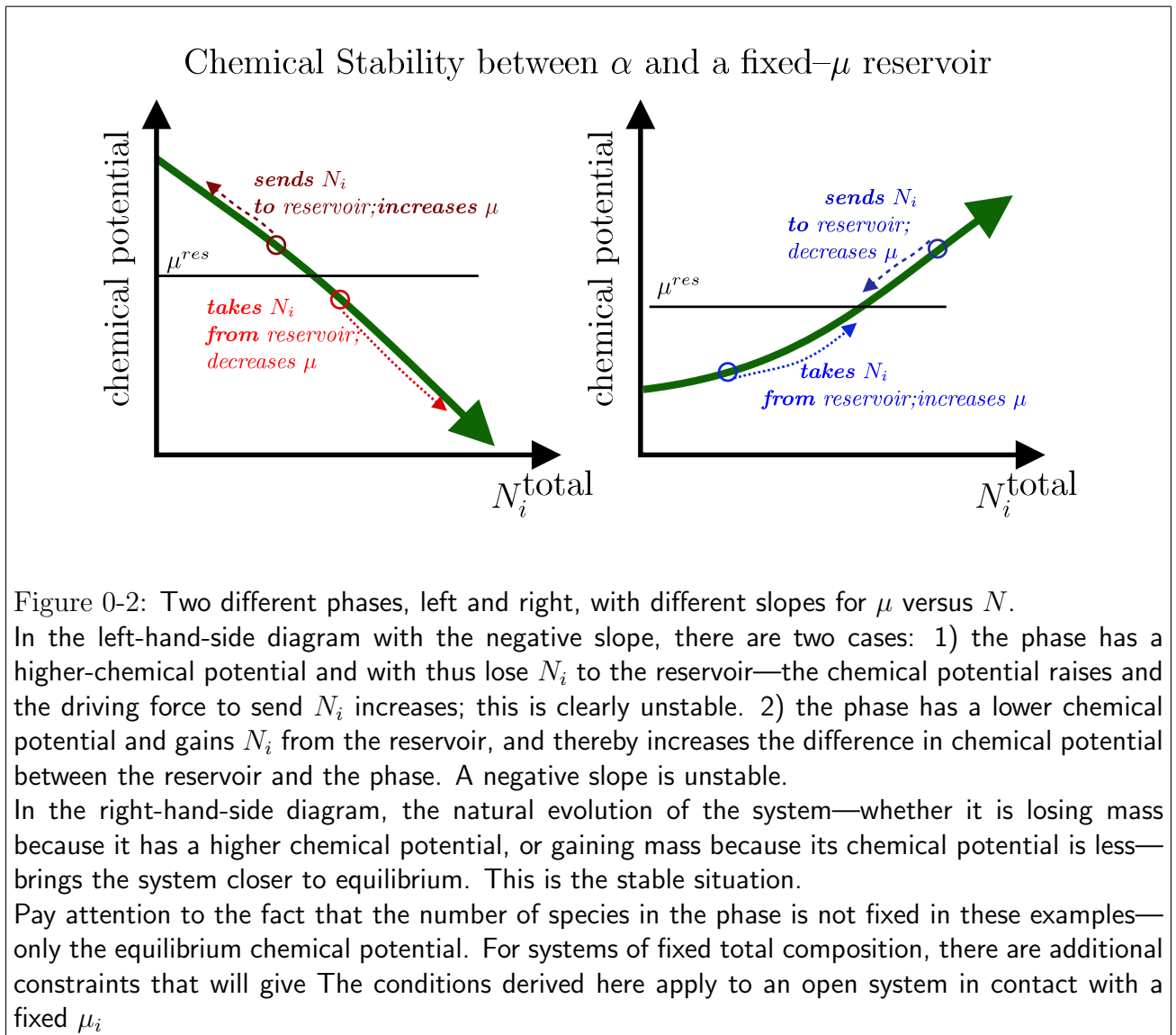
Figure 0-1: Modes by which the amount of a species within a phase can change.

Consider the last of the conditions, $\mu_i^\alpha(N_i^\alpha) = \mu_i^\beta(N_i^\beta)$, which is equilibrium; so we clarify that with the notation: $\mu_i^\alpha(N_i^{\alpha,eq}) = \mu_i^\beta(N_i^{\beta,eq})$ (which defines the two "equilibrium" amounts of N_i in each phase). To second order,

$$
\begin{aligned}
dU &= \left[\mu_i^\alpha(N_i^{\alpha,eq}) - \mu_i^\beta(N_i^{\beta,eq})\right] dN_i^\alpha + \frac{1}{2}\left[\left.\frac{\partial\mu_i^\alpha}{\partial N_i}\right|_{N_i=N_i^{\alpha,eq}} - \left.\frac{\partial\mu_i^\beta}{\partial N_i}\right|_{N_i=N_i^{\beta,eq}}\right](dN_i^\alpha)^2 \\
&= \frac{1}{2}\left[\left.\frac{\partial\mu_i^\alpha}{\partial N_i^\alpha}\right|_{N_i=N_i^{\alpha,eq}} - \left.\frac{\partial\mu_i^\beta}{\partial N_i^\alpha}\right|_{N_i=N_i^{\beta,eq}}\right](dN_i^\alpha)^2 \quad \text{because } \frac{dN_i^\alpha}{dN_i^\beta} = -1
\end{aligned}
\tag{1}
$$

which is a condition on the slopes of the curves at the crossing point: the slope of the α–curve must be greater than that of the β—curve. *Students should draw a sketch of curves and convince themselves they understand how the curves must cross.*

To further illustrate the relation between a phase's $\mu(N_i)$ and the slope $d\mu/dN_i$, consider the following diagram:

Chemical Stability between α and a fixed–μ reservoir

Figure 0-2: Two different phases, left and right, with different slopes for μ versus N.

In the left-hand-side diagram with the negative slope, there are two cases: 1) the phase has a higher-chemical potential and with thus lose N_i to the reservoir—the chemical potential raises and the driving force to send N_i increases; this is clearly unstable. 2) the phase has a lower chemical potential and gains N_i from the reservoir, and thereby increases the difference in chemical potential between the reservoir and the phase. A negative slope is unstable.

In the right-hand-side diagram, the natural evolution of the system—whether it is losing mass because it has a higher chemical potential, or gaining mass because its chemical potential is less—brings the system closer to equilibrium. This is the stable situation.

Pay attention to the fact that the number of species in the phase is not fixed in these examples—only the equilibrium chemical potential. For systems of fixed total composition, there are additional constraints that will give The conditions derived here apply to an open system in contact with a fixed μ_i

It will be more instructive to consider the conditions for equilibrium for a system of fixed composition—to do this we will define the mole fractions below.

Further more, consider the chemical stability of a single phase, just as we did for other material properties, we must have that:

$$\frac{\partial^2 G}{\partial N_i{}^2} = \frac{\partial \mu_i}{\partial N_i} > 0 \tag{2}$$

The curvature of G must be positive and the slope of μ must also be positive. If this were not the case, then for a system that is in equilibrium with a reservoir at fixed μ_i (i.e., the composition is the equilibrium composition), a small fluctuation in uniform composition would always decrease G.

Independent Chemical Species

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

$$dU = TdS - PdV + \vec{\mu}d\vec{N} \tag{3}$$

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.

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 and OH could form.

Thus, should the system to be composed of three substances. How many of these are independent? If only only on 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:

$$H + OH \rightleftharpoons H_2O \tag{4}$$

There must be mass balance that accounts for the fact that the disappearance of one species cannot take place with out a cooperative change in another (the definition of dependence).

$$dN_{H_2O} = -dN_{OH} = -dN_H \tag{5}$$

Therefore, the condition for equilibrium can be written in terms of any one independent variables (here, we pick N_{H_2O}) by using the above two equation to eliminate two dependent quantities.

$$
\begin{aligned}
dU &= TdS - PdV + \mu_{H_2O}dN_{H_2O} + \mu_{OH}dN_{OH} + \mu_H dN_H \\
&= TdS - PdV + (\mu_{H_2O} - \mu_{OH} - \mu_H)dN_{H_2O}
\end{aligned}
\tag{6}
$$

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.

We will generalize this result to several independent species and allow for charge transfer (which would be dominant in the example above) later.

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.*

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).

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,

$$dU = TdS - PdV + \phi^{res}dq^{res} + \phi^{\alpha}dq^{\alpha} + \mu^{res}dN^{res} + \mu^{\alpha}dN^{\alpha} \tag{7}$$

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

$$dU = TdS - PdV + [\mathcal{F}(\phi^{res} - \phi^{\alpha}) + \mu^{res} - \mu^{\alpha}]dN^{res} \tag{8}$$

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

Molar and Partial Molar Quantities

Why do we need to define molar quantities & partial molar quantities? Because in multi-component/multi-phase systems, chemical equilibrium calculations are complicated. Rather than calculating total amounts for extensive quantities, it is often convenient to define *molar quantities* for single component systems. Further for multi-component systems, *partial molar quantities* are used to define extensive variables per mole of each component.

Molar Quantities

Let's start with a system that only contains a single chemical component ($i = a$ instead of $i = a, b, \ldots, m$) with a single phase. The internal energy (PV and chemical work only with summation convention) can be represented as

$$dU = TdS - PdV + \mu_a dN_a = TdS - PdV + \mu dN \tag{9}$$

where dN is the number of mole of this chemical component a.

Similarly, The enthalpy can be represented as

$$dH = TdS + VdP + \mu dN \tag{10}$$

We can define the extensive variables (proportional to the size of the system) in equations above, U, S, V, H, into *molar quantities* as

$$u = \frac{U}{N}, \ s = \frac{S}{N}, \ v = \frac{V}{N}, \ h = \frac{H}{N} \tag{11}$$

From equations above, changes in the internal energy, entropy, volume, and enthalpy can be represented as

$$\begin{aligned}
dU &= u \ dN + Ndu \\
dS &= s \ dN + Nds \\
dV &= v \ dN + Ndv \\
dH &= h \ dN + Ndh
\end{aligned} \tag{12}$$

Equation (10) with molar quantities in extensive variables can be rewritten as

$$\begin{aligned}
h \ dN + Ndh &= T(sdN + Nds) + NvdP + \mu dN \\
N(dh - Tds - vdP) &= (\mu - h + Ts)dN
\end{aligned} \tag{13}$$

Applying the definition of Homogeneous Degree 1 (HD1) into enthalpy in equation (10)

$$H = TS + \sum_i \mu_i N_i, \tag{14}$$

and for a single component $N_i = N$, thus

$$h = Ts + \mu \tag{15}$$

Substitute equation (15) into equation (13) and we get:

$$dh = Tds + vdP \tag{16}$$

    `Question:  Can you tell the differences between eqns (10), (14), (15) & (16)?`

Similarly, we can find the change in the molar quantity of internal energy is

$$du = Tds - Pdv \tag{17}$$

Alternative derivation for equation (15): From previous lectures we know that $U + PV = H$ and from equation (14):

$$U + PV = TS + \mu N \tag{18}$$

Applying the ideas of molar quantities in the extensive variables, equation(12), we get

$$\begin{aligned}
Nu + PNv &= TNs + \mu N \\
u + vP &= Ts + \mu, \text{ thus} \\
h &= Ts + \mu \quad \text{Q.E.D.}
\end{aligned} \tag{19}$$