# Recap

Before the break we were concerned with the conditions of thermodynamic stability of a material and derived that there are *material-physical* constraints on the second derivatives of energy quantities. For example:

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V}\left[\frac{\partial^2 U(S,V)}{\partial V^2}\right]^{-1} \tag{1}$$

However, in everything that preceded, we didn't consider that the chemical content of a body may be variable.

# Considerations of an Open System (one which exchange different kinds of chemical species with the environment)

We now consider a system that can exchange chemical specifies with its environment.

For historical reasons, the system in question is called a *phase*. It will be supposed that the phase is a spatially continuous subsystem. The entire system is composed of the subsystem and the rest of the system. The rest of the system may also have phases.

***Extra Information and Notes***

***Potentially interesting but currently unnecessary***

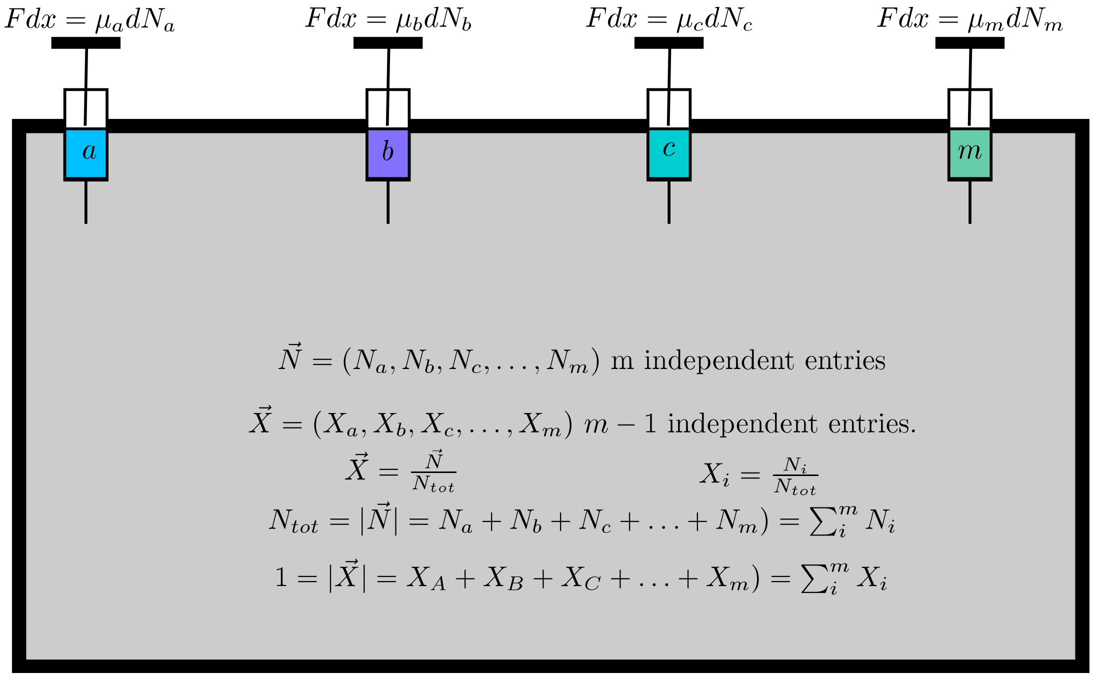
To be more concrete, we usually think of a phase as a liquid, solid, or vapor. These may be distinguished by their separate state functions.

The state function (or, practically, our *model* of a state function) determines the material properties as a function of the independent thermodynamic variables. This state function will determine how we might distinguish two phases; i.e., there may be a density change, or a bulk modulus change, that can be measured as we cross an *phase-separating interface, or interphase boundary*.

We will defer a strict definitions of phase and the position of a phase boundary. surface. Each type of simple, intuitive, phase described above, can have further catagories of distinct phases; for example:

1. Two solid phases could differ in their crystal structure.
2. Two liquid phases may differ in their equilbrium compositions.
3. Solid phases may differ in their equilbrium compositions
4. etc.

Just as we used a picture to represent an isolated, or adiabatic, etc, system, there is a picture that is traditionally used to represent a phase that exchanges chemicals with its environment:



$$\vec{N} = (N_a, N_b, N_c, \ldots, N_m) \text{ m independent entries}$$

$$\vec{X} = (X_a, X_b, X_c, \ldots, X_m)\ m-1 \text{ independent entries.}$$

$$\vec{X} = \frac{\vec{N}}{N_{tot}} \qquad X_i = \frac{N_i}{N_{tot}}$$

$$N_{tot} = |\vec{N}| = N_a + N_b + N_c + \ldots + N_m) = \sum_i^m N_i$$

$$1 = |\vec{X}| = X_A + X_B + X_C + \ldots + X_m) = \sum_i^m X_i$$

Figure 0-1: Van't Hoff Reaction Box: Each independent species can be exchanged with the environment by adding or subracting an amount of that species $dN$: the chemical potential *or each species* is defined as the $\mu_i = F_i(dx_i/dN_i)$ fo each equilibrium $F_i$. (Box design inspired by Tina Turner's *Acid Queen* scene in Ken Russell's 1975 film "Tommy," *Cav. Not, Prof. Kenneth Russel the materials scientist famous for his work on nucleation*)

**Consider a general case that additional work (other than PV work) on the system is composed by various forces, and the total work done can be represented as**

$$\sum_i F_i dx_i,\ i = a, b, \ldots, m \tag{2}$$

**where $x_i$ were the extensive variables that changed according to those forces.**

**Now consider a chemical system that the additional work is generated by $m$ syringes. These syringes are adding or subtracting $N_i$ number of species. The work done by each syringe $i$ on the system is**

$$F_i dx_i = \mu_i dN_i,\ i = a, b, \ldots, m \tag{3}$$

**With a positive or negative sign in equation (3), it refers to adding or subtracting species in the system (i.e., exchanging species with the environment). $\mu_i$ is the chemical potential *of each species* and is defined as $\mu_i = F_i(dx_i/dN_i)$ for each equilibrium $F_i$.**

**Before going details of chemical potential, $\mu_i$, let's discuss the differences between number of species, $N_i$ $(\vec{N})$ and the average composition, $X_i$ $(\vec{X})$. (*Note, later in the lecture of multiphase system, we will introduce the "actual composition", which is different from the average composition aforementioned*)**

**Total amount of species in this chemical system can be represented as**

$$N_{tot} = |\vec{N}| = N_a + N_b + N_c + \ldots + N_m = \sum_i^m N_i \tag{4}$$

**The <u>fractions</u> of the species, $i$, in this chemical system is**

$$\begin{aligned} X_i &= \frac{N_i}{N_{tot}}, \; i = a, b, \ldots, m \\ \vec{X} &= \frac{\vec{N}}{N_{tot}} \end{aligned} \tag{5}$$

**Note, in equation (5) $N_i$ is an extensive variable but $X_i$ is an *derived* intensive variable.**
**If we sum up all fractions of the all species, $i = a, b, \ldots, m$**

$$\begin{aligned} \sum_i^m X_i &= X_a + X_b + X_c + \ldots + X_m \\ &= \frac{N_a}{N_{tot}} + \frac{N_b}{N_{tot}} + \frac{N_b}{N_{tot}} + \ldots + \frac{N_m}{N_{tot}} \\ &= \frac{\sum_i^m N_i}{N_{tot}} \\ &= 1 \end{aligned} \tag{6}$$

***Extra Information and Notes***

***Potentially interesting but currently unnecessary***

Students should compare this graphical illustration to those that were used to derive the equilibrium conditions $P^\alpha = P^\beta$, $T^\alpha = T^\beta$. They are, in principle the same, and we will get the same result; i.e., $\mu_i^\alpha = \mu_i^\beta$—a necessary condition for two phases that can exchange a chemical species $i$ must have the same chemical potential in each phase. This is another example of, "everything is the same when reduced to the same mathematical structure".

This introduces the concept of an ideal open system. Each of the needles is capped by an osmotic membrane that allows passage of the relevant chemical species only. Thus, we relate the chemical potential *of each possible chemical species* **within each phase** to a physical force that we can measure.

The emphasis in the last paragraph should be taken quite seriously. Errors creep in if the student doesn't recognize the physical distinction between the sub-scripts and super-scripts in $N_i^\alpha$.

As in any idealization, the picture should be understood conceptually. It would be impossible to construct such a Van't Hoff box physically: there are no perfect osmotic membranes, and it is impossible to purify any substance so that only one chemical species is isolated. However, the concept does not prevent us from using the idea as a limiting case, and then just proceeding.

***Extra Information and Notes***

***Potentially interesting but currently unnecessary***

How many needles are needed to define a chemical system? We need one for each *independent* chemical species for the constituents that are under consideration. For example, with hydrogen, oxygen, water, and hydrogen peroxide, how many needles are needed? It's two, because there are two mass balance equations that reduce the four possible amounts to two—if we had more needles, we couldn't vary one of the independent parameters (i.e., $S$, $V$, $N_i$) without having one of the needles (or $S$ or $V$) necessarily change in a reversible equilibrium process.

The system pictured above is meant to convey as an adiabatic and constant volume (or mechanical work) example, which are the conditions for the internal energy $U(S, V)$ And thus, we extend our definition of internal energy to include chemical work terms explicitly:

For an entire sytem as a black box (ignoring the possibility of multiple phases)

| | |
|---|---|
| $dU = dq_{\text{rev}} + dw$ | all forms of work |
| $dU = TdS + dw$ | all forms of work |
| $dU(S, V) = TdS - PdV$ | PV work only |
| $dU(S, V, N_a, N_b, \dots N_m) = TdS - PdV + \sum_{i=1}^{m} \mu_i dN_i$ | PV and chemical work only |
| $dU(S, V, N_a, N_b, \dots N_m) = TdS - PdV + \mu_i dN_i$ | PV and chemical work only, summation convention |
| $dU(S, V, \vec{N}) = TdS - PdV + \vec{\mu} \cdot d\vec{N}$ | PV and chemical work only, vector notation |
| $dU = T(S, V, \vec{N})dS - P(S, V, \vec{N})dV + \vec{\mu}(S, V, \vec{N}) \cdot d\vec{N}$ | PV and chemical work only, vector notation—function dependence in differential coefficients |
| $dU(\vec{E}) = \vec{I}(\vec{E}) \cdot d\vec{E}$ | maximally dense and obscure, written in terms of extensive variables and intensive differential coefficients; useful for comparison |

If one is concerned about the internal distribution of species, entropy, and volume, then there must be a summation over all the phases that are present inside the system. Using a double summation condition—one sum over all the phases ($j$ for $\alpha, \beta, \gamma, \dots, \zeta$) and one over all the independent chemical species ($i$ for $N_a, N_b, N_c, \dots, N_m$):

$$dU = TdS - PdV + \mu_i^j dN_i^j \tag{7}$$

for the total system entropy and volume change in each phase, and where $PdV$ is the only work involved. We could write the total entropy and volume in terms of each phase, e.g.,

$$dS = \sum_j dS^j; \quad dV = \sum_j dV^j \tag{8}$$

where $dV^j$ is the change in volume of each consituent phase—but there is one relation between all of the $(dV^\alpha, dV^\beta, \dots, dV^\zeta)$ and therefore they are not all independent. In other words, we cannot specify $dV$ and *all* of the $dV^j$ independently. However, if it were desireable, one could pick the changes of volume of each phase to be independent; but then $dV$ for the entire system would be dependent on the sum. The same statements of independence and choice of variables applies to the system's total entropy and that of the phases.

# Conditions for Internal Equilibrium for Phases that can Exchange a Chemical Component

These conditions for internal equilibrium will be derived in the same manner in which it was shown that $T$ and $P$ must be uniform when $S$ and $V$ can be exchanged between two phases.

***Extra Information and Notes***

***Potentially interesting but currently unnecessary***

This is the general rule: "If a extensive quantity can be exchange between two subsystems (e.g., phases), then a necessary condition for thermodynamic equilibrium is that that extensive quantity's conjugate intensive quantity must be uniform (i.e., the same in all phases)". I think this is simple, organized, easy to remember, and beautiful.

We will consider two phases $\alpha$ and $\beta$ that can exchange a chemical species $i$. This result is easily generalized to an arbitrary number of phases and species—the result will always be the same: $\mu_i^j = \mu_i^k$ for any species, $i$ that can be transfered between phases $j$ and $k$ (*note once again, the equality refers to the sub-scripts (chemical species) and not super-scripts (phase)*).

We consider a closed, isolated, system that is composed of two phases $\alpha$ and $\beta$ in contact which can exhange $dN_i$. Because the $N_i$ can carry heat and volume with them, then it follows that the pressure and temperature in $\alpha$ and $\beta$ must be the same and uniform at equilibrium—there is no need to carry a super-script.

Thus, for the entire closed system $dN_i = 0 = dN_i^\alpha + dN_i^\beta$, and the total volume and entropy cannot change (or the internal energy at fixed volume and entropy is minimized at equilibrium) $dS = dV = 0$:

$$\begin{aligned} dU &= \mu_i^\alpha dN_i^\alpha + \mu_i^\beta dN_i^\beta \\ &= (\mu_i^\alpha - \mu_i^\beta) dN_i^\alpha \qquad \text{because } dN_i^\beta = -dN_i^\alpha \end{aligned} \tag{9}$$

There are three cases:

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

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

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

# Conditions of Equilbrium for Other Types of Systems

Here, we could redraw the boxes to indicated that the system is in equilbrium with a reservoir that fixes an intensive variables (i.e., constant $P$ or $T$), in these cases we derive:

| Fundamental Equation | Natural Variables |
|---|---|
| $dU(S,V,\vec{N}) = T(S,V,\vec{N})dS - P(S,V,\vec{N})dV + \vec{\mu}(S,V,\vec{N}) \cdot d\vec{N}$ | $S, V, \vec{N}$ |
| $dH(S,P,\vec{N}) = T(S,P,\vec{N})dS + V(S,P,\vec{N})dV + \vec{\mu}(S,P,\vec{N}) \cdot d\vec{N}$ | $S, P, \vec{N}$ |
| $dF(T,V,\vec{N}) = S(T,V,\vec{N})dS - P(T,V,\vec{N})dV + \vec{\mu}(T,V,\vec{N}) \cdot d\vec{N}$ | $T, V, \vec{N}$ |
| $dG(T,P,\vec{N}) = -S(T,P,\vec{N})dT + V(T,P,\vec{N})dV + \vec{\mu}(T,P,\vec{N}) \cdot d\vec{N}$ | $T, P, \vec{N}$ |

And, we will derive the Gibbs-Duhem relations by doing an integration of $U$ over its intensive variables.