At equilibrium, each $\mu_i$ must be uniform (constant) throughout a system, just like $T$ and $P$ must be.

Suppose two different regions, I and II, of a system have different values, $\mu_i^I$ and $\mu_i^{II}$, of the chemical potential of its $i^{th}$ component, $\mu_i$. In particular, suppose that $\mu_i^I > \mu_i^{II}$. Then, if we move $dn_i (> 0)$ moles of the component $i$ from region I to region II, at constant $T$ and $P$, we have $dn_i^I = -dn_i$ and $dn_i^{II} = +dn_i$, implying

$$dG = dG^I + dG^{II} = \mu_i^I dn_i^I + \mu_i^{II} dn_i^{II} = \mu_i^I (-dn_i) + \mu_i^{II} (+dn_i) = -(\mu_i^I - \mu_i^{II})(+dn_i) < 0.$$ 

**THUS, THE DIRECTION OF SPONTANEOUS CHANGE CORRESPONDS TO MOLECULES MOVING FROM REGIONS OF HIGHER CHEMICAL POTENTIAL TO REGIONS OF LOWER CHEMICAL POTENTIAL (THEREBY EQUALIZING/UNIFORMIZING THE CHEMICAL POTENTIAL).**

Consider the figure below – Fig. 6.2 in the textbook (3rd edition) – showing a two-component system equilibrated at temperature $T$. Pure H$_2$ gas is on the left, and a mixture of H$_2$ gas and Ar gas is on the right; the partition dividing them is only permeable to H$_2$ gas.

As established in the beginning of this lecture, the equilibrium condition for a mixture involves equality of the chemical potentials of all components throughout the system, wherever the components are found.

In our particular example, this condition requires $\mu_{H_2}^{pure}(T, p_{H_2}) = \mu_{H_2}^{mixed}(T, p_{H_2})$.

But the left hand side here can be written as

$$\frac{G_{H_2}^{pure}(T, p_{H_2})}{n_{H_2}} = \frac{G_{H_2}^{left}(T, p_{H_2})}{n_{H_2}} = G_{H_2}^o + n_{H_2}RT \ln \frac{p_{H_2}}{p^o} = \mu_{H_2}^o(T) + RT \ln \frac{p_{H_2}}{p^o}.$$ 

Note that $\mu_{H_2}^o(T) = \frac{g_{H_2}^o(T)}{n_{H_2}} = G_{m,H_2}^o(T)$ is the chemical potential – molar Gibbs free energy – of a pure-H$_2$ system at temperature $T$ and pressure $p^o = 1 \ atm$.

Writing $p_{H_2} = X_{H_2} P$, where $X_{H_2}$ and $P$ are the H$_2$ mole fraction and the total pressure of the H$_2$/Ar mixture, we have (from the above equations)

$$\mu_{H_2}^{mix}(T, P) = \mu_{H_2}^o(T) + RT \ln \frac{p_{H_2}=X_{H_2}P}{p^o} = \mu_{H_2}^o(T) + RT \ln \frac{P}{p^o} + RT \ln X_{H_2} = \mu_{H_2}^{pure}(T, P) + RT \ln X_{H_2}.$$
More generally, for component $i$ at mole fraction $X_i$ in a mixture at temperature $T$ and total pressure $P$,

$$\mu^\text{mixture}_i(T, P) = \mu^\text{pure}_i(T, P) + RT \ln X_i.$$  

NOTE: $RT \ln X_i < 0$ implies $\mu^\text{mixture}_i(T, P) < \mu^\text{pure}_i(T, P)$, which – as we’ll see in later lectures – is the physical, thermodynamic, basis for the phenomenon of osmosis.

→ FREE ENERGY OF MIXING

Consider Fig. 6.3 (3rd edition of textbook), showing the initial, unmixed state of 4 inert gases.

$$G_{\text{initial}} = \sum_{i=1}^{4} (\mu^\text{pure}_i) n_i.$$  

But

$$G_{\text{final}} = \sum_{i=1}^{4} \left( \mu^\text{pure}_i + RT \ln X_i \right) (n_i = X_i n_T) = \sum_{i=1}^{4} (\mu^\text{pure}_i) + n_T RT \sum_{i=1}^{4} X_i \ln X_i,$$

and thus

$$\Delta G = \Delta G_{\text{mixing}} = G_f - G_i = n_T RT \sum_{i} X_i \ln X_i.$$  

NOTE, AGAIN: $X_i \ln X_i < 0$ implies that $\Delta G_{\text{mixing}} < 0$, i.e., MIXING IS SPONTANEOUS!

→ Another route to this result comes from calculating directly the entropy change upon mixing gases (say, A and B), each initially at the same pressure, $P$, and temperature, $T$.

![Diagram](image)

Now, we have $\Delta S_{\text{mixing}} = \Delta S_A(V \rightarrow V) + \Delta S_B(V \rightarrow V) = n_A R \ln \frac{V}{V_A} + n_B R \ln \frac{V}{V_B}$, which

- using $n_{A(B)} = X_{A(B)} n_T$ and $V_{A(B)} = \frac{n_{A(B)}}{n_T}$ (from $n_{A(B)} RT = PV_{A(B)}$ and $n_T RT = PV$) – gives

$$\Delta S_{\text{mixing}} = -n_T R (X_A \ln X_A + X_B \ln X_B), > 0.$$  

But because $\Delta H = 0$ for these ideal gases, it follows from $\Delta G = \Delta H - T \Delta S$ that

$$\Delta G_{\text{mixing}} = n_T RT (X_A \ln X_A + X_B \ln X_B) \rightarrow n_T RT \sum_{i} X_i \ln X_i < 0,$$

i.e., mixing of gases is entropy-driven (with more volume available to each component).