2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 12

Room 3-442
Friday, March 15, 11:00am - 1:00pm

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Stable-equilibrium properties of MIXTURES (within the simple-system model)

Partial properties
Gibbs-Dalton ideal mixtures
Mixing and separation
Osmotic pressure and blue energy
Stratification

Experimental measurement of SES properties of mixtures:

Partial properties from the chemical potentials

$$G = E - TS + pV = G(T,p,\boldsymbol{n}) \qquad \mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$$

$$\left(\frac{\partial G}{\partial T}\right)_{T,p,\boldsymbol{n}} = -S(T,p,\boldsymbol{n}) \quad \left(\frac{\partial G}{\partial p}\right)_{T,p,\boldsymbol{n}} = V(T,p,\boldsymbol{n}) \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = \mu_i(T,p,n\boldsymbol{y})$$

$$\mathrm{d}\mu_i = \underbrace{\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}}}_{-s_i}\mathrm{d}T + \underbrace{\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}}}_{v_i}\mathrm{d}p + \sum_{j=1}^{r}\underbrace{\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j}}_{\mu_{i,j}\,=\,\mu_{i,j}}\mathrm{d}n_j = -s_i\,\mathrm{d}T + \underbrace{v_i\,\mathrm{d}p + \textstyle\sum_{j=1}^{r}\mu_{i,j}\,\mathrm{d}n_j}_{\mathrm{d}\mu_i|_T}$$

where we define

$$-\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial^2 G}{\partial T\partial n_i}\right)_{p,\boldsymbol{n}'_i} = \left(\frac{\partial S}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = s_i(T,p,n\boldsymbol{y}) \quad \textbf{Partial entropy of constituent } i$$

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial^2 G}{\partial p\partial n_i}\right)_{T,\boldsymbol{n}'_i} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = v_i(T,p,n\boldsymbol{y}) \quad \textbf{Partial volume of constituent } i$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} = \left(\frac{\partial^2 G}{\partial n_j\partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_{ij}} = \mu_{i,j}(T,p,n\boldsymbol{y}) = \mu_{j,i}(T,p,n\boldsymbol{y})$$

notice that, from $\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ and $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \boldsymbol{\mu}\cdot\mathrm{d}\boldsymbol{n}$ we also have

$$\left(\frac{\partial E}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = e_i(T,p,n\boldsymbol{y}) = T\,s_i - p\,v_i + \mu_i \quad \textbf{Partial energy of constituent } i$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{T,p,\boldsymbol{n}'_i} = h_i(T,p,n\boldsymbol{y}) = T\,s_i + \mu_i = \left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_{p,\boldsymbol{n}} \quad \textbf{Partial enthalpy of constituent } i$$

All partial properties can be evaluated once we know the chemical potentials as functions of T, p, $\boldsymbol{y}$ and n, i.e., $\mu_i = \mu_i(T,p,n\boldsymbol{y})$.

Of course, the dependence on n vanishes for large n and $\mu_i = \mu_i(T,p,\boldsymbol{y})$.

Experimental measurement of SES properties of mixtures:

Mixture properties from the partial properties

So, in general (i.e., for small and large systems) we proved

$$S = \sum_{i=1}^{r} n_i\, s_i - \left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{S = \sum_{i=1}^{r} n_i\, s_i}$$

$$V = \sum_{i=1}^{r} n_i\, v_i + \left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{V = \sum_{i=1}^{r} n_i\, v_i}$$

$$\sum_{i=1}^{r} n_i\, \mu_{i,j} = -\left(\frac{\partial Eu}{\partial n_j}\right)_{T,p,\boldsymbol{n}'_j} \quad \xrightarrow{n \text{ large}} \quad \boxed{\sum_{i=1}^{r} n_i\, \mu_{i,j} = 0} \quad \textbf{Duhem-Margules relation}$$

Moreover, recalling the definitions of Eu and partial properties

$$Eu = E - TS + pV - \boldsymbol{\mu} \cdot \boldsymbol{n} = F + pV - \boldsymbol{\mu} \cdot \boldsymbol{n} = G - \boldsymbol{\mu} \cdot \boldsymbol{n} = H - TS - \boldsymbol{\mu} \cdot \boldsymbol{n}$$

$$\mu_i = e_i - Ts_i + pv_i = f_i + pv_i = g_i = h_i - Ts_i$$

we also find the following relations, which justify calling partial properties that way:

$$E = \sum_{i=1}^{r} n_i\, e_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{E = \sum_{i=1}^{r} n_i\, e_i}$$

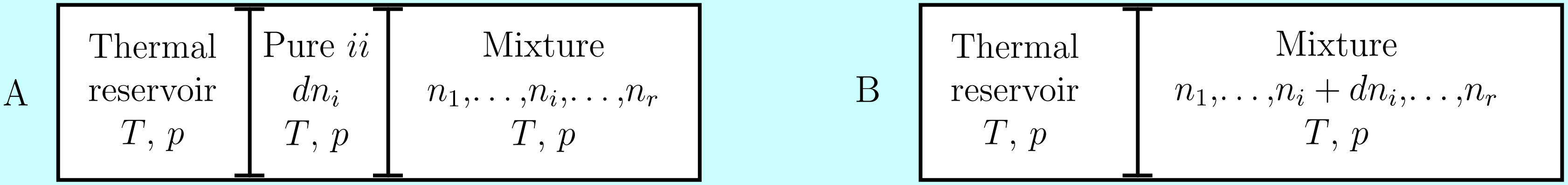
$$F = \sum_{i=1}^{r} n_i\, f_i + Eu - p\left(\frac{\partial Eu}{\partial p}\right)_{T,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{F = \sum_{i=1}^{r} n_i\, f_i}$$

$$G = \sum_{i=1}^{r} n_i\, g_i + Eu = \sum_{i=1}^{r} n_i\, \mu_i + Eu \quad \xrightarrow{n \text{ large}} \quad \boxed{G = \sum_{i=1}^{r} n_i\, g_i = \sum_{i=1}^{r} n_i\, \mu_i}$$

$$H = \sum_{i=1}^{r} n_i\, h_i + Eu - T\left(\frac{\partial Eu}{\partial T}\right)_{p,\boldsymbol{n}} \quad \xrightarrow{n \text{ large}} \quad \boxed{H = \sum_{i=1}^{r} n_i\, h_i}$$

Experimental measurement of SES properties of mixtures:

Partial properties from properties of isothermobaric mixing



Enthalpy of Tp-mixing*

$$\Delta h_i^{\text{mix}} = \frac{H(T,p,n_1,\dots,n_i+dn_i,\dots,n_r) - \left[H(T,p,n_1,\dots,n_i,\dots,n_r) + h_{ii}(T,p)\,dn_i\right]}{dn_i}$$

$$= \lim_{dn_i\to 0}\frac{H_{\text{B}} - H_{\text{A}}}{dn_i} = \left(\frac{\partial H}{\partial n_i}\right)_{T,p,\boldsymbol{n}_i'} - h_{ii}(T,p) = h_i(T,p,n\boldsymbol{y}) - h_{ii}(T,p)$$

Similarly, we define the volume, energy, and entropy of Tp-mixing

$$\Delta v_i^{\text{mix}} = v_i(T,p,n\boldsymbol{y}) - v_{ii}(T,p) \qquad \Delta e_i^{\text{mix}} = e_i(T,p,n\boldsymbol{y}) - e_{ii}(T,p) \qquad \Delta s_i^{\text{mix}} = s_i(T,p,n\boldsymbol{y}) - s_{ii}(T,p)$$

They are all measurable and allow the measurement of partial properties, once the pure-substance properties of the mixture components are known. as a result, we can write

$$\mu_i = h_i - Ts_i = h_{ii} + \Delta h_i^{\text{mix}} - Ts_{ii} - T\Delta s_i^{\text{mix}} = \mu_{ii}(T,p) + \Delta h_i^{\text{mix}} - T\Delta s_i^{\text{mix}} = \mu_{ii}(T,p_{ii})$$

$$\mu_{ii}(T,p_{ii}) - \mu_{ii}(T,p) = \int_p^{p_{ii}} v_{ii}(T,p')\,dp' = \Delta h_i^{\text{mix}} - T\Delta s_i^{\text{mix}} = \begin{cases} RT\ln\dfrac{p_{ii}}{p} & \text{ideal gas} \\ -(p-p_{ii})v_{ii} & \text{ideal liquid or solid} \end{cases}$$

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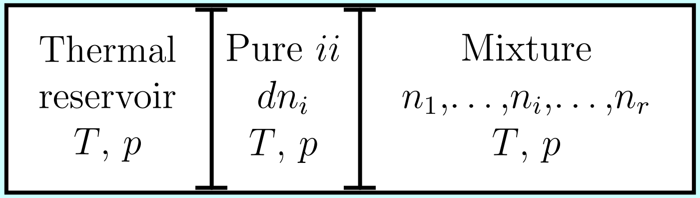
* Recall that the enthalpy is additive for systems in SES at the same pressure.

Experimental measurement of SES properties of mixtures:

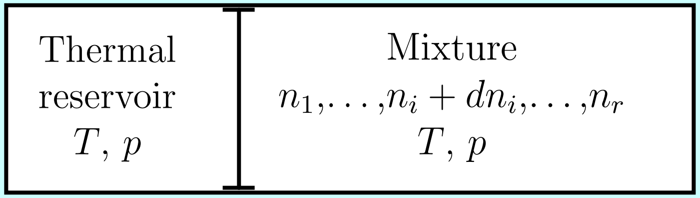
Example: enthalpies of isothermobaric mixing of molten salts

A



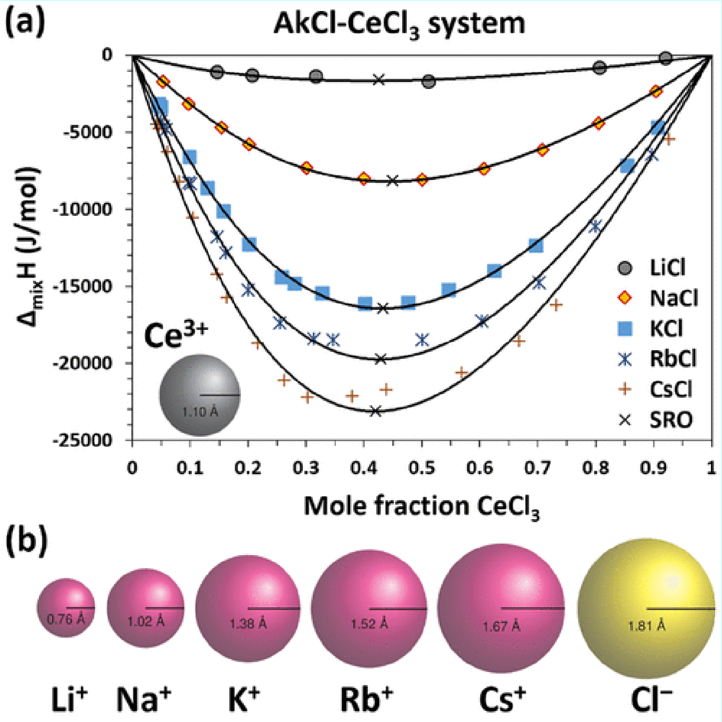
Thermal reservoir T, p | Pure ii dn_i T, p | Mixture $n_1, \ldots, n_i, \ldots, n_r$ T, p

B



Thermal reservoir T, p | Mixture $n_1, \ldots, n_i + dn_i, \ldots, n_r$ T, p

$$\Delta h_i^{\text{mix}} = h_i(T, p, n\boldsymbol{y}) - h_{ii}(T, p)$$



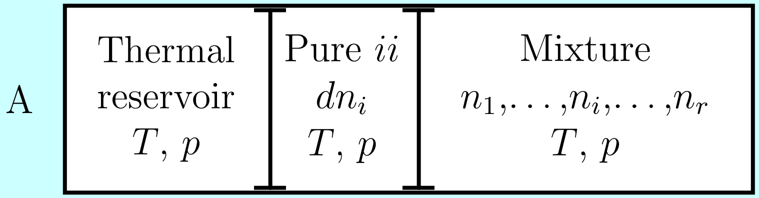
Last decade applications in molten salt systems:

- solvents for metals, particularly for extraction processes
- recycling and reprocessing of rare-earth elements used in electronics and magnets and nuclear fuels
- heat transfer media for solar-thermal systems and in molten salt reactors, which use salts as a coolant for solid fuel or as a solvent for a liquid fuel containing actinides

Fig.1 from: J. Schorne-Pinto, et al., Correlational Approach to Predict the Enthalpy of Mixing for Chloride Melt Systems, *ACS Omega* **2022** *7* (1), 362-371

Experimental measurement of SES properties of mixtures:

Example: volumes of isothermobaric mixing of molten salts

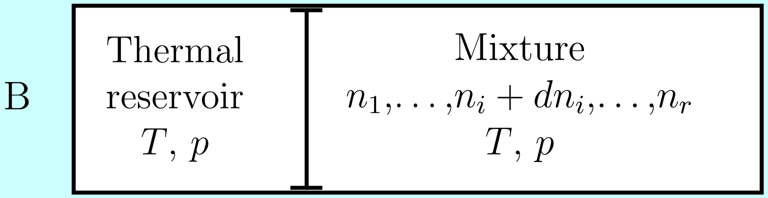


A

Thermal reservoir T, p

Pure ii dn_i T, p

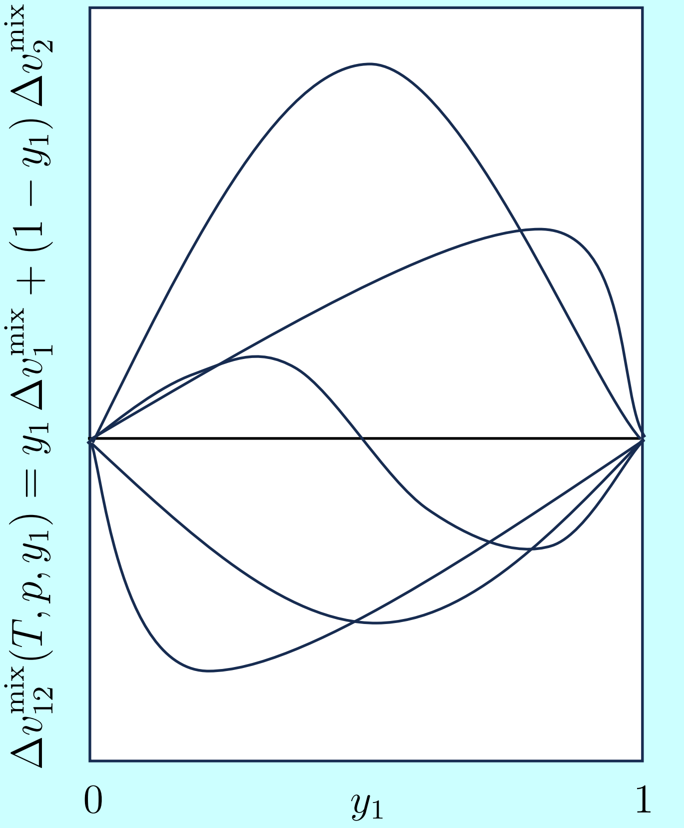
Mixture $n_1,\dots,n_i,\dots,n_r$ T, p



B

Thermal reservoir T, p

Mixture $n_1,\dots,n_i+dn_i,\dots,n_r$ T, p



$$\Delta v_i^{\rm mix} = v_i(T,p,n\boldsymbol{y}) - v_{ii}(T,p)$$

Reviews of experimental data:

Y.P. Handa, G.C. Benson, **Volume changes on mixing two liquids: A review of the experimental techniques and the literature data**, Fluid Phase Equilibria 3, 185 (1979).

R. Battino, **Volume changes on mixing for binary mixtures of liquids,** Chemical Reviews 71, 5 (1971).

Are mixture properties determined by the pure-substance properties of its constituents?

Partial properties in terms of partial pressures and pure-substance properties

As discussed in Section 26.5 of G&B2005, it is noteworthy that the meaning of the term "partial" in the expression "partial pressure" is not the same as in the definition of "partial properties." In fact, the partial pressure p_{ii} is not defined by a partial derivative with respect to amount n_i at constant T, p, and $\boldsymbol{n}_i'$. Nevertheless, partial properties can be expressed in terms of partial pressures and its derivatives as follows.

Recall that, by the definition of partial pressure, $\mu_{ii}(T,p_{ii}) = \mu_i(T,p,\boldsymbol{n}) = \mu_i(T,p,\boldsymbol{y})$ so that $p_{ii} = p_{ii}(T,p,\boldsymbol{y})$. Moreover, for the pure substance, $\mu_{ii}(T,p_{ii}) = g_{ii}(T,p_{ii})$ and $\mathrm{d}g_{ii} = -s_{ii}(T,p_{ii})\,\mathrm{d}T + v_{ii}(T,p_{ii})\,\mathrm{d}p_{ii}$. We find

$$s_i(T,p,\boldsymbol{y}) = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = -\left(\frac{\partial \mu_{ii}}{\partial T}\right)_{p_{ii}} - \left(\frac{\partial \mu_{ii}}{\partial p_{ii}}\right)_T \left(\frac{\partial p_{ii}}{\partial T}\right)_{p,\boldsymbol{n}}$$

$$= s_{ii}(T,p_{ii}) - v_{ii}(T,p_{ii})\,p_{ii,T}(T,p,\boldsymbol{y}) \qquad \text{where we defined} \quad p_{ii,T} = \left(\frac{\partial p_{ii}}{\partial T}\right)_{p,\boldsymbol{y}}$$

$$v_i(T,p,\boldsymbol{y}) = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = \left(\frac{\partial \mu_{ii}}{\partial p_{ii}}\right)_T \left(\frac{\partial p_{ii}}{\partial p}\right)_{T,\boldsymbol{y}}$$

$$= v_{ii}(T,p_{ii})\,p_{ii,p}(T,p,\boldsymbol{y}) \qquad \text{where we defined} \quad p_{ii,p} = \left(\frac{\partial p_{ii}}{\partial p}\right)_{T,\boldsymbol{y}}$$

$$h_i(T,p,\boldsymbol{y}) = \mu_i(T,p,\boldsymbol{n}) + T\,s_i(T,p,\boldsymbol{y}) = h_{ii}(T,p_{ii}) - T\,v_{ii}(T,p_{ii})\,p_{ii,T}(T,p,\boldsymbol{y})$$

$$u_i(T,p,\boldsymbol{y}) = h_i(T,p,\boldsymbol{n}) - p\,v_i(T,p,\boldsymbol{y})$$

$$= u_{ii}(T,p_{ii}) + v_{ii}(T,p_{ii})\Big[p_{ii} - p_{ii,T}(T,p,\boldsymbol{y})\,T - p_{ii,p}(T,p,\boldsymbol{y})\,p\Big]$$

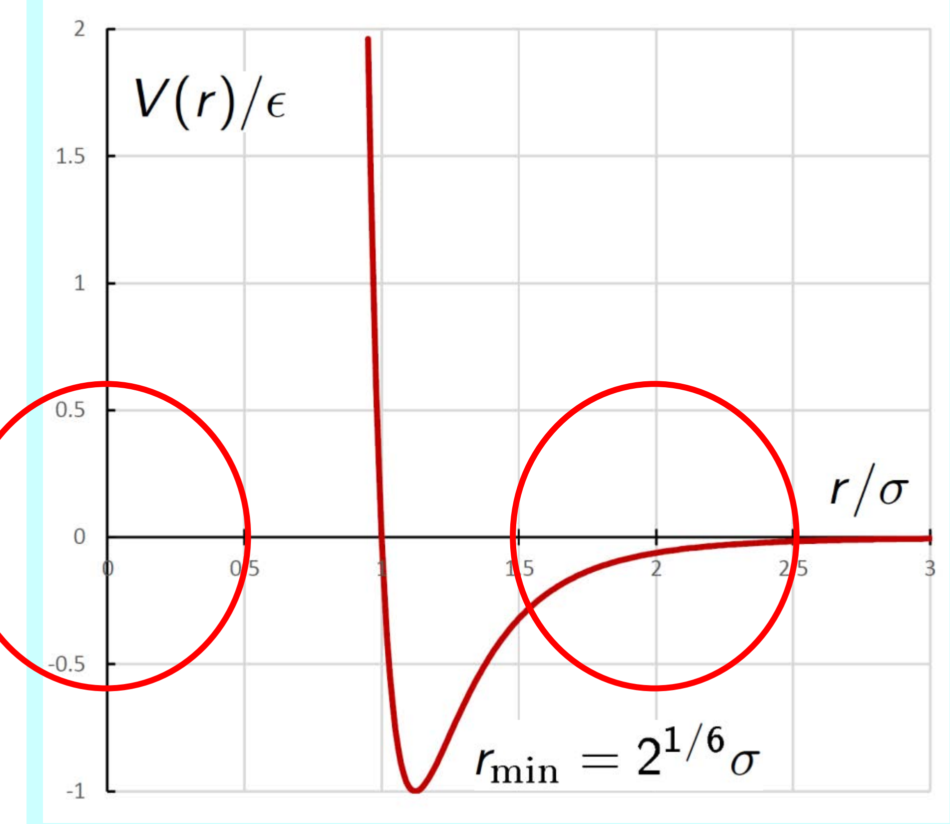
Lennard-Jones potential (model of intermolecular forces)

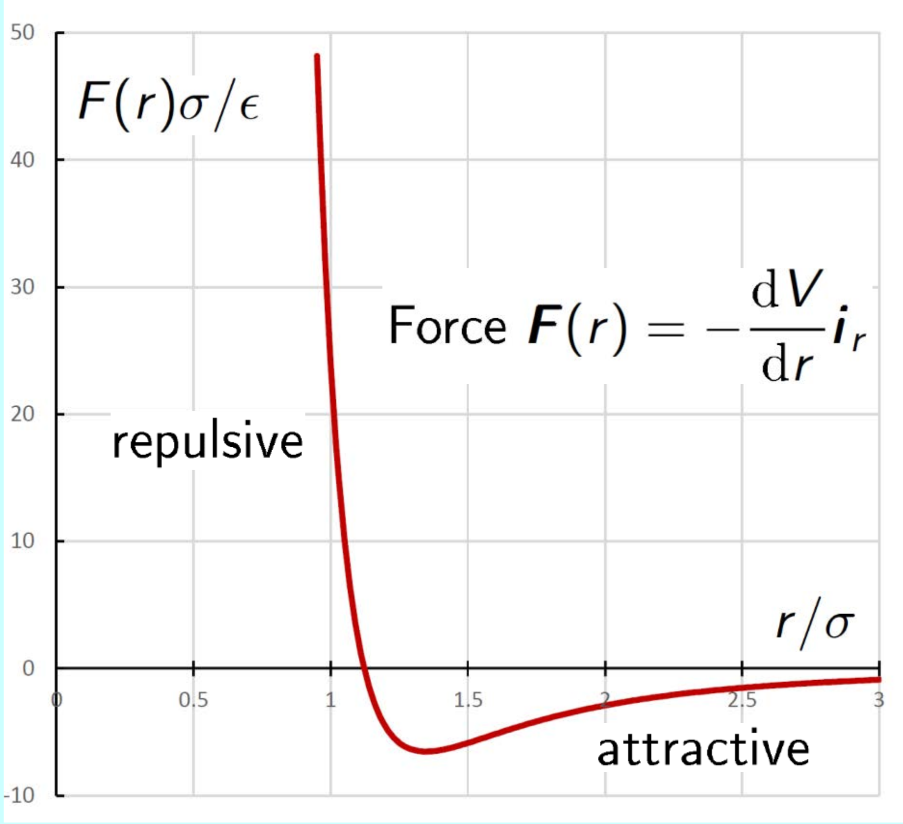
$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$= \epsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]$$

$$F(r) = 24\frac{\epsilon}{\sigma}\left(\frac{\sigma}{r}\right)^{3}\left[2\left(\frac{\sigma}{r}\right)^{6} - 1\right]$$

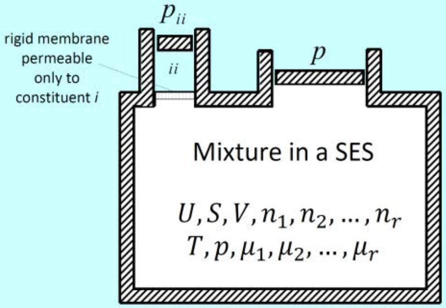
$$= 12\frac{2^{2/3}\epsilon}{r_{\min}}\left(\frac{r_{\min}}{r}\right)^{3}\left[\left(\frac{r_{\min}}{r}\right)^{6} - 1\right]$$





Are mixture properties determined by the pure-substance properties of its constituents?

Ideal Gibbs-Dalton behavior



Ideal Gibbs-Dalton behavior is defined by

Assumption 1: $U = \sum_{i=1}^{r} n_i u_{ii}(T, p_{ii})$

Assumption 2: $S = \sum_{i=1}^{r} n_i s_{ii}(T, p_{ii})$

Assumption 3: $V = n_i v_{ii}(T, p_{ii}) \quad \forall i$

This derivation assumes the simple-system approximation.

Subtract from the Euler relation of the mixture, $U = TS - pV + \sum_{i=1}^{r} \mu_i n_i$, the specific Euler relations of its pure constituents, $u_{ii} = Ts_{ii} - p_{ii}v_{ii} + \mu_{ii}$, evaluated at T and p_{ii}, and each multiplied by the amount n_i of the corresponding constituent in the mixture

$$\left(U - \sum_{i=1}^{r} n_i u_{ii}(T, p_{ii})\right) = T\left(S - \sum_{i=1}^{r} n_i s_{ii}(T, p_{ii})\right) - pV + \sum_{i=1}^{r} n_i p_{ii} v_{ii}(T, p_{ii}) + \sum_{i=1}^{r} (\mu_i - \mu_{ii}) n_i$$

The last summation is zero because at the specified conditions $\mu_i = \mu_i(T, p, \boldsymbol{n}) = \mu_{ii}(T, p_{ii}) = \mu_{ii}$. Now, solve for p (we may call this Dalton's theorem) to obtain a relation between the pressure of the mixture and the partial pressures of its components

$$p = \frac{1}{V} \sum_{i=1}^{r} n_i p_{ii} v_{ii}(T, p_{ii}) - \frac{1}{V}\left(U - \sum_{i=1}^{r} n_i u_{ii}(T, p_{ii})\right) + \frac{T}{V}\left(S - \sum_{i=1}^{r} n_i s_{ii}(T, p_{ii})\right)$$

Using the three assumptions that define ideal Gibbs-Dalton behavior, we obtain Dalton's law of partial pressures, $p = \sum_{i=1}^{r} p_{ii}$ (which clearly holds only in that very special limit).

Are mixture properties determined by the pure-substance properties of its constituents?

Ideal Gibbs-Dalton behavior

Ideal Gibbs-Dalton behavior is defined by

Assumption 1: $U = \sum_{i=1}^r n_i u_i(T,p,\boldsymbol{y}) = \sum_{i=1}^r n_i u_{ii}(T,p_{ii})$

Assumption 2: $S = \sum_{i=1}^r n_i s_i(T,p,\boldsymbol{y}) = \sum_{i=1}^r n_i s_{ii}(T,p_{ii})$

Assumption 3: $V = \sum_{i=1}^r n_i v_i(T,p,\boldsymbol{y}) = n_i v_{ii}(T,p_{ii})\ \forall i$ (no sum!)

here the first equalities recall the relations in terms of partial properties.
The assumptions can be interpreted like this:

$$\boxed{\begin{array}{c}\text{Mixture}\\ n_1,\dots,n_i,\dots,n_r\\ T,\ p\\ U,\ S\\ V\end{array}} = \boxed{\begin{array}{c}\text{Pure } n_1\\ T,\ p_{11}\\ u_{11}(T,p_{11})\\ s_{11}(T,p_{11})\\ V\end{array}} + \cdots + \boxed{\begin{array}{c}\text{Pure } n_i\\ T,\ p_{ii}\\ u_{ii}(T,p_{ii})\\ s_{ii}(T,p_{ii})\\ V\end{array}} + \cdots + \boxed{\begin{array}{c}\text{Pure } n_r\\ T,\ p_{rr}\\ u_{rr}(T,p_{rr})\\ s_{rr}(T,p_{rr})\\ V\end{array}}$$

Ideal Gibbs-Dalton mixture of ideal gases

$\forall i$ we have $v_{ii}(T,p_{ii}) = \dfrac{RT}{p_{ii}}$ $\qquad v_{ii}(T,p) = \dfrac{RT}{p}$ $\qquad V = n_i v_{ii}(T,p_{ii}) = n_i \dfrac{RT}{p_{ii}}$

$$p_{ii} = n_i \frac{RT}{V} \qquad p = \sum_i p_{ii} = \sum_i n_i \frac{RT}{V} = n\frac{RT}{V} \qquad \frac{p_{ii}}{p} = \frac{n_i}{n} = y_i \quad \Rightarrow \quad \boxed{p_{ii} = y_i p}$$

$$\mu_i(T,p,\boldsymbol{y}) = \mu_{ii}(T,p_{ii}) = \mu_{ii}(T,p) + \int_p^{p_{ii}} \left(\frac{\partial \mu_{ii}}{\partial p}\right)_T dp' = \mu_{ii}(T,p) + \int_p^{p_{ii}} v_{ii}(T,p')\,dp'$$

$$= \mu_{ii}(T,p) + \int_p^{p_{ii}} \frac{RT}{p'}\,dp' = \mu_{ii}(T,p) + RT\ln\frac{p_{ii}}{p} = \boxed{\mu_{ii}(T,p) + RT\ln y_i}$$

Are mixture properties determined by the pure-substance properties of its constituents?

Ideal Gibbs-Dalton mixtures of ideal gases

$$\forall i \text{ we have } v_{ii}(T,p_{ii}) = \frac{RT}{p_{ii}} \qquad v_{ii}(T,p) = \frac{RT}{p} \qquad V = n_i v_{ii}(T,p_{ii}) = n_i\frac{RT}{p_{ii}}$$

$$p_{ii} = n_i\frac{RT}{V} \qquad p = \sum_i p_{ii} = \sum_i n_i \frac{RT}{V} = n\frac{RT}{V} \qquad \frac{p_{ii}}{p} = \frac{n_i}{n} = y_i \quad \Rightarrow \quad p_{ii} = y_i p$$

$$\mu_i(T,p,\boldsymbol{y}) = \mu_{ii}(T,p_{ii}) = \mu_{ii}(T,p) + \int_p^{p_{ii}} \left(\frac{\partial \mu_{ii}}{\partial p}\right)_T dp' = \mu_{ii}(T,p) + \int_p^{p_{ii}} v_{ii}(T,p')\,dp'$$

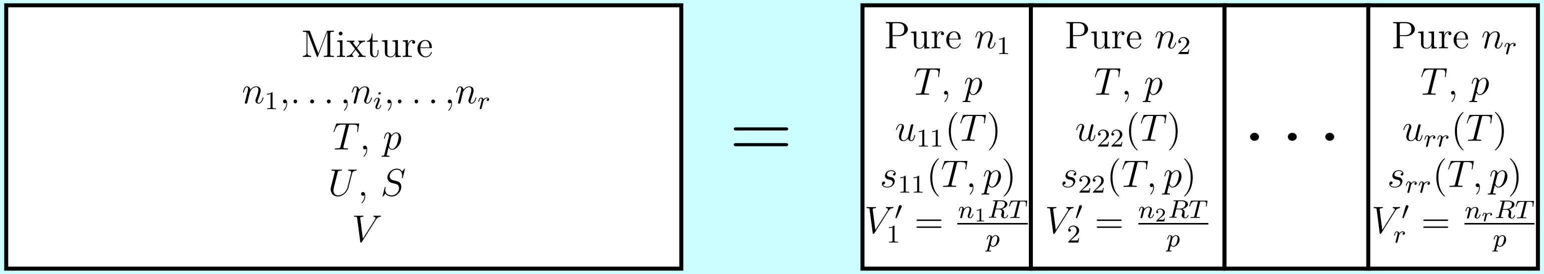
$$= \mu_{ii}(T,p) + \int_p^{p_{ii}} \frac{RT}{p'}\,dp' = \mu_{ii}(T,p) + RT\ln\frac{p_{ii}}{p} = \mu_{ii}(T,p) + RT\ln y_i$$

$$s_i(T,p,\boldsymbol{y}) = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\boldsymbol{n}} = s_{ii}(T,p) - R\ln y_i = s_{ii}(T,p_{ii}) \qquad v_i(T,p,\boldsymbol{y}) = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\boldsymbol{n}} = v_{ii}(T,p) = \frac{RT}{p}$$

$$h_i(T,p,\boldsymbol{y}) = \left(\frac{\partial(\mu_i/T)}{\partial(1/T)}\right)_{p,\boldsymbol{n}} = h_{ii}(T) \qquad u_i(T,p,\boldsymbol{y}) = T\,s_i - p\,v_i + \mu_i = u_{ii}(T)$$

Note also that $V = \sum_{i=1}^{r} V_i' = \sum_{i=1}^{r} n_i v_{ii}(T,p)$ (Amagat law of additive volumes)

where $V_i' = n_i v_{ii}(T,p)$ is called proper volume of i



Mixture
$n_1,\ldots,n_i,\ldots,n_r$
$T,\ p$
$U,\ S$
V

$=$

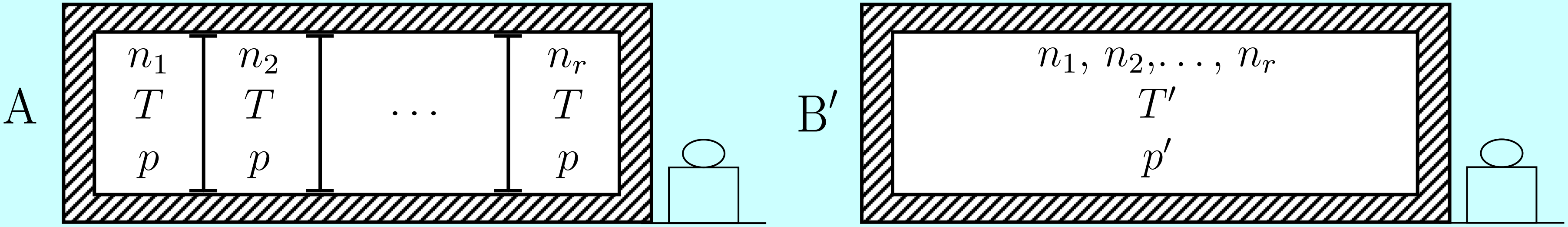
Pure n_1
$T,\ p$
$u_{11}(T)$
$s_{11}(T,p)$
$V_1' = \frac{n_1 RT}{p}$

Pure n_2
$T,\ p$
$u_{22}(T)$
$s_{22}(T,p)$
$V_2' = \frac{n_2 RT}{p}$

$\cdots$

Pure n_r
$T,\ p$
$u_{rr}(T)$
$s_{rr}(T,p)$
$V_r' = \frac{n_r RT}{p}$

Entropy of spontaneous mixing



Remove partitions allowing spontaneous mixing. Using energy, volume, and entropy additivity for A, and ideal G-D-mixture model for B′,

$$U_{\rm A}=\sum_i n_i u_{ii}(T) \qquad V_{\rm A}=\sum_i n_i v_{ii}(T,p)=\frac{nRT}{p} \qquad S_{\rm A}=\sum_i n_i s_{ii}(T,p)$$

$$U_{\rm B'}=\sum_i n_i u_{ii}(T') \qquad V_{\rm B'}=\sum_i n_i v_{ii}(T',p')=\frac{nRT'}{p'} \qquad S_{\rm B'}=\sum_i n_i s_{ii}(T',p'_{ii})$$

Energy balance for the isolated system, $U_{\rm B'}-U_{\rm A}=0$, recalling $du_{ii}=c_{v,ii}(T)\,dT$,

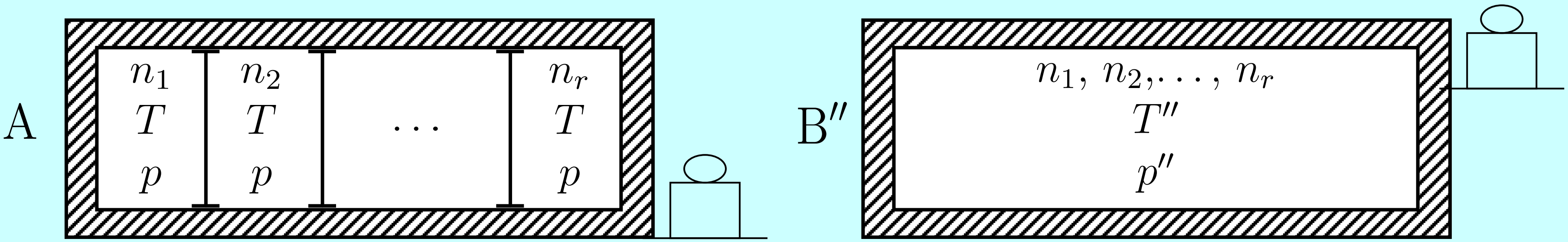
$$U_{\rm B'}-U_{\rm A}=\sum_i n_i[u_{ii}(T')-u_{ii}(T)]=\sum_i n_i\int_T^{T'} c_{v,ii}(\theta)\,d\theta=0$$

Since $c_{v,ii}(T)>0$ for any T, the integral can only be zero if $T'=T$. Therefore, the volume balance $V_{\rm B'}=V_{\rm A}$ yields $p'=p$.

Entropy balance for the isolated system, $S_{\rm B'}-S_{\rm A}=S_{\rm irr}$, recalling $ds_{ii}=c_{p,ii}(T)\,dT/T-R\,dp/p$, so that $s_{ii}(T',p'_{ii})=s_{ii}(T',p')-R\ln y_i$, yields (for $T'=T$ and $p'=p$)

$$S_{\rm irr}=S_{\rm B'}-S_{\rm A}=\sum_i n_i[s_{ii}(T',p'_{ii})-s_{ii}(T,p)]=\sum_i n_i\Delta s_i^{\rm mix}=\sum_i n_i[-R\ln y_i]=-nR\sum_i y_i\ln y_i\ge 0$$

Extracting the adiabatic availability of mixing



Do the mixing with a reversible weight process. Using energy, volume, and entropy additivity for A, and ideal G-D-mixture model for B$''$,

$$U_{\rm A} = \sum_i n_i u_{ii}(T) \qquad V_{\rm A} = \sum_i n_i v_{ii}(T,p) = \frac{nRT}{p} \qquad S_{\rm A} = \sum_i n_i s_{ii}(T,p)$$

$$U_{\rm B''} = \sum_i n_i u_{ii}(T'') \qquad V_{\rm B''} = \sum_i n_i v_{ii}(T'',p'') = \frac{nRT''}{p''} \qquad S_{\rm B''} = \sum_i n_i s_{ii}(T'',p''_{ii})$$

The volume balance $V_{\rm B''} = V_{\rm A}$ imposes $p''/T'' = p/T$. Thus, recalling $p''_{ii} = y_i\, p''$, assuming constant specific heats, defining $c_{v,mix} = \sum_i y_i\, c_{v,ii}$, and using

$$s_{ii}\left(T'', p''_{ii} = y_i \frac{T''}{T} p\right) - s_{ii}(T,p) = c_{p,ii} \ln \frac{T''}{T} - R \ln \left(y_i \frac{T''}{T} \right) = c_{v,ii} \ln \frac{T''}{T} - R \ln y_i$$

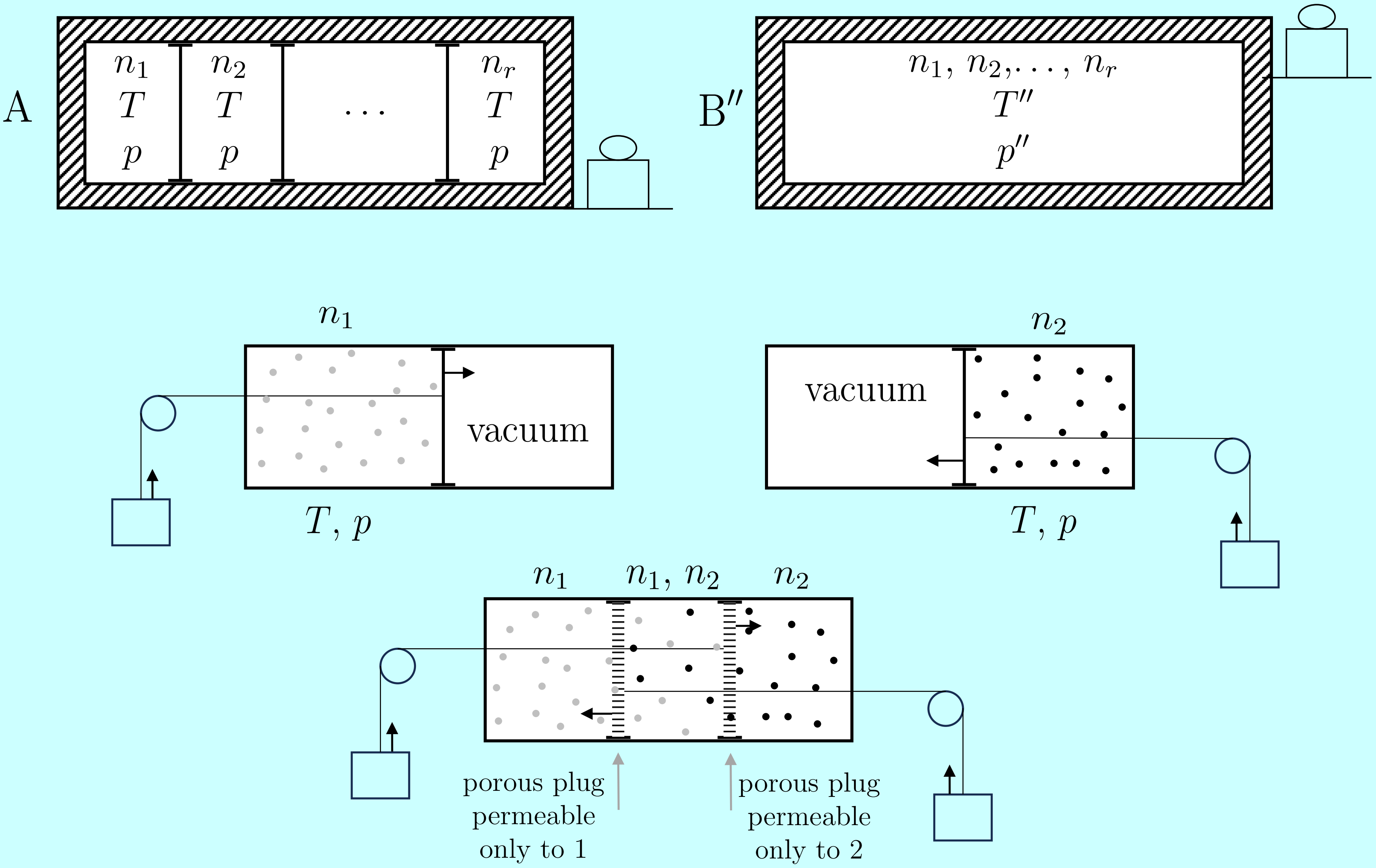
the entropy balance for the reversible weight process, $S_{\rm B''} - S_{\rm A} = 0$, becomes

$$0 = S_{\rm B''} - S_{\rm A} = \sum_i n_i [s_{ii}(T'',p''_{ii}) - s_{ii}(T,p)] = \sum_i n_i [c_{v,ii} \ln \frac{T''}{T} - R \ln y_i] = n [c_{v,mix} \ln \frac{T''}{T} - R \sum_i y_i \ln y_i]$$

and yields $T'' = T \exp\left(\frac{R}{c_{v,mix}} \sum_i y_i \ln y_i\right)$ (clearly $T'' < T$). Therefore, the energy balance for the weight process, $U_{\rm B''} - U_{\rm A} = -W^{\rightarrow}_{\rm rev}$, yields

$$W^{\rightarrow}_{\rm rev} = U_{\rm A} - U_{\rm B''} = \sum_i n_i [u_{ii}(T'') - u_{ii}(T)] = n\, c_{v,mix} (T - T'') = \boxed{n\, c_{v,mix} T \left[1 - \exp\left(\frac{R}{c_{v,mix}} \sum_i y_i \ln y_i \right) \right]}$$

Extracting the adiabatic availability of mixing



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Slide 6:

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Spring 2024