2.43 ADVANCED THERMODYNAMICS

Spring Term 2024
LECTURE 13

Room 3-442
Tuesday, March 19, 2:30pm - 4:30pm

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Room 3-351d

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

Partial properties

Gibbs-Dalton ideal mixtures

Mixing and separation

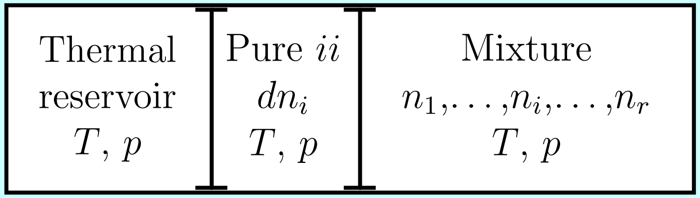
Osmotic pressure and blue energy

Stratification

Experimental measurement of SES properties of mixtures:

Partial properties from properties of isothermobaric mixing

A

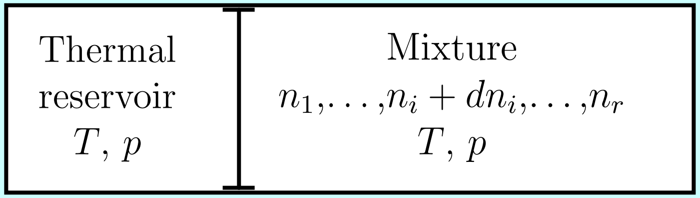


Thermal reservoir T, p

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

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

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

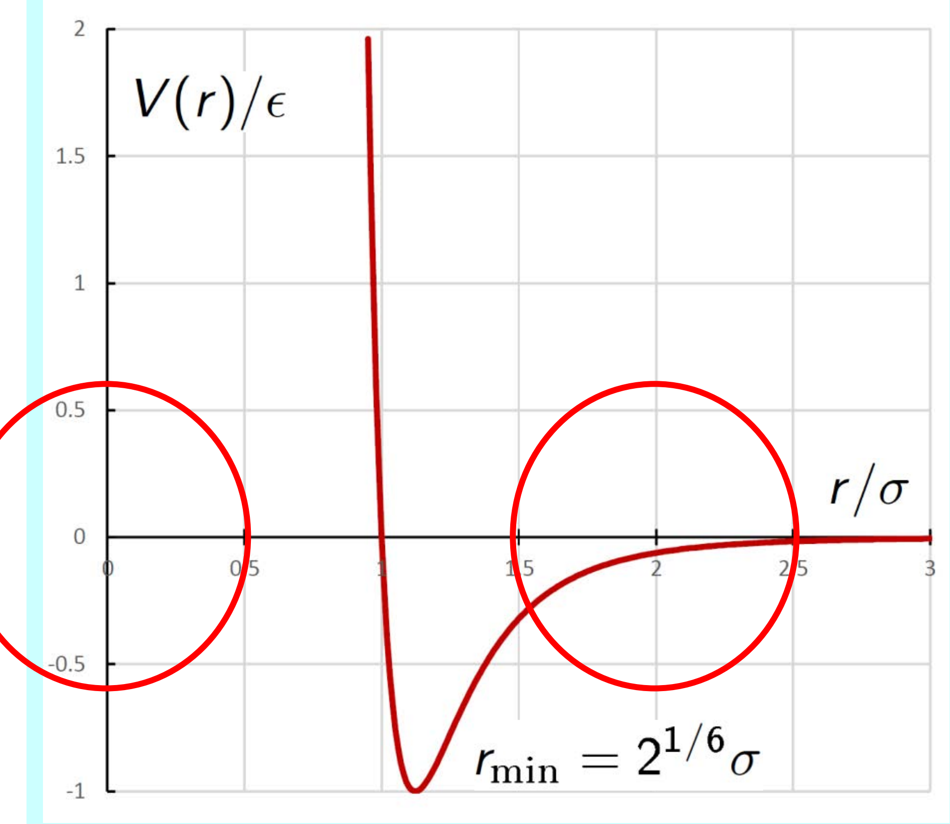
$$\mu_{ii}(T,p_{ii}) - \mu_{ii}(T,p) = \int_p^{p_{ii}} v_{ii}(T,p')\,dp' = \Delta h_i^{\text{mix}} - T\Delta s_i^{\text{mix}} = \begin{cases} RT\ln\dfrac{p_{ii}}{p} & \text{ideal gas} \\ -(p-p_{ii})v_{ii} & \text{ideal liquid or solid} \end{cases}$$

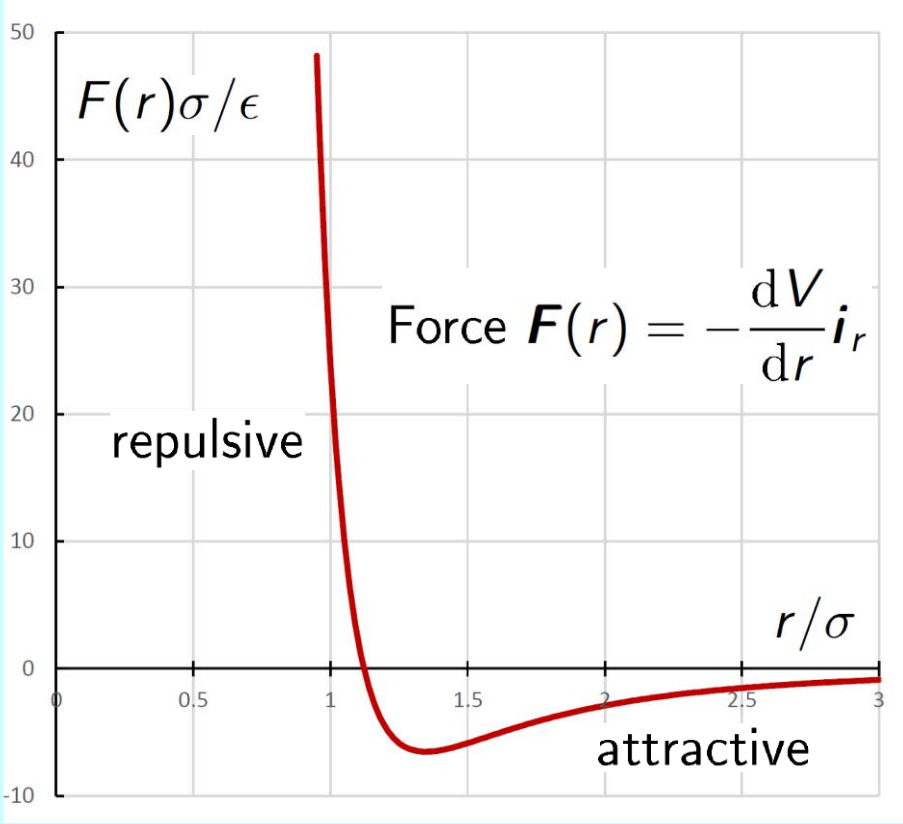
* Recall that the enthalpy is additive for systems in SES at the same pressure.

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

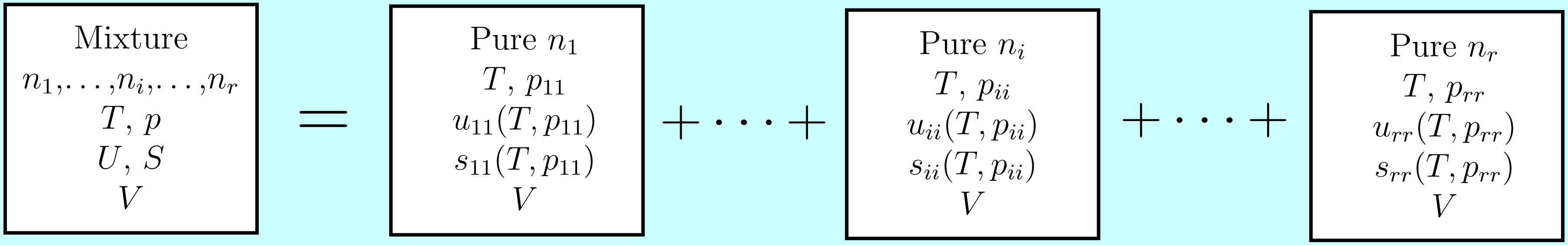
Assumption 1: $U = \sum_{i=1}^r n_i u_i(T,p,\boldsymbol{y}) = \sum_{i=1}^r n_i u_{ii}(T,p_{ii})$

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:



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

Ideal Gibbs-Dalton mixture of ideal gases

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

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

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

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

Ideal Gibbs-Dalton mixtures of ideal gases

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

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

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

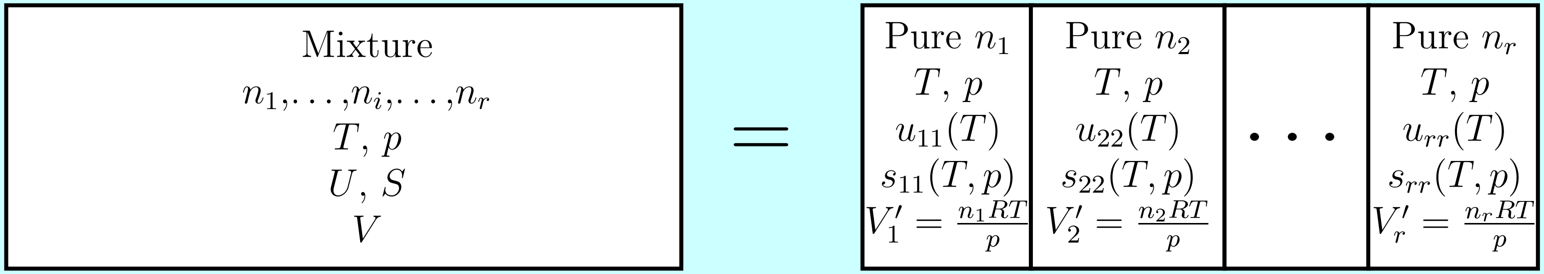
$$= \mu_{ii}(T,p) + \int_p^{p_{ii}} \frac{RT}{p'}\,dp' = \mu_{ii}(T,p) + RT\ln\frac{p_{ii}}{p} = \mu_{ii}(T,p) + RT\ln y_i$$

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

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

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

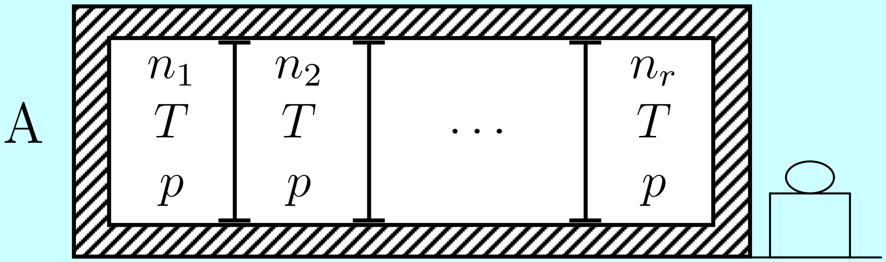
Pure n_2
$T,\ p$
$u_{22}(T)$
$s_{22}(T,p)$
$V_2' = \frac{n_2 RT}{p}$

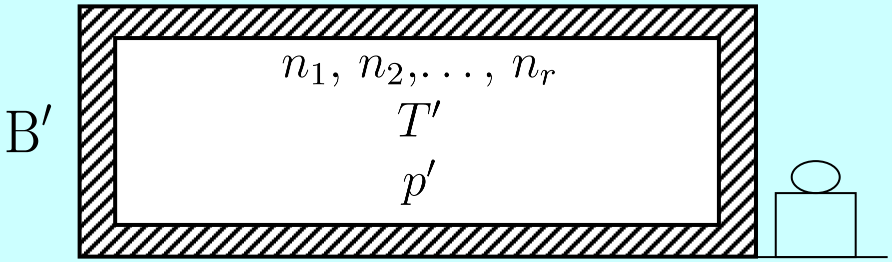
$\cdots$

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

Isothermobaric mixing of ideal gases

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 $du_{ii} = c_{v,ii}(T)\,dT$,

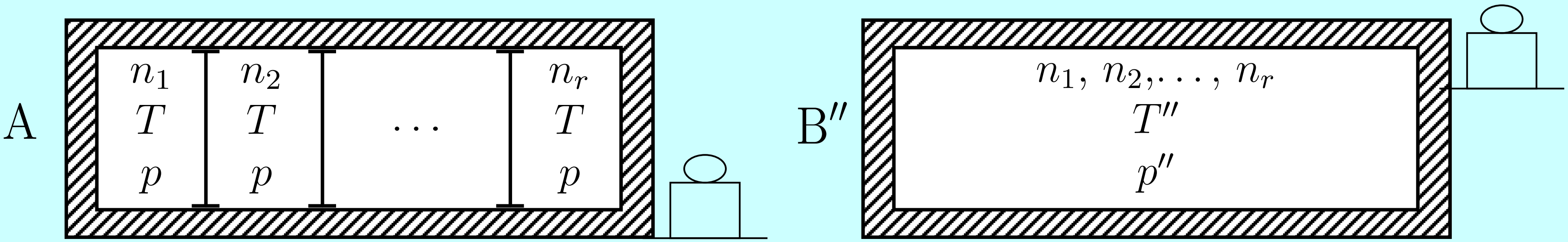
$$U_{\rm B'} - U_{\rm A} = \sum_i n_i [u_{ii}(T') - u_{ii}(T)] = \sum_i n_i \int_T^{T'} c_{v,ii}(\theta)\,d\theta = 0$$

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

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

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

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

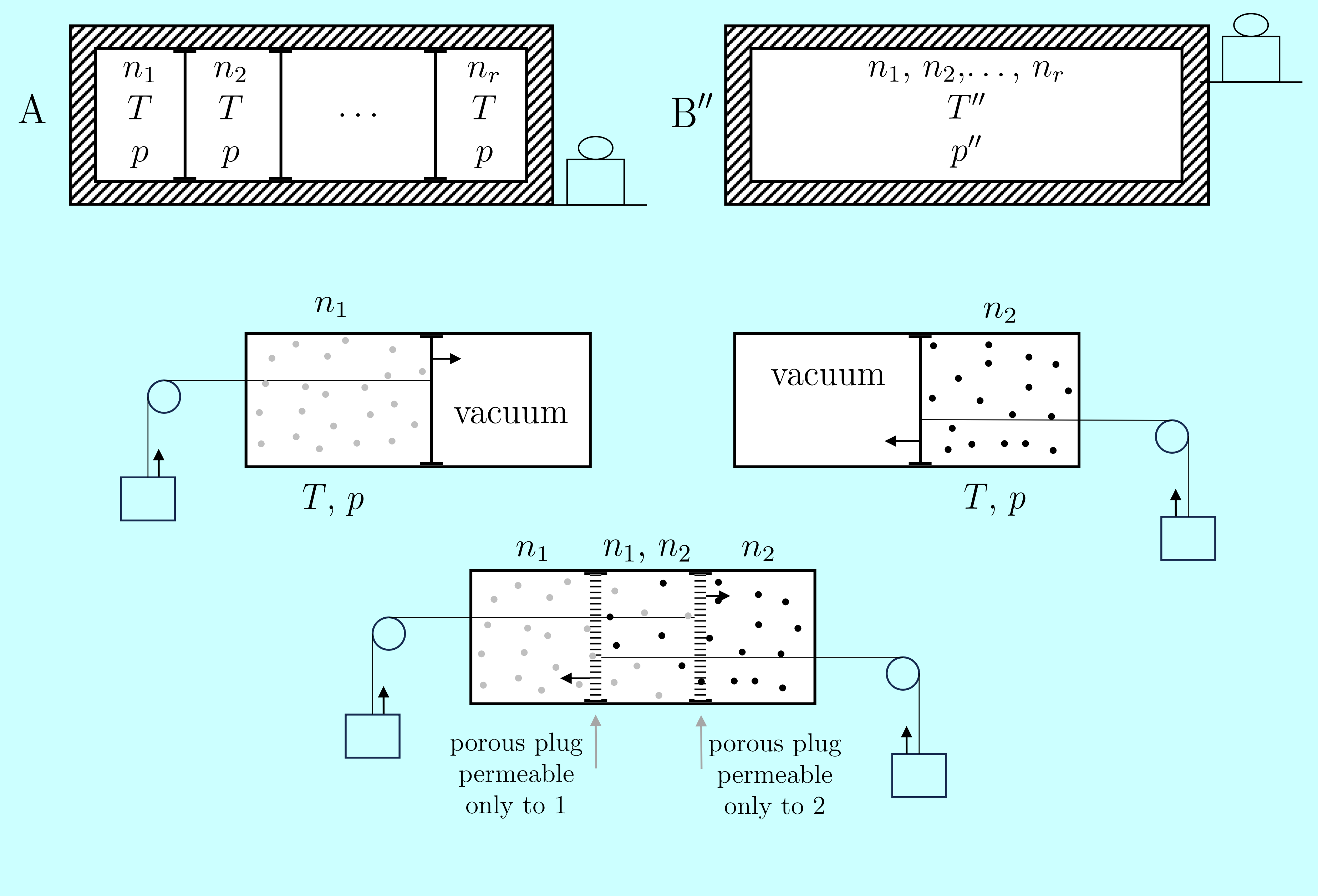
the entropy balance for the reversible weight process, $S_{\rm B''} - S_{\rm A} = 0$, becomes

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

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

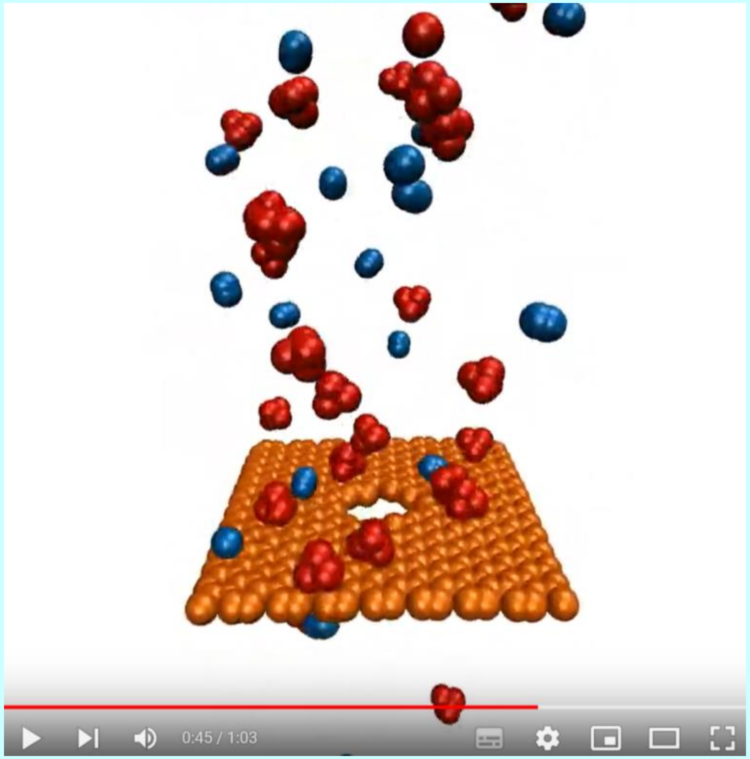
$$W^{\rightarrow}_{\rm rev} = U_{\rm A} - U_{\rm B''} = \sum_i n_i [u_{ii}(T'') - u_{ii}(T)] = n\, c_{v,mix}(T - T'') = \boxed{n\, c_{v,mix} T \left[1 - \exp\left(\frac{R}{c_{v,mix}} \sum_i y_i \ln y_i\right)\right]}$$

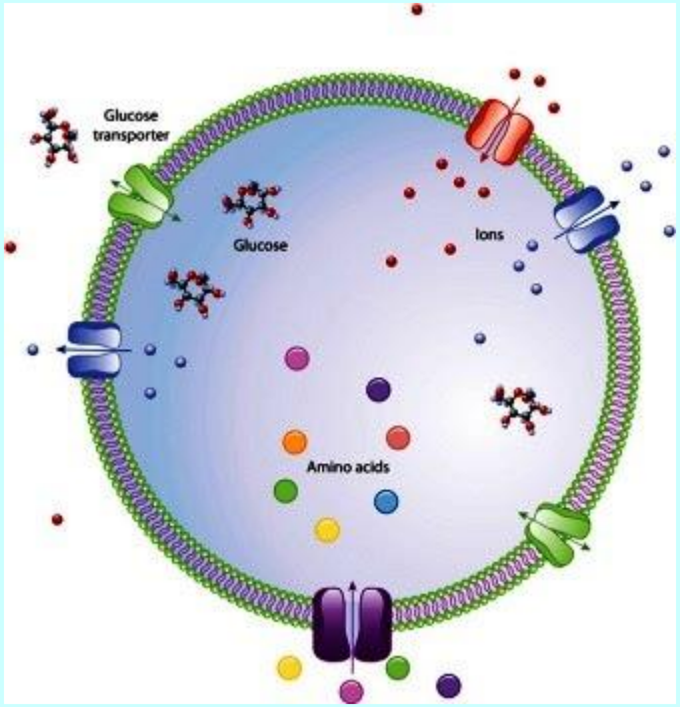
Extracting the adiabatic availability of mixing



Semipermeable (passive transport) vs selective (active transport)

Membranes





https://www.youtube.com/watch?v=hxFj8qgejek

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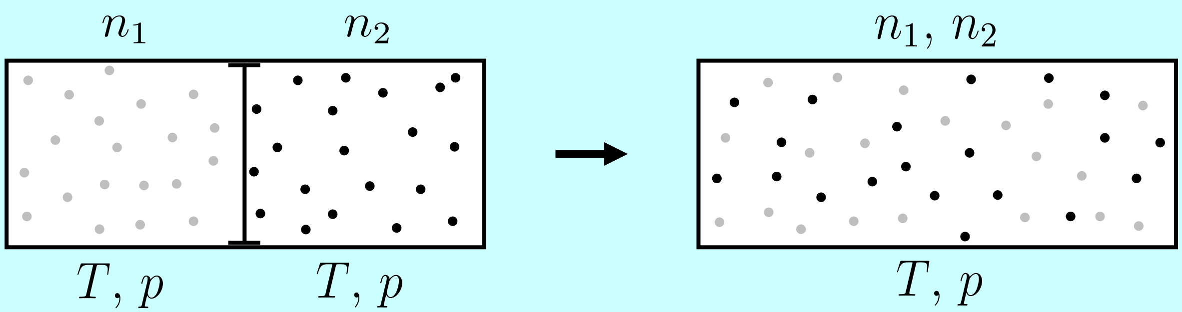
Entropy of spontaneous mixing (**Gibbs paradox** resolved)

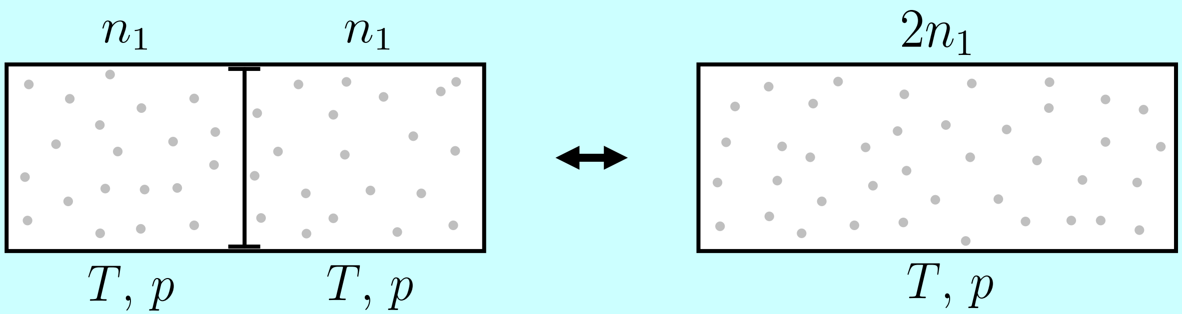


$$y_1 = \frac{n_1}{n} \qquad y_2 = 1 - y_1 = \frac{n_2}{n} \qquad n = n_1 + n_2$$

$$S_{\text{irr}} = -nR \sum_i y_i \ln y_i = -nR[y_1 \ln y_1 + (1-y_1)\ln(1-y_1)] \geq 0$$

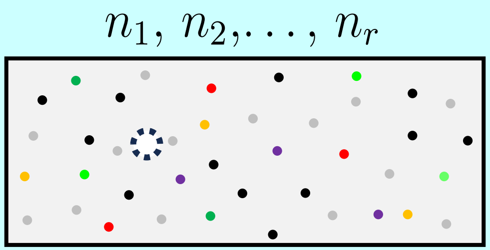
For example, for $n_1 = n_2 = n/2$, $y_1 = y_2 = 1/2$, $S_{\text{irr}} = nR\ln 2$.

However, if particles 1 and 2 are identical, removing (and adding) partitions, within the simple system model, changes no SES property. So, in this case $S_{\text{irr}} = 0$.



Information theory interpretation:

Shannon information entropy



	probability	surpise	normalized
	p	**-ln(p)**	**-ln(p)/-ln(0.5)**
	1	0.0	0
N2	0.79	0.2	0.3
50%	0.5	0.7	1
O2	0.21	1.6	2
Ar	0.009	4.7	7
CO2	0.0005	7.6	11

Suppose we have r possible types of particles, with molecular masses $M_1, \ldots, M_r$.

The probability to observe a particle of type i is $p_i = \dfrac{n_i}{n} = y_i$. Note: $p_i \geq 0$ and $\sum_{i=1}^r p_i = 1$

The mean or expected value of the mass is $\langle M \rangle = \sum_{i=1}^r p_i M_i$.

The degree of uncertainty, about which M_i will be observed next, is measured by the

Shannon information entropy $$S_I = -\sum_{i=1}^{r} p_i \ln p_i$$

Example. Suppose we do not know the y_i's, but we have measured $\langle M \rangle$.

What is the **least biased assignment of y_i's** compatible with the measured $\langle M \rangle$?

Maximize $-\sum_{i=1}^r p_i \ln p_i$ subject to the constraints $\sum_{i=1}^r p_i = 1$ and $\sum_{i=1}^r p_i M_i = \langle M \rangle$.

With the method of Lagrange multipliers obtain $p_i = \dfrac{\exp(-\lambda_M M_i)}{\sum_i \exp(-\lambda_M M_i)}$.

Inserting these in the constraint, $\sum_{i=1}^r M_i \exp(-\lambda_M M_i)/Z = \langle M \rangle$, yields $\lambda_M = \lambda_M(\langle M \rangle)$.

Classic reference: E.T. Jaynes, **Information theory and statistical mechanics**, Physical Review 106, 620 (1957).

Quantum model of a structureless particle in a box:

Ideal gas equation of state for a single particle in a box

For a system consisting of a single particle ($n = 1\,\text{molecule} = 1/N_{\text{Av}}$ mol) of mass m with no internal structure and only translational degrees of freedom, confined in a parallelepiped-shaped container with sides ℓ_1, ℓ_2, ℓ_3 (and volume $V = \ell_1\ell_2\ell_3$), the quantized energy levels are

$$\epsilon_{j_1,j_2,j_3} = \epsilon_{j_1} + \epsilon_{j_2} + \epsilon_{j_3} = \frac{h^2}{8m}\left(\frac{j_1^2}{\ell_1^2} + \frac{j_2^2}{\ell_2^2} + \frac{j_3^2}{\ell_3^2}\right) \quad \text{where } j_1, j_2, j_3 = 1, 2, 3\ldots, \infty$$

The maximum entropy principle implies that the SES probability distribution $\{p_{j_1,j_2,j_3}\}$ is given by the solution of the constrained maximization problem

$$\max_{\{p_{j_1,j_2,j_3}\}} S = -nR\sum_{\boldsymbol{j}} p_{j_1,j_2,j_3}\ln p_{j_1,j_2,j_3} \quad \text{subject to} \quad \sum_{\boldsymbol{j}} p_{j_1,j_2,j_3} = 1 \quad \text{and} \quad \sum_{\boldsymbol{j}} p_{j_1,j_2,j_3}\epsilon_{j_1,j_2,j_3} = E$$

where $\sum_{\boldsymbol{j}} = \sum_{j_1=1}^{\infty}\sum_{j_2=1}^{\infty}\sum_{j_3=1}^{\infty}$. Assigning the Lagrange multiplier $1/k_{\text{B}}T$ to the energy constraint, and noting that $nR = R/N_{\text{Av}} = k_{\text{B}}$ (the Boltzmann constant), we find the SES distribution

$$p_{j_1,j_2,j_3} = \frac{\exp(-\epsilon_{j_1,j_2,j_3}/k_{\text{B}}T)}{\mathcal{Q}} = p_{j_1}p_{j_2}p_{j_2} = \frac{\exp(-\epsilon_{j_1}/k_{\text{B}}T)}{\mathcal{Q}_1}\frac{\exp(-\epsilon_{j_2}/k_{\text{B}}T)}{\mathcal{Q}_2}\frac{\exp(-\epsilon_{j_3}/k_{\text{B}}T)}{\mathcal{Q}_3}$$

where we define the partition functions $\mathcal{Q} = \mathcal{Q}_1\mathcal{Q}_2\mathcal{Q}_3$, $\mathcal{Q}_i = \sum_{j_i=1}^{\infty}\exp(-\epsilon_{j_i}/k_{\text{B}}T)$. It easy to verify that the probabilities and all the properties can be obtained from derivatives of the $\mathcal{Q}_i$'s and that $T = \left(\partial E/\partial S\right)_{\ell_1,\ell_2,\ell_3}$, i.e., the Lagrange multiplier indeed represents the temperature

$$E = k_{\text{B}}T^2\left(\frac{\partial\ln\mathcal{Q}}{\partial T}\right)_{\boldsymbol{\ell}} = E_1 + E_2 + E_3 \qquad E_i = \sum_{j_i} p_{j_i}\epsilon_{j_i} = k_{\text{B}}T^2\left(\frac{\partial\ln\mathcal{Q}_i}{\partial T}\right)_{\ell_i} \qquad p_{j_i} = -k_{\text{B}}T\left(\frac{\partial\ln\mathcal{Q}_i}{\partial\epsilon_{j_i}}\right)_T$$

$$S = k_{\text{B}}\left(\frac{\partial T\ln\mathcal{Q}}{\partial T}\right)_{\boldsymbol{\ell}} = S_1 + S_2 + S_3 \qquad S_i = -k_{\text{B}}\sum_{j_i} p_{j_i}\ln p_{j_i} = k_{\text{B}}\left(\frac{\partial T\ln\mathcal{Q}_i}{\partial T}\right)_{\ell_i} = \frac{E_i}{T} + k_{\text{B}}\ln\mathcal{Q}_i$$

Quantum models of particles:

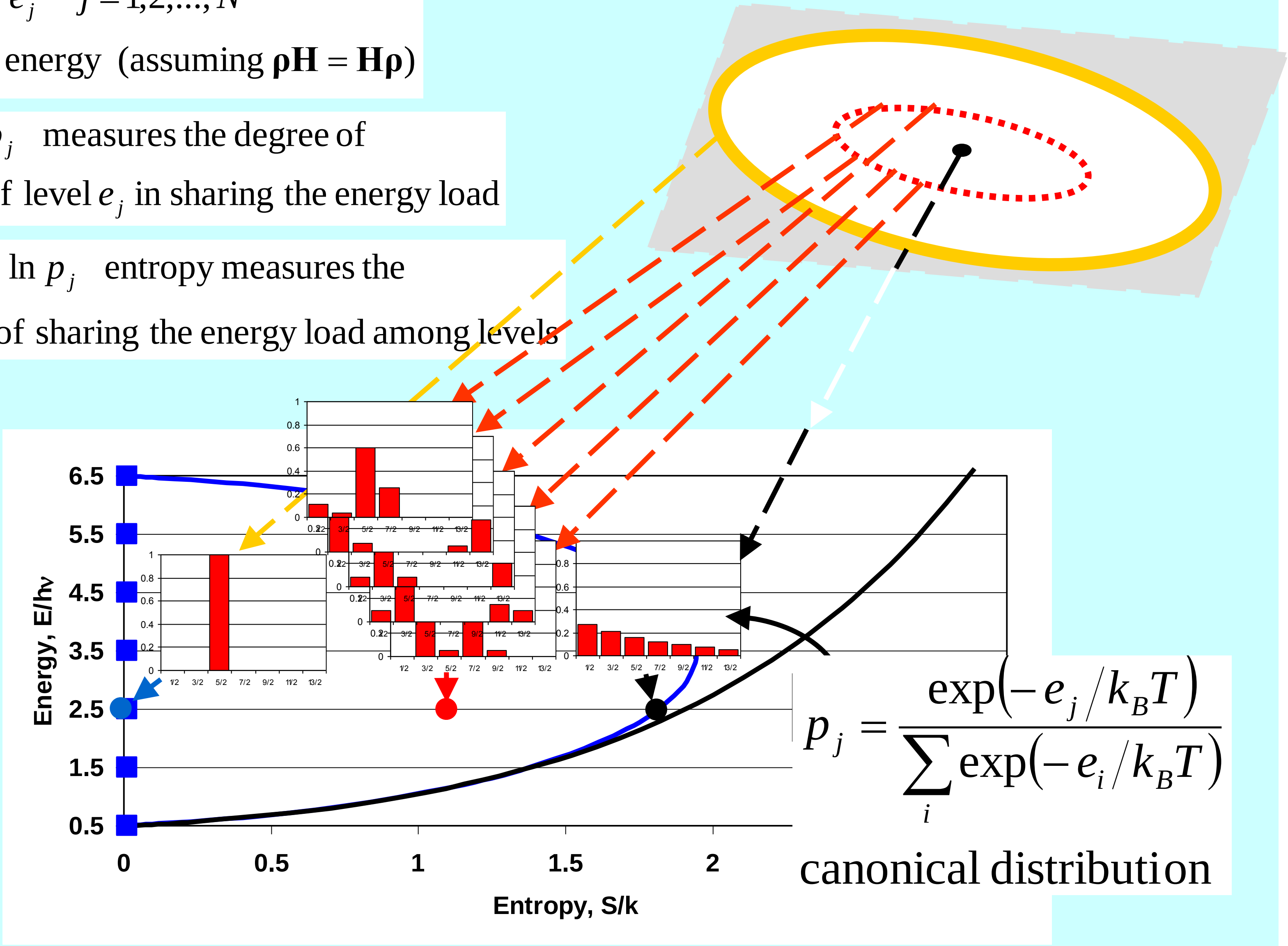
Upper bounded vs unbounded energy spectrum

energy levels $e_j \quad j = 1, 2, \ldots, N$

$E = \sum_j p_j e_j$ energy (assuming $\boldsymbol{\rho}\mathbf{H} = \mathbf{H}\boldsymbol{\rho}$)

probability p_j measures the degree of involvement of level e_j in sharing the energy load

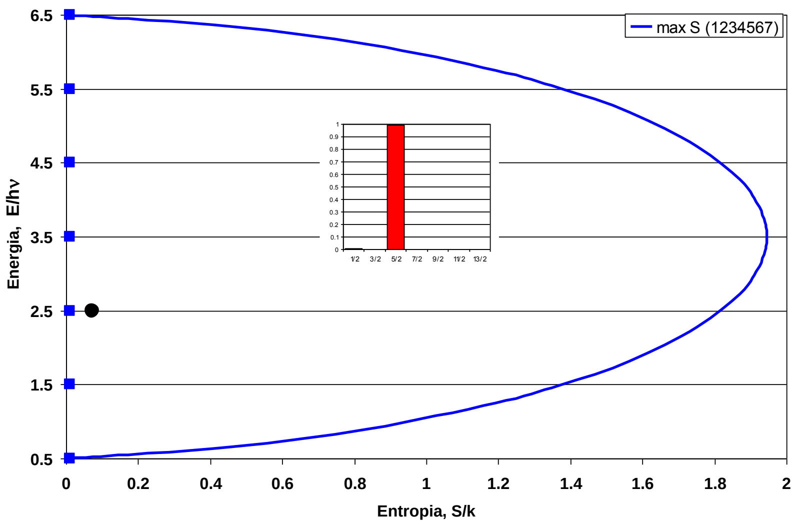
$S = -k_B \sum_j p_j \ln p_j$ entropy measures the global degree of sharing the energy load among levels

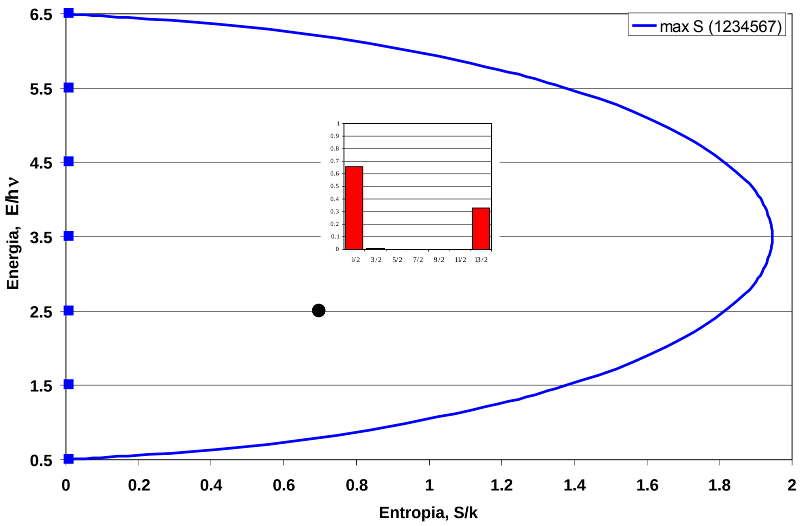


$$p_j = \frac{\exp\left(-e_j / k_B T\right)}{\sum_i \exp\left(-e_i / k_B T\right)}$$

canonical distribution

Steepest entropy ascent equation of motion models the
time evolution of the state (probability distribution) towards SES





Ideal gas equation of state for a single particle in a box

For $i=1,2,3,$ $\quad \epsilon_{j_i} = \frac{h^2}{8m}\left(\frac{j_i^2}{\ell_i^2}\right) \qquad \mathcal{Q}_i = \sum_{j_i=1}^{\infty} \exp\left(-\frac{\epsilon_{j_i}}{k_{\rm B}T}\right) = \sum_{j_i=1}^{\infty} \exp\left(-\frac{h^2 j_i^2}{8mk_{\rm B}T\ell_i^2}\right)$

$$\mathcal{Q}_i = \mathcal{Q}_i(T,\ell_i) \qquad {\rm d}\ln\mathcal{Q}_i = \frac{E_i}{k_{\rm B}T^2}{\rm d}T + \frac{2E_i}{k_{\rm B}T}\frac{{\rm d}\ell_i}{\ell_i} \qquad \left(\frac{\partial\ln\mathcal{Q}_i}{\partial T}\right)_{\ell_i} = \frac{E_i}{k_{\rm B}T^2} \qquad \left(\frac{\partial\ln\mathcal{Q}_i}{\partial\ln\ell_i}\right)_T = \frac{2E_i}{k_{\rm B}T}$$

$$S_i = \frac{E_i}{T} + k_{\rm B}\ln\mathcal{Q}_i \qquad {\rm d}S_i = \frac{1}{T}{\rm d}E_i + \frac{2E_i}{T}\frac{{\rm d}\ell_i}{\ell_i} \qquad {\rm d}E_i = T\,{\rm d}S_i - 2E_i\frac{{\rm d}\ell_i}{\ell_i} = T\,{\rm d}S_i - \pi_i V\frac{{\rm d}\ell_i}{\ell_i}$$

where we defined the directional pressure $\pi_i = -\left(\frac{\partial E_i}{\partial V}\right)_{S,\boldsymbol{\ell}'_i} = -\frac{1}{V}\left(\frac{\partial E_i}{\partial\ln\ell_i}\right)_{S,\boldsymbol{\ell}'_i} = \frac{2E_i}{V}$

representing the change in energy ∂E_i at constant S_i due to a change in the volume $V = \ell_1\ell_2\ell_3$ obtained by changing only ℓ_i, so that $\partial V/V = \partial\ell_i/\ell_i$. We finally obtain,

$$E = E_1 + E_2 + E_3 = (\pi_1 + \pi_2 + \pi_3)\frac{V}{2} \qquad {\rm d}E = T\,{\rm d}S - \pi_1 V\frac{{\rm d}\ell_1}{\ell_1} - \pi_2 V\frac{{\rm d}\ell_2}{\ell_2} - \pi_3 V\frac{{\rm d}\ell_3}{\ell_3}$$

For 'practical' values of m, ℓ_1, ℓ_2, ℓ_3, and T, the values of $h^2/8mk_{\rm B}T\ell_i^2$ are much smaller than one, and therefore the sum in $\mathcal{Q}_i$ can be approximated by an integral,

$$\mathcal{Q}_i = \sum_{j_i=0}^{\infty} {\rm e}^{-\frac{h^2}{8mk_{\rm B}T}\frac{j_i^2}{\ell_i^2}} \approx \int_0^{\infty} {\rm e}^{-\frac{h^2}{8mk_{\rm B}T}\frac{x^2}{\ell_i^2}}\,dx = \left(\frac{2\pi mk_{\rm B}T\ell_i^2}{h^2}\right)^{1/2} \quad\Rightarrow\quad \mathcal{Q} = \mathcal{Q}_1\mathcal{Q}_2\mathcal{Q}_3 \approx \left(\frac{2\pi mk_{\rm B}TV^{2/3}}{h^2}\right)^{3/2}$$

Consequently, the details of the shape of the container become irrelevant, given the same volume V, as the separate dependence of $\mathcal{Q}$ on the individual ℓ_i's disappears.

$$\left(\frac{\partial\ln\mathcal{Q}_i}{\partial T}\right)_{\ell_i} = \frac{1}{2T} \qquad E_i = \frac{1}{2}k_{\rm B}T \qquad \pi_i = \frac{k_{\rm B}T}{V} \qquad S_i = \frac{1}{2}k_{\rm B} + \frac{1}{2}k_{\rm B}\ln\frac{2\pi mk_{\rm B}T\ell_i^2}{h^2}$$

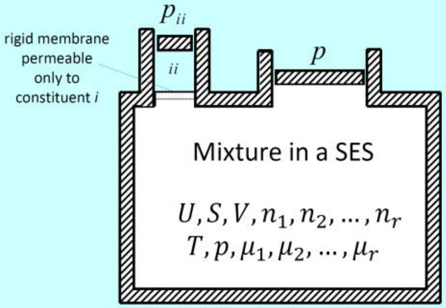
$$E = \frac{3}{2}k_{\rm B}T \qquad {\rm d}E = T\,{\rm d}S - k_{\rm B}T\left(\frac{{\rm d}\ell_1}{\ell_1} + \frac{{\rm d}\ell_2}{\ell_2} + \frac{{\rm d}\ell_3}{\ell_3}\right) = {\rm d}E = T\,{\rm d}S - k_{\rm B}T\frac{{\rm d}V}{V} \quad\Rightarrow\quad p = \frac{k_{\rm B}T}{V}$$

$$S = \frac{3}{2}k_{\rm B}\left(1 + \ln\frac{2\pi mk_{\rm B}TV^{2/3}}{h^2}\right)$$

Recall: valid at large T for given V so that $TV^{2/3} \gg \frac{h^2}{8mk_{\rm B}}$

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

Ideal solution behavior

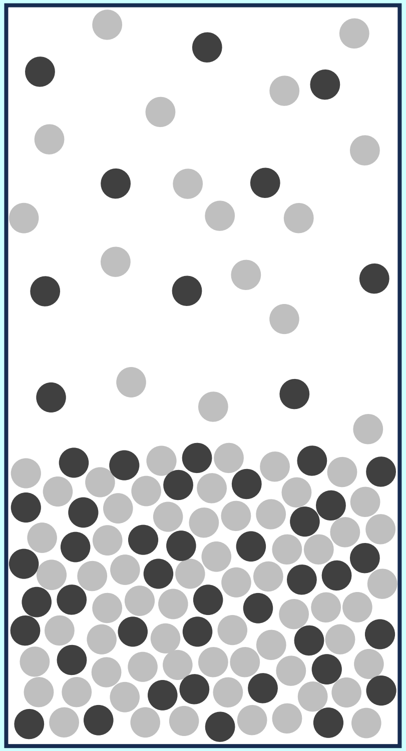


Ideal solution behavior is defined by

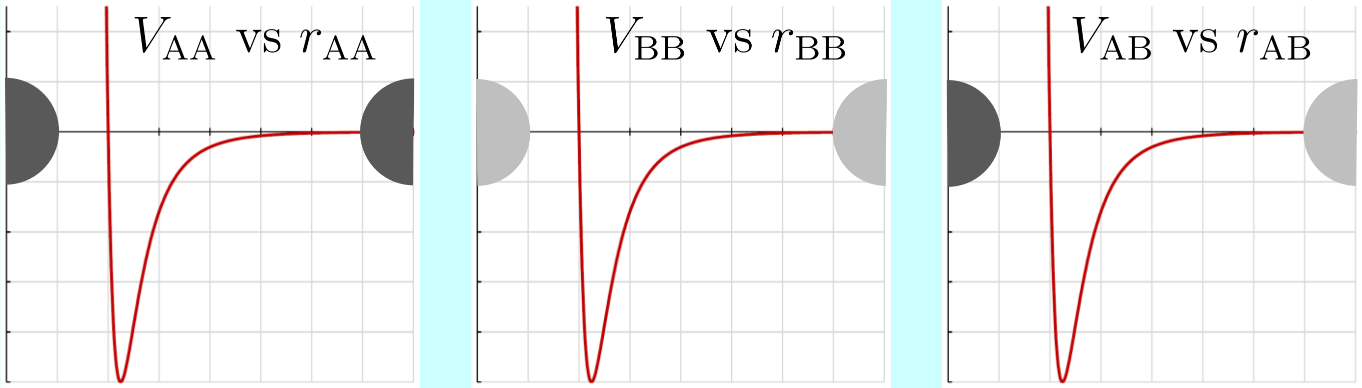
Assumption 1: $\Delta h_i^{\mathrm{mix}} = 0 \quad \forall i$

Assumption 2: $\Delta s_i^{\mathrm{mix}} = -R \ln y_i \quad \forall i$

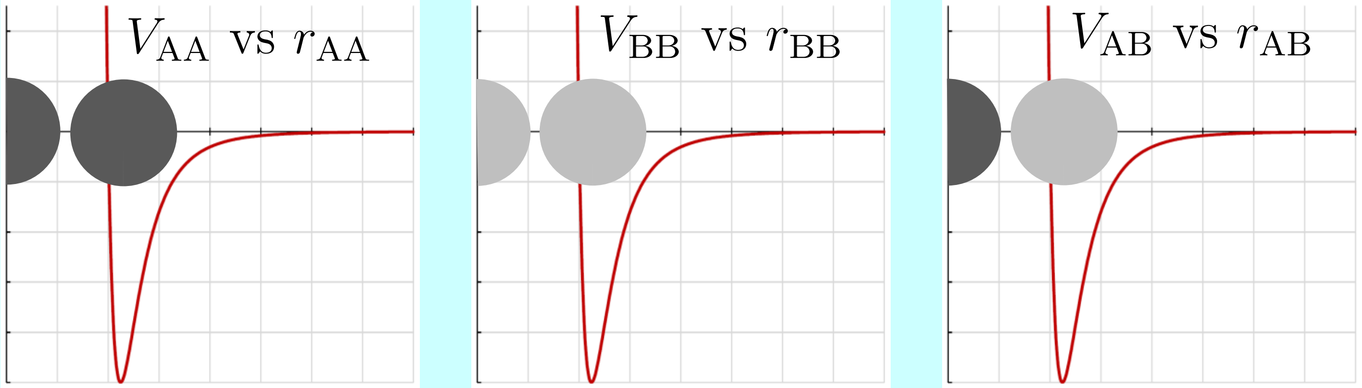
Assumption 3: $\Delta v_i^{\mathrm{mix}} = 0 \quad \forall i$



Ideal GD mixture of ideal gases: $\langle V_{\mathrm{AA}} \rangle \approx \langle V_{\mathrm{BB}} \rangle \approx \langle V_{\mathrm{AB}} \rangle \approx 0$ because $\langle r_{\mathrm{AA}} \rangle \gg r_{\min}^{\mathrm{AA}}$, $\langle r_{\mathrm{BB}} \rangle \gg r_{\min}^{\mathrm{BB}}$, $\langle r_{\mathrm{AB}} \rangle \gg r_{\min}^{\mathrm{AB}}$.



Ideal solution: $\langle V_{\mathrm{AA}} \rangle \approx \langle V_{\mathrm{BB}} \rangle \approx \langle V_{\mathrm{AB}} \rangle$.



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