2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 14

Room 3-442
Friday, March 22, 11:00am - 1:00pm

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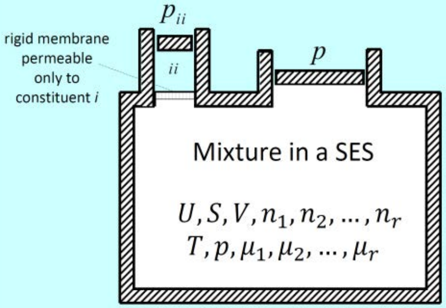
Room 3-351d

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

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

Ideal solution behavior

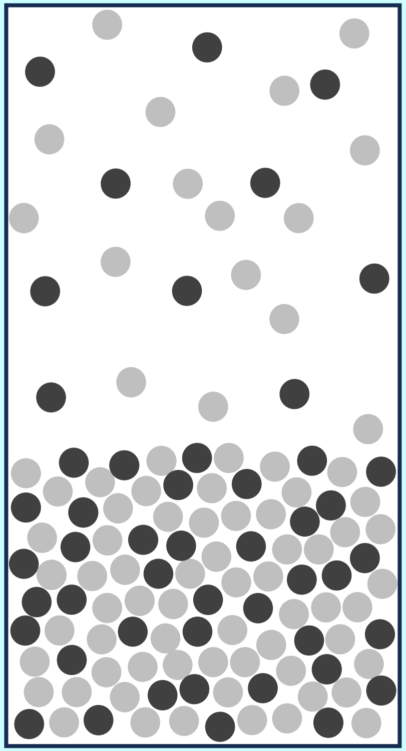


Ideal solution behavior is defined by

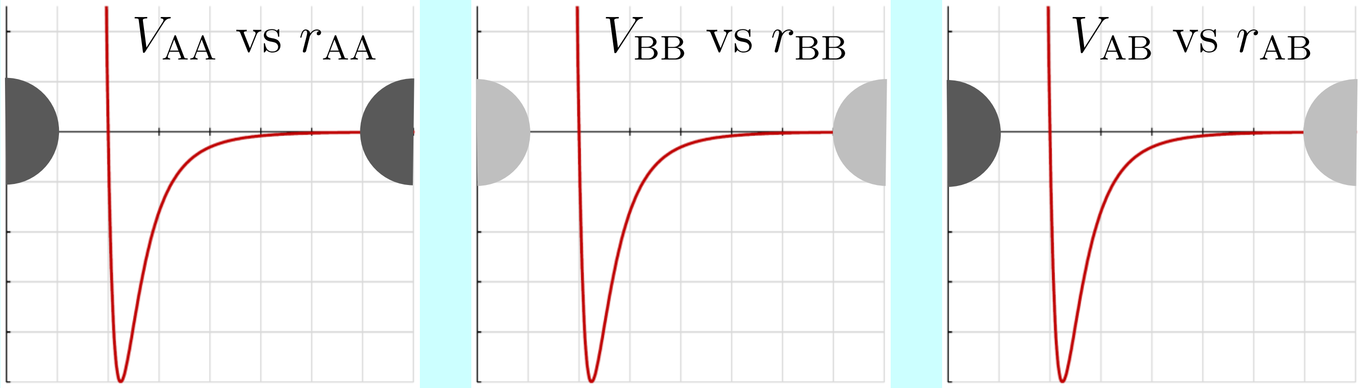
Assumption 1: $\Delta h_i^{\text{mix}} = 0 \quad \forall i$

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

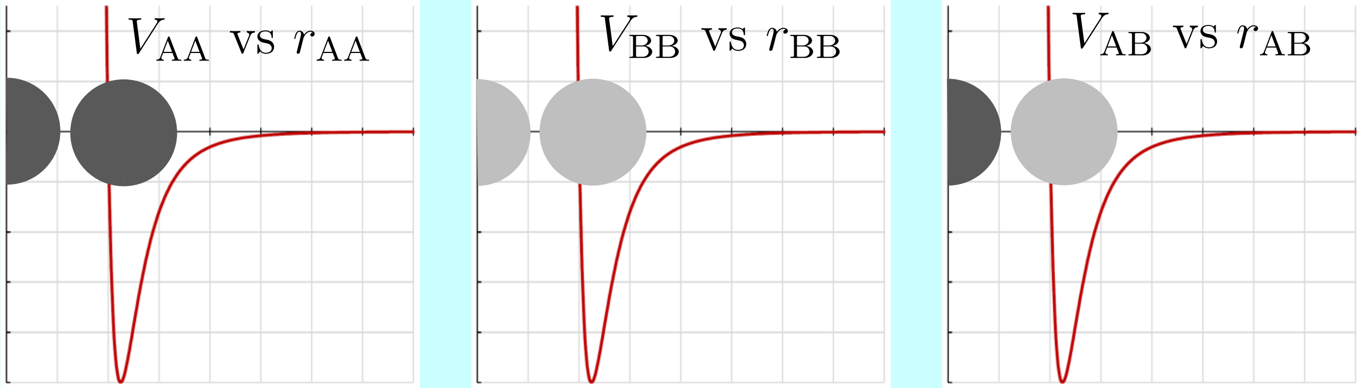
Assumption 3: $\Delta v_i^{\text{mix}} = 0 \quad \forall i$



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



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



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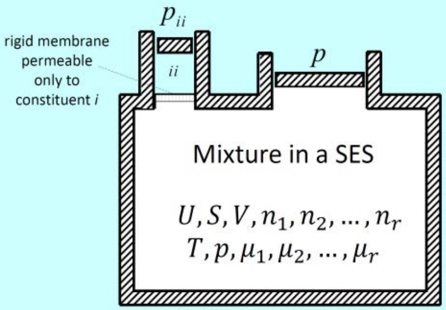
Ideal solution behavior



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Start from the relation $\mu_i = h_i - T\, s_i$ that we proved in general when we defined partial properties and recall that for the pure substance $\mu_{ii}(T,p) = h_{ii}(T,p) - T\, s_{ii}(T,p)$. Using the definitions of the properties of mixing, $h_i = h_{ii}(T,p) + \Delta h_i^{\text{mix}}$, $s_i = s_{ii}(T,p) + \Delta s_i^{\text{mix}}$, $v_i = v_{ii}(T,p) + \Delta v_i^{\text{mix}}$, we may rewrite as

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

Using the three assumptions above, that define ideal solution behavior, we obtain

$$V = \sum_{i=1}^{r} n_i v_i = \sum_{i=1}^{r} n_i \left[v_{ii}(T,p) + \Delta v_i^{\text{mix}} \right] = \sum_{i=1}^{r} n_i v_{ii}(T,p)$$

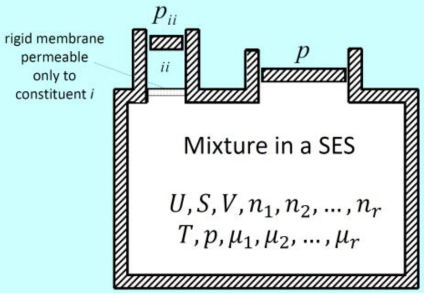
Amagat law of additive volumes

$$S_{\text{irr}}^{Tp\,\text{mix}} = S - \sum_{i=1}^{r} n_i s_{ii}(T,p) = -nR \sum_{i} y_i \ln y_i$$

Entropy of mixing
(like for GDmix of ideal gases)

$$\mu_i = \mu_i(T,p,\boldsymbol{y}) = \mu_{ii}(T,p) + RT \ln y_i$$

Osmotic pressure of the solvent of a dilute solution:
van’t Hoff relation



The **osmotic pressure of constituent i in a mixture** is defined as the difference between the pressure of the mixture and the partial pressure of that component:

$$p_i^{\rm osm} = p - p_{ii}(T, p, \boldsymbol{y})$$

Start from the following general relation we already proved

$$\mu_{ii}(T, p_{ii}) - \mu_{ii}(T, p) = \int_p^{p_{ii}} \left(\frac{\partial \mu_{ii}}{\partial p}\right)_{T,\boldsymbol{y}} dp' = \int_p^{p_{ii}} v_{ii}(T, p')\, dp' = \Delta h_i^{\rm mix} - T\Delta s_i^{\rm mix} \qquad (1)$$

Consider a **dilute** solution where constituent 1 is the **solvent** and constituents 2, …, r are the **solutes**. Dilute means that $1 - y_1 = \sum_{k=2}^r y_k \ll 1$. Van’t Hoff observed that when the solution is dilute, a molecule of solvent added to the mixture is most likely going to be surrounded by other molecules of solvent, and therefore the intermolecular interactions produce negligible energy and volume effects, i.e., $\Delta h_1^{\rm mix} = 0$ and $\Delta v_1^{\rm mix} = 0$. So, the only effect is the additional dilution which affects the entropy of mixing. In fact, rewrite $S_{\rm mix} = -nR\sum_{i=1}^r y_i \ln y_i$ as $S_{\rm mix} = -Rn_1 \ln \frac{n_1}{n_1+n_s} - R\sum_{k=2}^r n_k \ln \frac{n_k}{n_1+n_s} = -Rn_1 \ln n_1 - R\sum_{k=2}^r n_k \ln n_k + R(n_1+n_s)\ln(n_1+n_s)$ where $n_s = \sum_{k=2}^r n_k$ denotes the total amount of solutes. We have

$$\Delta s_1^{\rm mix} = \left(\frac{\partial S_{\rm mix}}{\partial n_1}\right)_{n_s} = -R - R\ln n_1 + R + R\ln(n_1+n_s) = -R\ln y_1$$

Therefore, the solvent of a dilute solution (only the solvent) satisfies the three conditions that define ideal solution behavior. We further assume incompressible liquid behavior for the solvent, $v_{11}(T, p') = v_{11} = \text{const}$. The last equality of Eq. (1) becomes

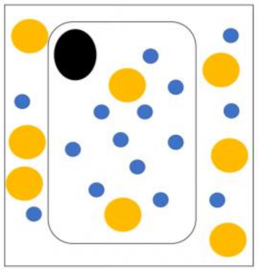
$$\int_p^{p_{11}} v_{11}(T, p')\, dp' = -(p - p_{11})v_{11} = \Delta h_1^{\rm mix} - T\Delta s_1^{\rm mix} = RT\ln y_1 = RT\ln(1 - \sum_{k=2}^r y_k)$$

which, using the approximation $\ln(1-x) \approx -x$, valid for small x, becomes the Van’t Hoff relation

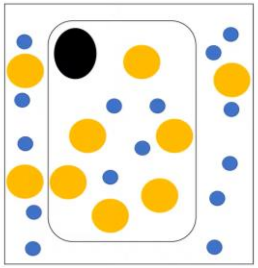
$$p_1^{\rm osm} = p - p_{11}(T, p, \boldsymbol{y}) \approx \frac{RT}{v_{11}} \sum_{k=2}^r y_k$$

Passive transport across biological membranes

Osmosis in biology

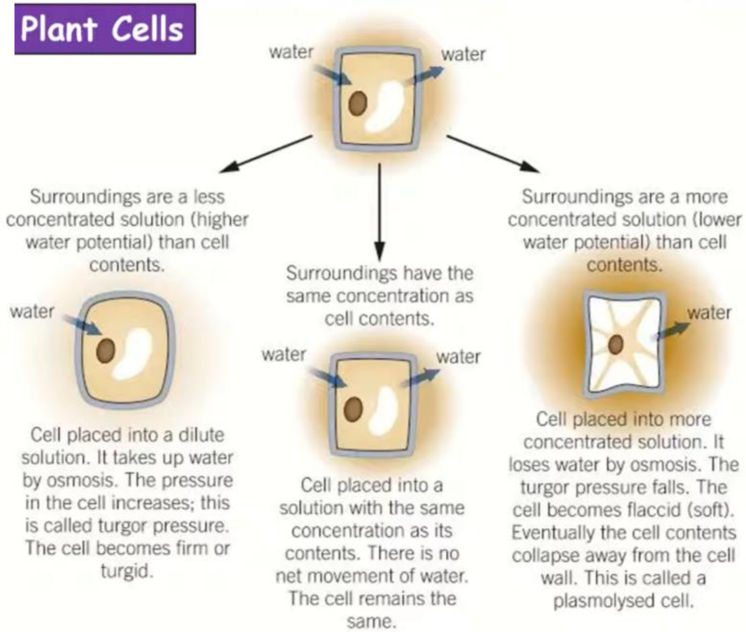


The cell is more dilute than the surrounding fluid so there is a net movement of water out of the cell.



The cell is more concentrated than the surrounding fluid so there is a net movement of water into the cell.

Plant Cells



Surroundings are a less concentrated solution (higher water potential) than cell contents.

Cell placed into a dilute solution. It takes up water by osmosis. The pressure in the cell increases; this is called turgor pressure. The cell becomes firm or turgid.

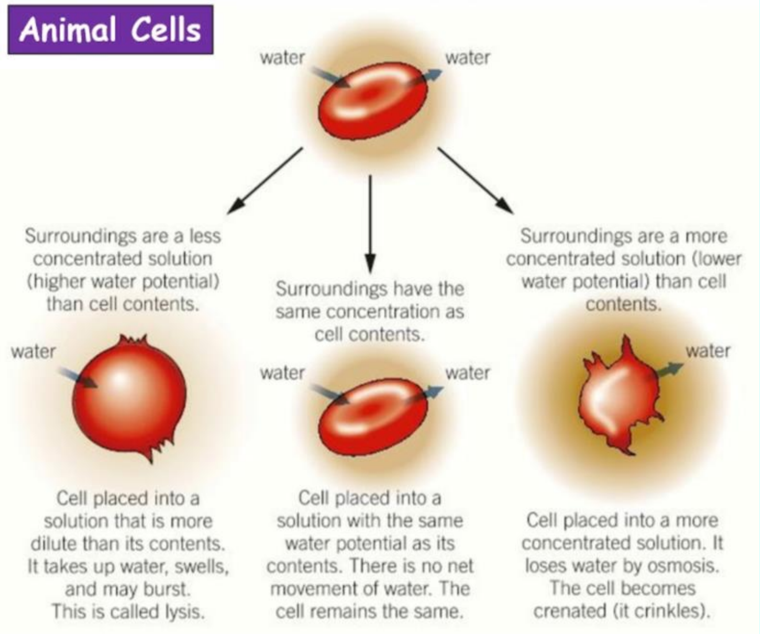
Surroundings have the same concentration as cell contents.

Cell placed into a solution with the same concentration as its contents. There is no net movement of water. The cell remains the same.

Surroundings are a more concentrated solution (lower water potential) than cell contents.

Cell placed into more concentrated solution. It loses water by osmosis. The turgor pressure falls. The cell becomes flaccid (soft). Eventually the cell contents collapse away from the cell wall. This is called a plasmolysed cell.

Animal Cells



Surroundings are a less concentrated solution (higher water potential) than cell contents.

Cell placed into a solution that is more dilute than its contents. It takes up water, swells, and may burst. This is called lysis.

Surroundings have the same concentration as cell contents.

Cell placed into a solution with the same water potential as its contents. There is no net movement of water. The cell remains the same.

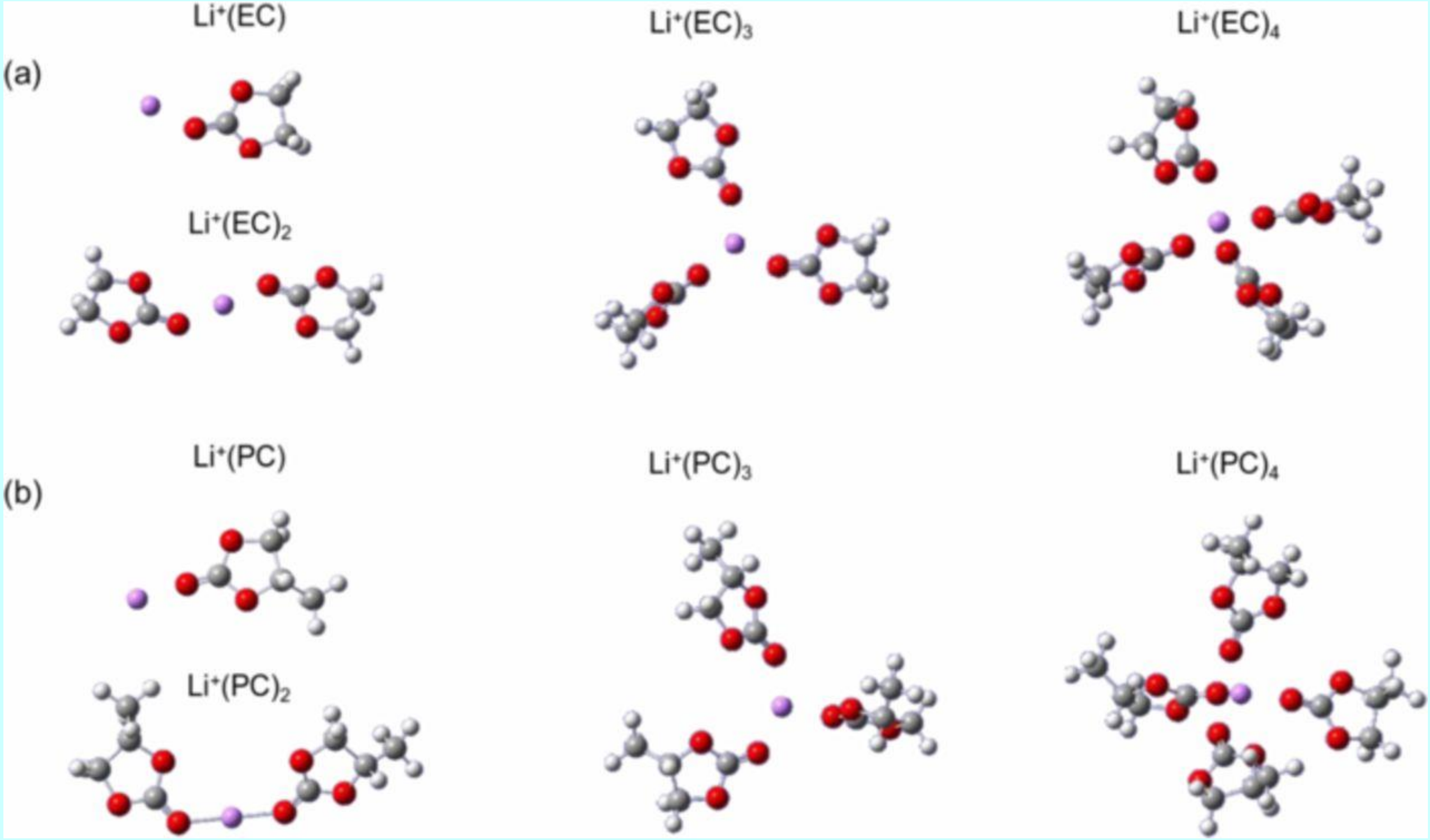
Surroundings are a more concentrated solution (lower water potential) than cell contents.

Cell placed into a more concentrated solution. It loses water by osmosis. The cell becomes crenated (it crinkles).

https://www.youtube.com/watch?v=Whv58DCm_CI

Osmosis in engineering applications:

Osmotic pressure of organic solvents in lithium-ion batteries



In some lithium-ion batteries, lithium salts such as LiPF6, LiBF4 or LiClO4 are solvated in organic solvents such as propylene carbonate (PC) and ethylene carbonate (EC). This picture shows solvation structures around a Li ion. Atom colors: oxygen (red), carbon (grey), hydrogen (white), lithium ion (purple).
Fig.5 from M.D. Bhatt and C. O'Dwyer, J. Electrochem. Soc. 161, A1415 (2014).

An important example:
Osmotic pressure of seawater

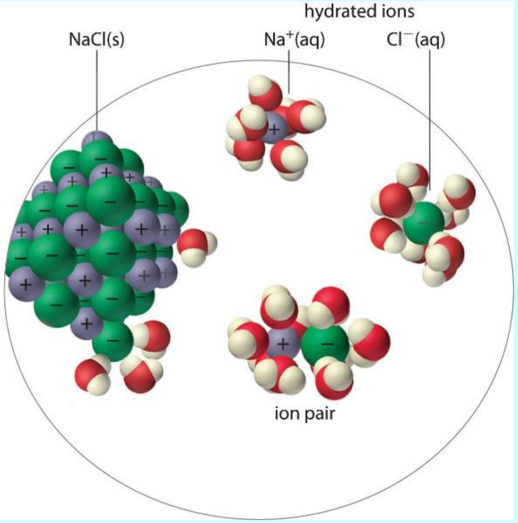


Fig.17.2 from General Chemistry Principles Patterns and Applications, Saylor Academy, 2012.

The average weight percent of salt per kg of seawater is $m_s = 35\,\mathrm{g}$. In a solution of NaCl in water, most of the Na^+ and Cl^- ions dissociate from each other due to the polar nature of water molecules, but some remain bound as ion pairs. The partially positively charged hydrogen atoms of water molecules orient themselves towards the Cl^- ions, while the partially negatively charged oxygen atoms orient towards the Na^+ ions. Thus, water molecules in close proximity to the ions tend to form relatively strong electrostatic attractions with them and are bound in the so-called solvation or hydration shell, subtracting some water molecules from their solvent role. The hydration number is typically around 6, meaning that each hydrated Cl^- ion, Na^+ ion and $\mathrm{Cl}^- * \mathrm{Na}^+$ ion pair is surrounded by approximately 6 water molecules in its hydration shell. Similarly, for the ion-pairs.

Neglecting all these non-ideal effects, and assuming 100% ion dissociation, the number of water molecules is $n_1 = m_1/M_1 = 965/18 = 53.61\,\mathrm{mol}$ and the numbers of Na^+ and Cl^- ions are $n_2 = n_3 = m_s/M_s = 35/58.5 = 0.598\,\mathrm{mol}$, so that the solvent mole fraction is $y_1 = 53.61/(53.61 + 0.598) = 0.9782$ and $-\ln y_1 = 0.02207$ which is indeed close to $\sum_{k=2}^{r} y_k = y_2 + y_3 = 1 - y_1 = 0.02183$. Thus, the osmotic pressure assuming ideal solution behavior is

$$p - p_{11} = \frac{RT}{v_{11}}(-\ln y_1) = \frac{8.314\frac{\mathrm{kJ}}{\mathrm{kmol\,K}}298\,\mathrm{K}}{10^{-3}\frac{\mathrm{m}^3}{\mathrm{kg}}18\frac{\mathrm{kg}}{\mathrm{kmol}}}0.02207 = 3038\,\mathrm{kPa} = 30.38\,\mathrm{bar} = 310\,\mathrm{m}_{\mathrm{H2O}}$$

the last equality uses Bernoulli's law $\Delta p = \rho g \Delta z$ to express the pressure in terms of the equivalent height of a column of water. Since this value exceeds the average measured value of osmotic pressure for salinities between 30 and 38, which range between 220 m and 290 m, we infer that non-ideality of the solution and the ion pairing effects mentioned above, are not negligible.

An important example:

Osmotic pressure of seawater

		Ideal solution	Average	Arctic Ocean	Mediterranean
subscript 11 = H2Opure					
T	K	298	298	298	298
R	kJ/kmol K	8.314	8.314	8.314	8.314
rho_11	kg/m3	1000	1000	1000	1000
v_11	m3/kmol	0.018	0.018	0.018	0.018
RT/v_11	kJ/m3=kPa	137643	137643	137643	137643
g	m/s2	9.81	9.81	9.81	9.81
(RT/v_11)/(rho_11 g)	m	14031	14031	14031	14031
M_NaCl	g/mol	58.5	58.5	58.5	58.5
M_11	g/mol	18	18	18	18
% Na+ Cl- hydrated	assumption	100%	82%	82%	82%
% Na+ Cl- ion-paired		0%	18%	18%	18%
hydration # for hydrated ions	assumption	0	6	6	6
hydration # for ion pairs	assumption	0	6	6	6
m_NaCl	g	35	35	30	38
m_11	g	965	965	970	962
m	g	1000	1000	1000	1000
x_NaCl		0.035	0.035	0.03	0.038
n_NaCl	mol	0.5983	0.5983	0.5128	0.6496
n_11	mol	53.61	53.61	53.89	53.44
y_NaCl (before solvation)		0.011	0.011	0.009	0.012
n_Na+	mol	0.5983	0.4906	0.4205	0.5326
n_Cl-	mol	0.5983	0.4906	0.4205	0.5326
n_NaCl	mol	0.0000	0.1077	0.0923	0.1169
n_Na+_hydrated_ion	mol	0.5983	0.4023	0.3448	0.4368
n_Cl-_hydrated_ion	mol	0.5983	0.4023	0.3448	0.4368
n_hydrated_ion_pair	mol	0.0000	0.0883	0.0757	0.0959
n_11 free	mol	53.61	48.25	49.30	47.63
n_total	mol	54.81	49.25	50.15	48.71
m_11 free	g	965.0	868.6	887.3	857.3
y_11 free		0.9782	0.9797	0.9829	0.9777
-ln y_11 free		0.0221	0.0205	0.0172	0.0226
1-y_11 free		0.0218	0.0203	0.0171	0.0223
P_osm	**m**	**310**	**288**	**242**	**316**
P_osm	bar	30.4	28.2	23.7	31.0

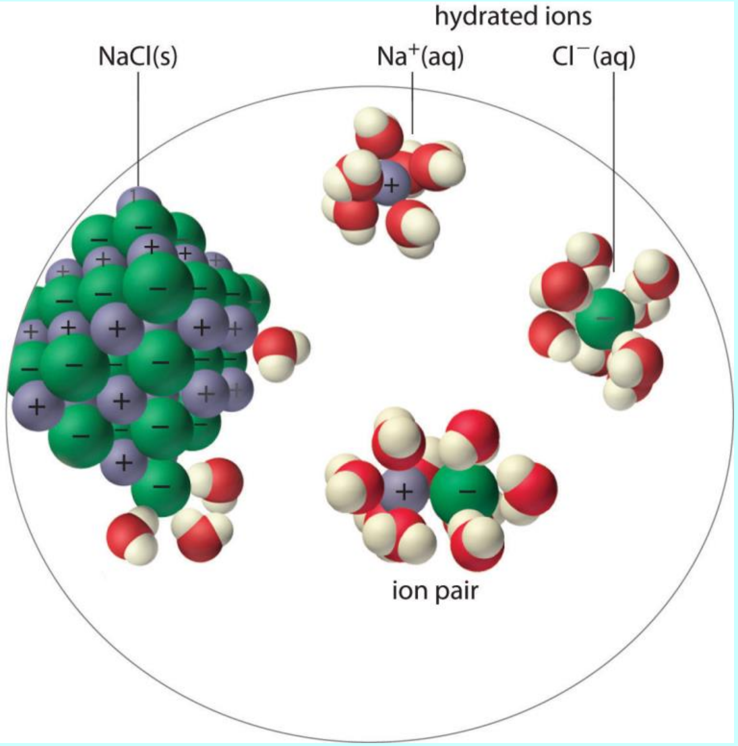


Fig.17.2 from General Chemistry Principles Patterns and Applications, Saylor Academy, 2012.

A vital application in many countries: fresh water production from saline waters

Pressure-driven reverse-osmosis desalination of seawater

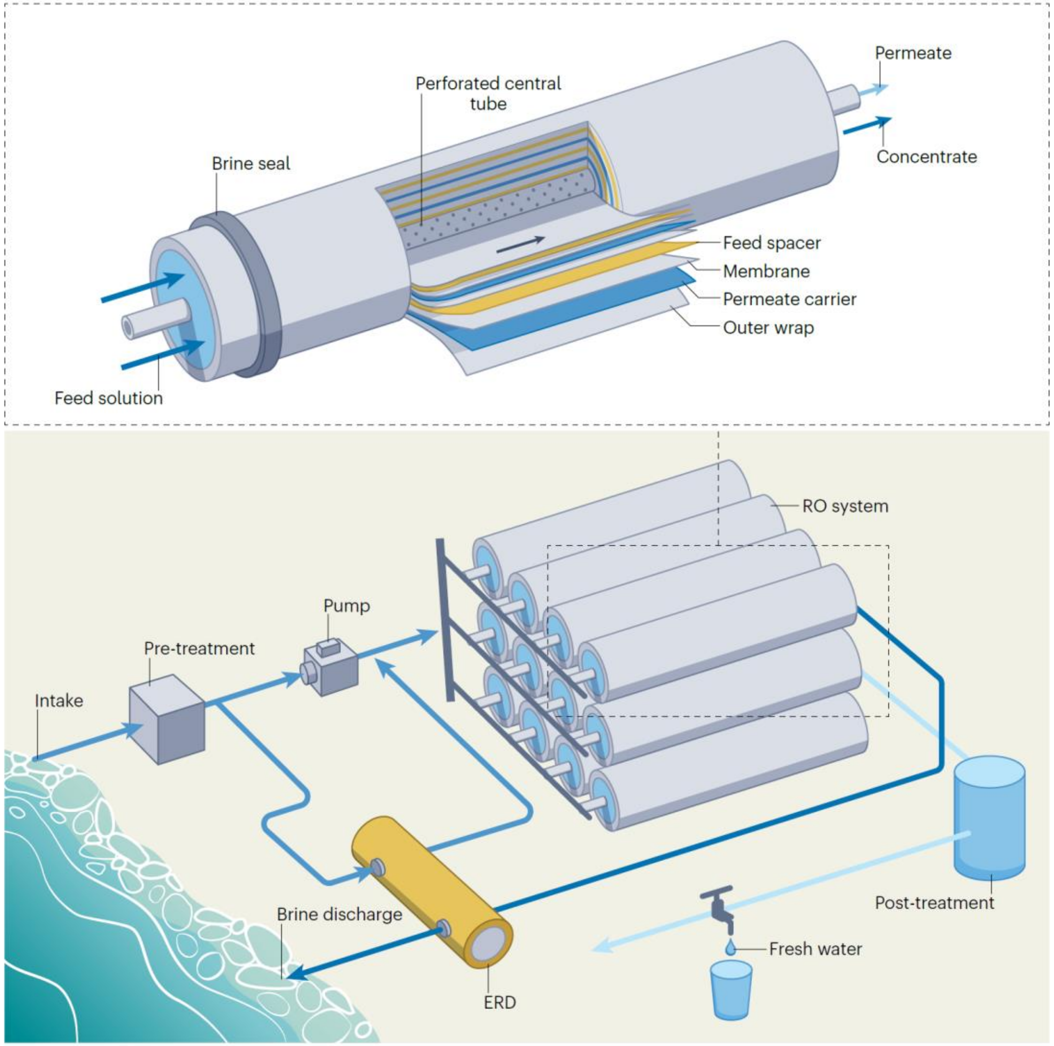
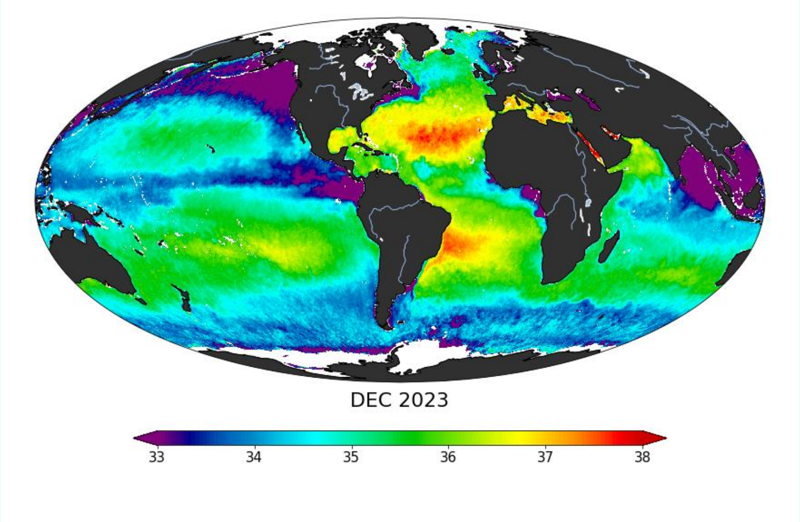


Fig. 1 | Schematic of a seawater reverse osmosis desalination plant and spiral-wound module. The treatment train includes seawater intake, pretreatment, reverse osmosis (RO), post-treatment and brine discharge. An energy recovery device (ERD) is commonly installed to retrieve the energy of the pressurized brine. The inset shows a spiral-wound RO module consisting of feed channel, spacer, RO membrane and permeate channel.

Fig.1 from: Liu, W., Livingston, J.L., Wang, L. *et al.* Pressure-driven membrane desalination. *Nat Rev Methods Primers* **4**, 10 (2024).

A potential renewable energy source:
Osmotic power (Blue energy)



https://salinity.oceansciences.org/smap-salinity.htm

Theoretical max from

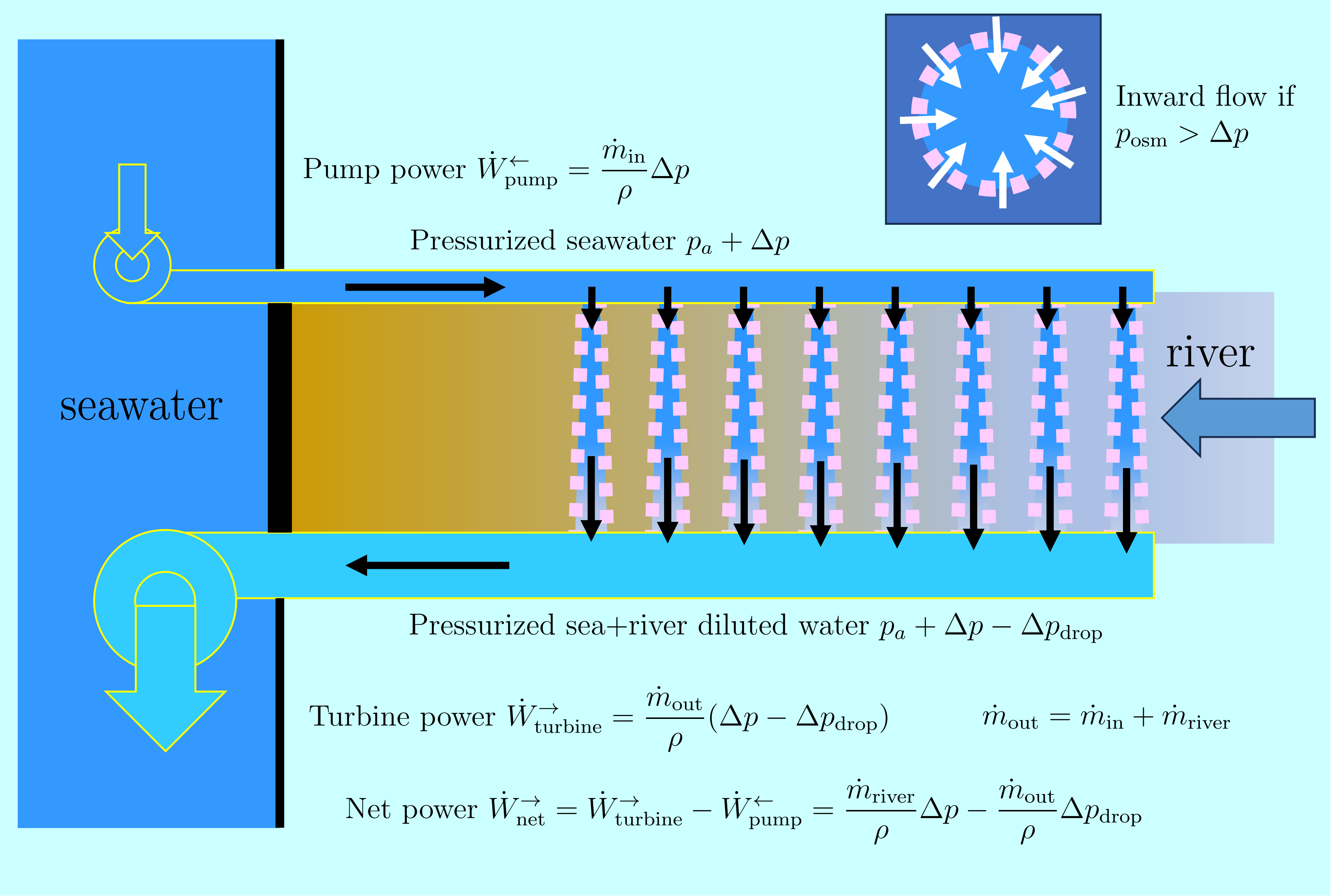
- **Reverse ElectroDialysis (RED)**
  = 1350 MW / (1000m^3/s)

- **Pressure-Retarded Osmosis (PRO)**
  = 2700 MW / (1000m^3/s)

River: average flow rate (country where it flows into the sea)

Amazon: 209000 m³/s (Brazil)
Congo: 41000 m³/s (Dem. Rep. of Congo)
Orinoco: 35000 m³/s (Venezuela)
Paraná: 22000 m³/s (Argentina, Uruguay)
Yangtze: 22000 m³/s (China)
Mississippi: 16000 m³/s (USA)
Amur: 15000 m³/s (Russia)
Niger: 14000 m³/s (Nigeria)
Mekong: 14000 m³/s (Vietnam)
Lena: 12000 m³/s (Russia)
Ganges: 12000 m³/s (India, Bangladesh)
...
Po: 6000 m³/s (Italy)

A potential renewable energy source:
Osmotic power (Blue energy)



Inward flow if $p_{\text{osm}} > \Delta p$

Pump power $\dot{W}^{\leftarrow}_{\text{pump}} = \dfrac{\dot{m}_{\text{in}}}{\rho}\Delta p$

Pressurized seawater $p_a + \Delta p$

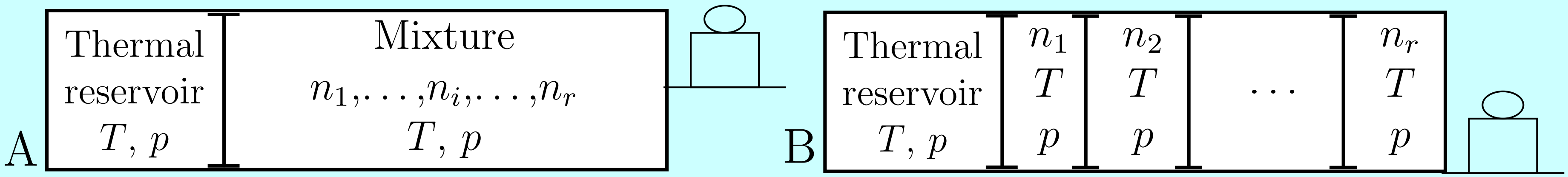
Pressurized sea+river diluted water $p_a + \Delta p - \Delta p_{\text{drop}}$

Turbine power $\dot{W}^{\rightarrow}_{\text{turbine}} = \dfrac{\dot{m}_{\text{out}}}{\rho}(\Delta p - \Delta p_{\text{drop}})$ $\qquad \dot{m}_{\text{out}} = \dot{m}_{\text{in}} + \dot{m}_{\text{river}}$

Net power $\dot{W}^{\rightarrow}_{\text{net}} = \dot{W}^{\rightarrow}_{\text{turbine}} - \dot{W}^{\leftarrow}_{\text{pump}} = \dfrac{\dot{m}_{\text{river}}}{\rho}\Delta p - \dfrac{\dot{m}_{\text{out}}}{\rho}\Delta p_{\text{drop}}$

Isothermobaric demixing of ideal gas mixtures or ideal solutions:

Minimum work of complete separation



Volume balance: $(V_B - V_A) + (V_B^R - V_A^R) = 0$

Energy balance: $(E_B - E_A) + (E_B^R - E_A^R) = W^{\leftarrow}_{\text{sep}}$

Entropy balance: $(S_B - S_A) + (S_B^R - S_A^R) = S_{\text{gen}}$

Fund.rel. for R: $E_B^R - E_A^R = T_R\,(S_B^R - S_A^R) - p_R\,(V_B^R - V_A^R)$

Eliminate $(V_B^R - V_A^R)$, $(E_B^R - E_A^R)$, and $(S_B^R - S_A^R)$, and use $T_A = T_B = T_R$ to yield:

$$W^{\leftarrow}_{\text{sep}} = E_B - E_A - T\,(S_B - S_A) + p\,(V_B - V_A) + T\,S_{\text{gen}} = W^{\leftarrow}_{\text{sep,rev}} + T\,S_{\text{gen}}$$

$$W^{\leftarrow}_{\text{sep,rev}} = G_B - G_A = \sum_i n_i\mu_{ii}(T,p) - \sum_i n_i\mu_i(T,p,\boldsymbol{y}) \underset{\text{or GDgasmix}}{\overset{\text{ideal solution}}{=}} -nRT\sum_i y_i \ln y_i$$

Assume dry air is just 1=N2, 2=O2, 3=Ar, 4=CO2, with $\{M_i\} = \{28.02, 32, 39.95, 44.01\}$

If we take $\boldsymbol{y}[\%] = \{78.08, 20.95, 0.93, 0.04\}$, $M = \sum_i y_i M_i = 28.97$ we obtain (at $T = 298\,\text{K}$)

$W^{\leftarrow}_{\text{sep,rev}}/nM = -(RT/M)\sum_i y_i \ln y_i = 48.5\,\text{kJ/kg}$

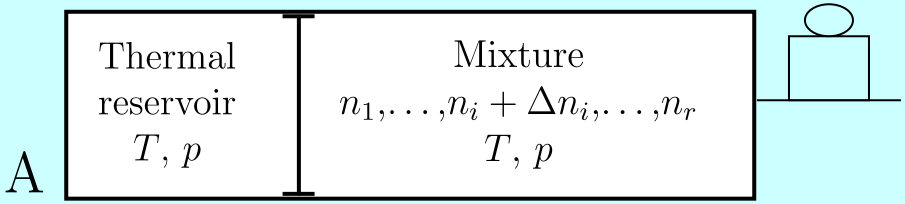
But note that for $\boldsymbol{y}[\%] = \{78.84, 21.16, 0, 0\}$, $M = 28.86$ we have $W^{\leftarrow}_{\text{sep,rev}}/nM = 44.3\,\text{kJ/kg}$

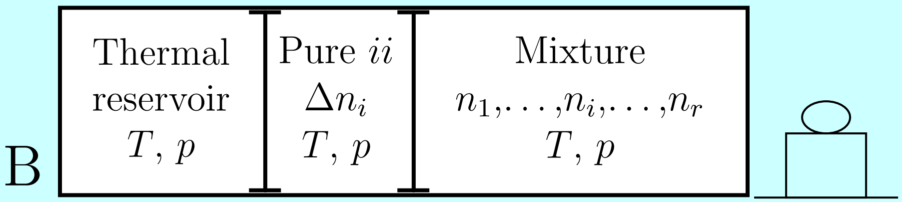
Consider ideal liquid solutions of 1=H2O and 2=CH3CH2OH, with $\{M_i\} = \{18.015, 46.07\}$ and $\{\rho_{ii}[\text{g/cm}^3]\} = \{1, 0.789\}$: For example, wine with volume fraction $\phi_2 = 14\%$ ($y_2 = 4.7\%$)

$W^{\leftarrow}_{\text{sep,rev}}/nM = -(RT/M)\sum_i y_i \ln y_i = 24.2\,\text{kJ/kg}$

Isothermobaric demixing of ideal gas mixtures or ideal solutions:

Minimum work of partial separation





$$W^{\leftarrow}_{\rm sep,rev} = G_B - G_A = \Delta n_i \mu_{ii}(T,p) + \sum_j n_j \mu_j(T,p,\boldsymbol{y}_B) - \Delta n_i \mu_i(T,p,\boldsymbol{y}_A) - \sum_j n_j \mu_j(T,p,\boldsymbol{y}_A)$$

assume ideal solution or GDgasmix and note that $y_{jB}/y_{jA} = 1 + \Delta n_i/n$ for $j \neq i$ ($n = n_B$),

$$\frac{W^{\leftarrow}_{\rm sep,rev}}{RT} = -\Delta n_i \ln y_{iA} + \sum_j n_j \ln(y_{jB}/y_{jA}) = -\Delta n_i \ln y_{iA} - n_i \ln\left(1+\frac{\Delta n_i}{n_i}\right) + n \ln\left(1+\frac{\Delta n_i}{n}\right)$$

For **complete removal** of i, i.e., $n_i = 0$, $y_{iA} = \Delta n_i/(n+\Delta n_i)$ ($n_A = n + \Delta n_i$), it reduces to

$$\frac{W^{\leftarrow}_{\rm sep,rev}}{\Delta n_i RT} \overset{n_i=0}{=} -\ln y_{iA} - \frac{1-y_{iA}}{y_{iA}} \ln(1-y_{iA}) \quad (1) \qquad \overset{y_{iA}\ll 1}{\approx} -\ln y_{iA} \qquad (2)$$

For **partial removal** of i, i.e., $n_i \neq 0$, $y_{iA} = (n_i+\Delta n_i)/(n+\Delta n_i)$, $\chi = \Delta n_i/(n_i+\Delta n_i)$, it gives

$$\frac{W^{\leftarrow}_{\rm sep,rev}}{\Delta n_i RT} = -\ln y_{iA} + \frac{1-\chi}{\chi}\ln(1-\chi) + \frac{1-\chi\, y_{iA}}{\chi\, y_{iA}} \ln\left(1+\frac{\chi\, y_{iA}}{1-\chi\, y_{iA}}\right) \quad (3) \qquad \overset{\chi\ll 1}{\approx} -\ln y_{iA} \qquad (4)$$

Assume dry air at 298 K with $\boldsymbol{y}[\%] = \{78.08, 20.95, 0.93, 0.04\}$ (1=N2, 2=O2, 3=Ar, 4=CO2)

For minor removals ($\chi \ll 1$) of just N2 or just O2 or just Ar or just CO2 Eq.(2) gives

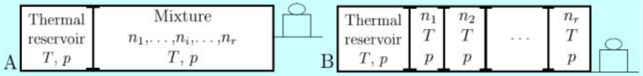
$$\frac{W^{\leftarrow}_{\rm sep,rev}}{\Delta n_i M_i} = \{21.9, 121.0, 290.1, 440.5\}\,\text{kJ/kg}$$

Note that $\displaystyle\sum_i \frac{W^{\leftarrow}_{\rm sep,rev}}{\Delta n_i M_i}\frac{\Delta n_i M_i}{nM} = \frac{W^{\leftarrow}_{\rm sep,rev}}{nM} = 48.5\,\text{kJ/kg}$ is equivalent to complete separation.

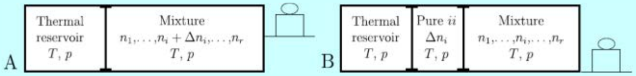
Minimum works of complete separation, partial minor removal, complete removal

Isothermobaric demixing of atmospheric air components

		N2	O2	Ar	CO2	sum
%		**78.08%**	**20.95%**	**0.93%**	**0.05%**	100.01%
M_i	kg/kmol	28.02	32	39.95	44.01	M
y_iM_i	kg/kmol	21.88	6.70	0.37	0.02	28.98
Complete separation						
(RT/M)*(-y_i\lny_i)	kJ/kg_air	16.5	28.0	3.7	0.3	**48.6**
Partial minor removal						
-lny_i (Eq.2)		0.2474	1.5630	4.6777	7.6009	
Eq.2 *RT/M_i	kJ/kg_i	**21.9**	**121.0**	**290.1**	**427.9**	
x_i (mass fraction)		0.7551	0.2314	0.0128	0.0008	100.00%
x_i*Eq.2*RT/M_i	kJ/kg_air	**16.5**	**28.0**	**3.7**	**0.3**	48.6
Complete removal						
-lny_i -... (Eq.1)		0.6735	2.4501	5.6731	8.6007	
Eq.1*RT/M_i	kJ/kg_i	**59.6**	**189.7**	**351.8**	**484.2**	

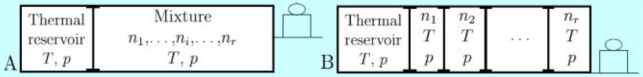


$\Delta n_i \ll n_i$

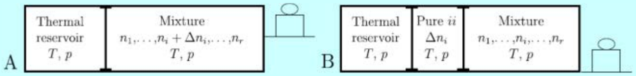


$n_i = 0$

		N2	O2	Ar	CO2	sum
%		**78.84%**	**21.16%**	0.00%	0.00%	100.00%
M_i	kg/kmol	28.02	32			M
y_iM_i	kg/kmol	22.09	6.77			28.86
Complete separation						
(RT/M)*(-y_i\lny_i)	kJ/kg_air	**16.1**	**28.2**			**44.3**
Partial minor removal						
-lny_i (Eq.2)		0.2377	1.5533			
Eq.2 *RT/M_i	kJ/kg_i	**21.0**	**120.3**			
x_i (mass fraction)		0.7654	0.2346			100.00%
x_i*Eq.2*RT/M_i	kJ/kg_air	**16.1**	**28.2**			44.3
Complete removal						
-lny_i -... (Eq.1)		0.6545	2.4391			
Eq.1*RT/M_i	kJ/kg_i	**57.9**	**188.8**			



$\Delta n_i \ll n_i$

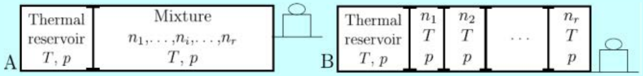


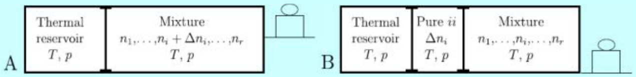
$n_i = 0$

Minimum works of complete separation, partial minor removal, complete removal

Isothermobaric demixing of a liquid solution

Wine		**water**	**ethanol**		
		H2O	**CH_3CH_2OH**		
phi_i	volume fraction	88%	**12%**		
M_i	kg/kmol	18.015	47.06		
rho_ii	g/cc	1	0.789	rho=	0.975
v_ii=M_i/rho_i	cc/mol	18.015	59.645		
phi_i/v_ii	mol/cc	0.04885	0.00201	sum=	0.05086
y_i	mole fraction	96.0%	4.0%		
y_iM_i	kg/kmol	17.30	1.86	M=	19.16
y_iv_ii	cc/mol	17.30	2.36	v=	19.66
x_i	mass fraction	90.3%	9.7%		
n_i/V=y_i/v	mol/liter	48.85	2.01	n/V=	50.86
Complete separation				C=	
-y_i\lny_i		0.03876	0.12777	sum=	0.16654
nRT/V*sum(-y_i\lny_i)	kJ/liter			W=	21.0
Partial removal of water to increase the alcohol content to					
final phi_2			**14%**		
Dn_1	mol/liter	7.930			
a=chi		0.162			
b=c*y		0.156			
-lny_1		0.040			
(1-a)/a*ln(1-a)		-0.914			
(1-b)/b*ln(1+b/(1-b))		0.918			
W/\delta n_i RT		0.044			
W	kJ/liter	0.864			



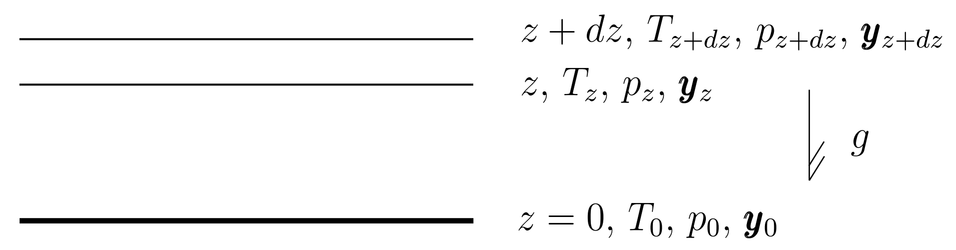


Stratification of ideal gas and liquid mixtures in gravitational field

$$E_z = U(S_z, V_z, \boldsymbol{n}_z) + m_z g z \qquad m_z = \textstyle\sum_i n_{iz} M_i$$

$$\mu^{\rm tot}_{i,z} = \left(\frac{\partial E_z}{\partial n_{iz}}\right)_{S_z, V_z, \boldsymbol{n}'_{iz}} = \mu_i(T_z, p_z, \boldsymbol{y}_z) + M_i g z$$

$$= \text{total potential of constituent } i$$



$z + dz,\ T_{z+dz},\ p_{z+dz},\ \boldsymbol{y}_{z+dz}$

$z,\ T_z,\ p_z,\ \boldsymbol{y}_z$

g

$z = 0,\ T_0,\ p_0,\ \boldsymbol{y}_0$

Assume (locally only) $T_{z+dz} \approx T_z$ and impose, for every constituent i, the equality of total potentials, $\mu^{\rm tot}_{i,z+dz} = \mu^{\rm tot}_{i,z}$, between adjacent layers

$$\mu^{\rm tot}_{i,z+dz} \approx \mu_i(T_z, p_{z+dz}, \boldsymbol{y}_{z+dz}) + M_i g(z+dz) = \mu_{ii}(T_z, p_{z+dz}) + RT_z \ln y_{i,z+dz} + M_i g(z+dz)$$

$\mu^{\rm tot}_{i,z} = \mu_i(T_z, p_z, \boldsymbol{y}_z) + M_i g z = \mu_{ii}(T_z, p_z) + RT_z \ln y_{i,z} + M_i g z$ (we assumed ideal mixture behavior).

Therefore, $\mu^{\rm tot}_{i,z+dz} = \mu^{\rm tot}_{i,z}$ implies $\mu_{ii}(T_z, p_{z+dz}) + RT_z \ln(y_{i,z} + dy_{i,z}) + M_i g\, dz = \mu_{ii}(T_z, p_z) + RT_z \ln y_{i,z}$

Finally, $v_{ii}(T_z, p_z)\, dp_z + RT_z\, dy_{i,z}/y_{i,z} + M_i g\, dz = 0$ where we used $\ln(1 + dy_{i,z}/y_{i,z}) = dy_{i,z}/y_{i,z}$

For a pure substance this is $v(T,p)\, dp = -M g\, dz$ and integration yields Bernoulli static equations

$$\Rightarrow \begin{cases} \text{ideal gas } p_z = p_0 \exp\left(-\dfrac{Mg}{R}\displaystyle\int_0^z \dfrac{dz}{T_z}\right) \\ \text{incompr.liquid } p_z = p_0 - \rho g z \qquad \rho = M/v \end{cases}$$

For a mixture of ideal gases, instead, recalling that under ideal behavior $y_{i,z} p_z = p_{ii,z}$, it becomes

$$RT_z\, dp_z/p_z + RT_z\, dy_{i,z}/y_{i,z} = RT_z\, dp_{ii,z}/p_{ii,z} = -M_i g\, dz \quad \Rightarrow \quad p_{ii,z} = p_{ii,0} \exp\left(-\frac{M_i g}{R}\int_0^z \frac{dz}{T_z}\right)$$

so that, once we have the $p_{ii,z}$'s, we find $p_z = \sum_i p_{ii,z}$ and $y_{i,z} = p_{ii,z}/p_z$.

For a binary mixture of incompressible liquids, setting $y_z = y_{11,z} = 1 - y_{22,z}$, it becomes

$v_{11}\, dp_z + RT_z\, dy_z/y_z = -M_1 g\, dz$ and $v_{22}\, dp_z - RT_z\, dy_z/(1 - y_z) = -M_2 g\, dz$ which combined yield

$$\frac{1}{v_{11}}\frac{dy_z}{y_z} + \frac{1}{v_{22}}\frac{dy_z}{1 - y_z} = (\rho_2 - \rho_1)\frac{g}{R}\frac{dz}{T_z} \quad \text{and integrated} \quad \frac{y_z}{y_0}\left(\frac{1 - y_0}{1 - y_z}\right)^{v_{11}/v_{22}} = \exp\left((\rho_2 - \rho_1)\frac{g v_{11}}{R}\int_0^z \frac{dz}{T_z}\right)$$

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2.43 Advanced Thermodynamics
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