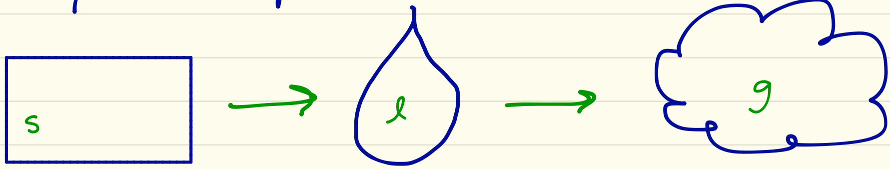
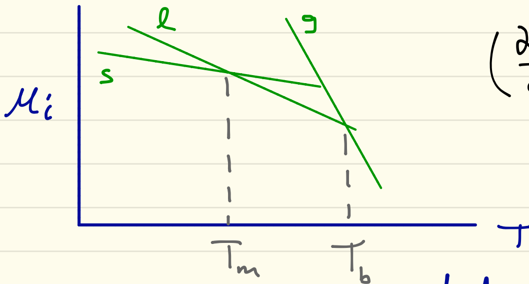
Lecture 10 – mixtures

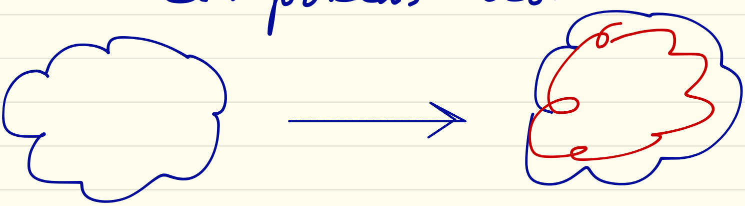
Single component world



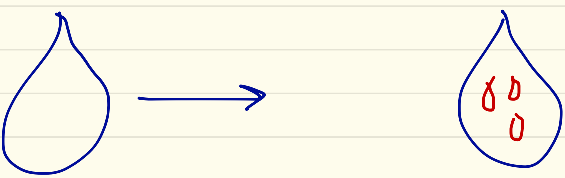


$$\left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -s(T,p)$$

Multi-component world



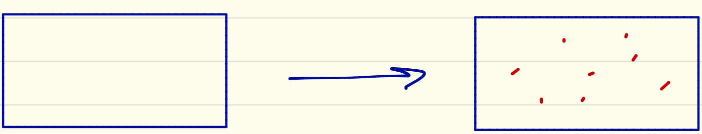
g + g



l + g

l + l

l + s

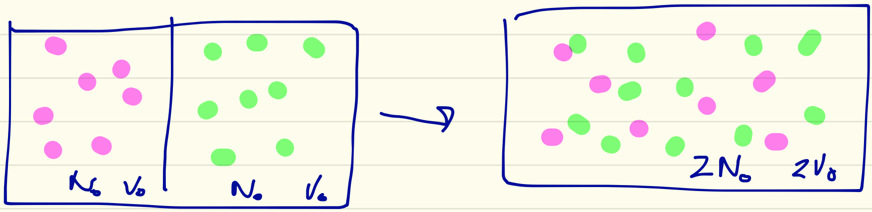


s + s

What is a mixture?

Intimate intermingling of chemically distinct components. Macroscopically behaves like a single substance.

Ideal gas mixture



Δu? Δh? Δp? Δs?

What if • ≡ •? Does answer change?

Assume monatomic ideal gas.

$$q_\ell = \frac{V}{\Lambda_\ell^3} \qquad Q_\ell = q_\ell^N/N! \qquad \Lambda \equiv \Lambda(\beta, m)$$

Ditto q_r, Q_r, Λ_r

What does "ideal" mean? Independent contributions to total.

$$Q_{\ell+r} = q_\ell'^N/N! \; q_r'^N/N! \qquad q_\ell' = V'/\Lambda_\ell^3 \qquad V' = 2V_0$$

Pressure? $p = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)$

$$\ln Q_\ell = N \ln q_\ell - \ln N!$$
$$= N(\ln V - 3\ln\Lambda) - \ln N!$$

Pure component

Let $v_A = v_B \quad T_A = T_B \implies P_A = P_B$

$$q_A = V_A/\Lambda_A^3 \qquad Q_A = q_A^{N_A}/N_A!$$

$$F_A = -k_B T \ln Q_A = -N_A k_B T \left(\ln V_A - 3 \ln \Lambda_A - N_A \ln N_A + N_A \right)$$

$$P_A = -\partial F_A/\partial V_A = N_A k_B T/V_A = k_B T/v_A$$

$$U_A = -N_A \frac{\partial \ln q}{\partial \beta} = \frac{3}{2} N_A k_B T$$

ditto B

Combine

$V = V_A + V_B \quad T = T_A = T_B \quad N = N_A + N_B \rightarrow v = v_A = v_B$

$$q_A = V/\Lambda_A^3 \qquad q_B = V/\Lambda_B^3$$

$$Q_{AB} = q_A^{N_A}/N_A! \; q_B^{N_B}/N_B!$$

$$= \left(\frac{V}{\Lambda_A^3}\right)^{N_A} \left(\frac{V}{\Lambda_B^3}\right)^{N_B} \cdot \frac{1}{N_A! N_B!}$$

$$= \left(\frac{V}{V_A}\right)^{N_A} \left(\frac{V}{V_B}\right)^{N_B} \left(V_A/\Lambda_A^3\right)^{N_A} \left(V_B/\Lambda_B^3\right)^{N_B} \frac{1}{N_A! N_B!}$$

$$F_{AB} = -k_B T \ln Q_{AB}$$

$$= F_A + F_B - k_B T \Big\{ \underbrace{N_A \ln \frac{V}{V_A} + N_B \ln \frac{V}{V_B}}_{\Delta F_{mix}} \Big\}$$

$$V_A/V = N_A/N = y_A \qquad V_B/V = N_B/N = y_B$$

$$F_{AB} = F_A + F_B + k_B T \{ N_A \ln y_A + N_B \ln y_B \} \qquad 1/N_A + N_B$$

$$f_{AB} = y_A f_A + y_B f_B + k_B T \underbrace{\{ y_A \ln y_A + y_B \ln y_B \}}_{\text{ideal free energy of mixing, } \Delta f_{mix}}$$

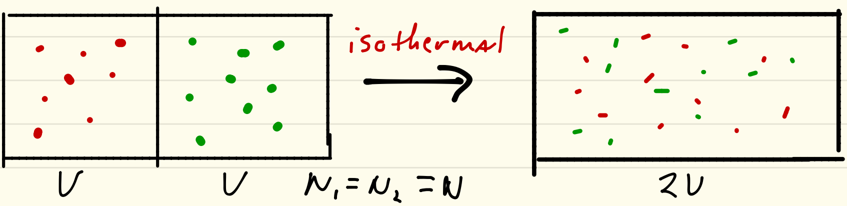
Entirely entropic:

$$U_{AB} = -\left(\partial \ln Q_{AB} / \partial \beta \right) = \tfrac{3}{2} N_A k_B T + \tfrac{3}{2} N_B k_B T$$

$$\boxed{\begin{array}{c} \Delta U_{mix} = 0 \\ \Delta S_{mix} = -N k_B \sum_i y_i \ln y_i > 0 \end{array}}$$

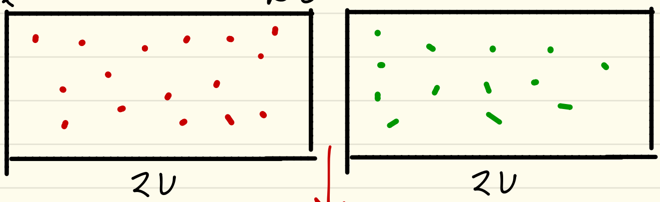
Follows that ΔU_{mix}^{IGM}, ΔV_{mix}^{IGM}, $\Delta H_{mix}^{IGM} = 0$

$$\Delta G_{mix}^{IGM} = RT \sum_i y_i \ln y_i \;, \quad \Delta S_{mix} = -R \sum_i y_i \ln y_i$$

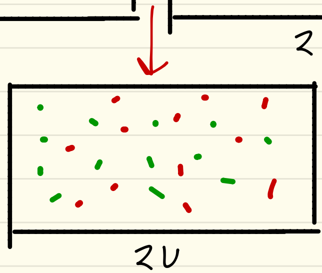


- Work necessary to "unmix"

Compare: $S_\ell = \ldots + NR \ln \frac{2V}{Nv}$ $\quad S_r = \ldots +$

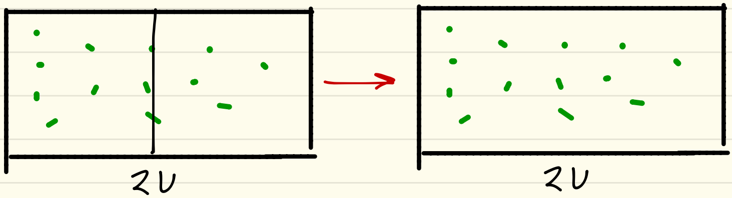


$\Delta S_{mix} = 0$!



$\Delta P \neq 0$

$$S_{mix} = \ldots + 2NR \ln \frac{2V}{2Nv_0} + 2NR \ln 2 = S_\ell + S_r$$



$\Delta S = 0$!!

Gibbs' "paradox"

What if $A = B$? $\quad y_A \to 1 \quad \Delta S_{mix} \to 0$

Why? $\quad N_A = N_B = N/2 \quad V_A = V_B = V/2$

$$Q_{AB} = \left(\frac{V}{\Lambda^3}\right)^N \cdot \frac{1}{N!} = \left(\frac{V}{\Lambda^3}\right)^{N_A}\left(\frac{V}{\Lambda^3}\right)^{N_B} \cdot \frac{1}{N!}$$

$$F_{AB} = -Nk_BT\left[\ln V - 3\ln\Lambda - \ln N + 1\right]$$

$$= -2N_Ak_BT\left[\ln 2V_A - 3\ln\Lambda - \ln 2N_A + 1\right]$$

$$= -2N_Ak_BT\left[\ln V_A - 3\ln\Lambda - \ln N_A + 1\right]$$

$$= 2F_A$$

Consequence of big N!!

μ view: 50:50 vastly dominates all else. If green are indistinguishable, opening door doesn't add any more μstates.

Pressure

$$p = -\frac{\partial F_{AB}}{\partial V} = -\frac{\partial F_A}{\partial V} - \frac{\partial F_B}{\partial V}$$

$$= \underbrace{\frac{N_A k_B T}{V} + \frac{N_B k_B T}{V}}_{\text{"partial" pressures}} = \frac{N k_B T}{V}$$

$$p_A = y_A p \quad p_B = y_B p$$

chemical potential

$$\mu_A = \left(\frac{\partial F_{AB}}{\partial N_A}\right)_{N_B, V, T}$$

$$F_{AB} = N_A f_A + N_B f_B + k_B T\Big[N_A\big(\ln N_A - \ln(N_A+N_B)\big) + N_B\big(\ln N_B - \ln(N_A+N_B)\big)\Big]$$

$$\mu_A = f_A + k_B T\left\{\cancel{N_A\left(\frac{1}{N_A} - \frac{1}{N_A+N_B}\right)} + \ln N_A - \ln(N_A+N_B) \cancel{+ N_B\left(\frac{-1}{N_A+N_B}\right)}\right\}$$

0

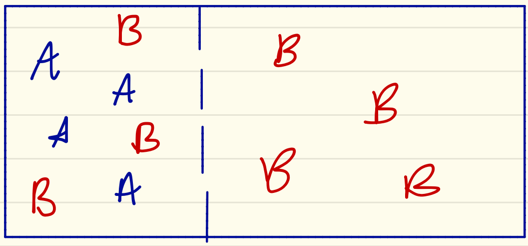
$$= f_A(v,T) + k_B T \ln y_A = \underbrace{f_A(v^\circ, T) + \left(f_A(v,T) - f_A(v^\circ,T)\right)}_{\mu_A^\circ(T)} + k_B T \ln y_A$$

$$= \mu_A^\circ(T) + k_B T \ln \underbrace{v/v^\circ}_{p/p^\circ} + k_B T \ln y_A$$

$$\boxed{\mu_A = \mu_A^\circ + k_B T \ln p_A/p^\circ}$$

μ_A° chemical pot'l of pure, ideal A at reference pressure.

Mixture equilibrium



semi-permeable membrane

General equilibrium requirement is that

$$\boxed{\mu_B^{mix} = \mu_B}$$

$$\mu_B^\circ(T) + k_B T \ln\left(\frac{P_{mix}\, y_B}{p^\circ}\right) = \mu_B^\circ(T) + k_B T \ln P/p^\circ$$

$$\boxed{P_{mix}\, y_B = P}$$

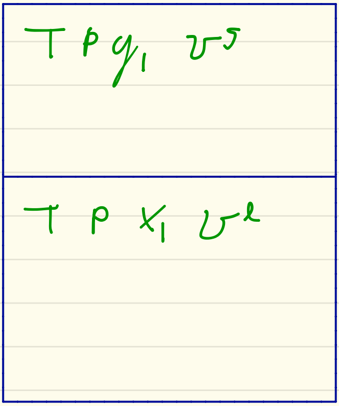
$\mu_B^{mix} \to -\infty$ as $y_B \to 0$ Yech!

$P_B = P_{mix}\, y_B \to 0$ as $y_B \to 0$ Nice!

$$P_B(T,P,y_B) = y_B P = p^\circ e^{(\mu_B - \mu_B^\circ)/kT}$$

nice form
suggests fugacity

Non-ideal gas mixture



Phase rule

$$\text{dof} = C - P + 2 = 2 - 2 + 2 = 2$$

eg specify T, x_1

determine P, v^l, v^g, y_1

mechanical: $P(T, v^l, x_1) = P(T, v^g, y_1)$

chemical: $\mu_1(T, v_l, x_1) = \mu_1(T, v_g, y_1)$

$$\Rightarrow f_1(T, v_l, x_1) = f_1(T, v_g, y_1)$$

ditto component 2

$$\boxed{\mu_B^{mix} = \mu_B \overset{\text{equivalent}}{\Longrightarrow} f_B^{mix} = f_B}$$

Need some expressions for these quantities

Fugacity

$$G^{res} = G(T,P) - G^{ig}(T,P) = \int_0^P \left(\frac{\partial G^{res}}{\partial P'}\right) dP'$$

$$= \int_0^P v^{res}\, dP' = \int_0^P \left(v - \frac{RT}{P'}\right) dP'$$

Convenient to define fugacity f such that

$$RT \ln f/P = \int_0^P \left(v - \frac{RT}{P'}\right) dP'$$

Thus $\mu(T,P) = \mu^\circ(T) + RT \ln f/P$

$$f(T,P) = P\, e^{\Delta\mu/RT}$$

As $P \to 0$, $f \to P$, $\mu^{ig} \to -\infty$ bad

Similarly for a mixture,

$$\mu_i(T,P,y_j) - \underline{\mu_i^{ig}(T,P,y_j)} = \int \left(\frac{\partial \bar{g}_{i\,res}}{\partial P}\right) dP'$$

$$= \int_0^P \left(\bar{v}_i - \frac{RT}{P'}\right) dP' = RT \ln \hat{f}_i/y_i P$$

$$\boxed{\mu_i(T,P) = \mu_i^\circ(T) + RT \ln \hat{f}_i/y_i P} \quad RT \ln \hat{f}_i/P^\circ$$

-or-

$$\hat{f}_i(T,P,y_j) = y_i P\, e^{\Delta\mu_i^{res}/RT}$$

$$\Delta\mu_i = \mu_i^{\text{real mix}} - \mu_i^{\text{ig mix}}$$

Define fugacity coefficient

$$\phi_k(T, P, y_j) = f_k / y_k P$$

$$\lim_{P \to 0} f_k = y_k P \qquad \lim_{P \to 0} \phi_k = 1$$

Fugacity better behaved then chemical potential, derivable from PvT / Z data or EOS.

Can also show

$$\left(\frac{\partial \ln \phi}{\partial T} \right) = - \left(\frac{h - h^{IG}}{RT^2} \right)$$

Gibbs-Helmholtz relation.

$$\left(\frac{\partial \ln \phi_i}{\partial T} \right) = - \left(\frac{\bar{h}_i - \bar{h}_i^{IG}}{RT^2} \right)$$

$$\left(\frac{\partial \ln \phi_i}{\partial P} \right) = \bar{v}_i^{res} / RT$$

Mixture EOS

EOS can capture mixture behavior

ex Virial EOS can be written in terms of pressure

$$Z = 1 + P\left(\frac{B}{RT}\right) + P^2\left(\frac{C - B^2}{(RT)^2}\right) + \cdots$$

Theory also shows $B = \sum_i \sum_j y_i y_j B_{ij}$ composition dependent

Compute or measure $B_{11}, B_{22}, B_{12} \cdots$

$$V = \frac{NRT}{P} + \frac{1}{N} \sum_i \sum_j N_i N_j B_{ij}$$

$$\bar{V}_k = \left(\frac{\partial V}{\partial N_k}\right) = \cdots$$

$$= \frac{RT}{P} + 2 \sum_i y_i B_{ik} - B$$

Suggests residual volume

$$\bar{V}_k - \bar{V}^{ig} = 2 \sum_i y_i B_{ik} - B = \bar{V}_k^{res}$$

For equilibrium calculations, want to know μ_k

Virial mixture EOS

$$\mu_k^{res}(T,P,\,) = \int_0^P \bar{v}_k^{res}\,dP$$

$$= \int_0^P \left(2\sum_i y_i B_{ik} - B\right) dP$$

$$= P\left(2\sum_i y_i B_{ik} - B\right)$$

$$f_k = y_k P \exp\left[P\left(2\sum y_i B_{ik} - B\right)/RT\right]$$

$$\phi_k(T,P,y_j) = \exp\left[P\left(2\sum y_i B_{ik} - B\right)/RT\right]$$

Same idea w/ more complex EOS

eg vdW

Lorentz-Berthelot mixing rules

$$b = \sum_i y_i b_i \qquad a = \sum_i \sum_j y_i y_j a_{ij} \qquad a_{ij} = \sqrt{a_i a_j}$$

for e.g. vdW EOS

$$\Rightarrow \ln \phi_i(T,v,x_i)$$

$$= \ln\left(\frac{v}{v-b}\right) + \frac{b_i}{v-b} - \frac{2\sqrt{a_i}\sum_j x_j\sqrt{a_j}}{vRT} - \ln Z$$

In general all this takes accurate EOS or PvT EOS data. Works well for gases, not as well for liquids.

May be hard to get mixture data.

Amagat's rule

Lewis fugacity rule $\hat{f}_i = y_i f$. Reliable if $\bar{v}_i \approx v$

$$\Rightarrow \mu_i(T,P,x_i) = \mu_i^*(T) + RT\ln x_i$$

pure i