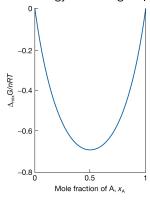
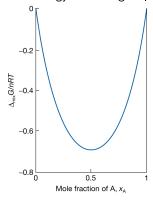


$$\mu = \mu^{\odot} + RT \ln p$$
  
Before mixing  $G_i = n_A \mu_A + n_B \mu_B$ 

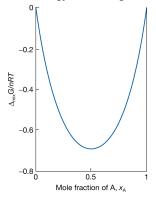


$$\mu = \mu^{\odot} + RT \ln p$$
  
Before mixing  $G_i = n_A \mu_A + n_B \mu_B$   
 $= n_A (\mu_A^{\odot} + RT \ln p) + n_B (\mu_B^{\odot} + RT \ln p)$ 



$$\mu = \mu^{\odot} + RT \ln p$$
Before mixing  $G_i = n_A \mu_A + n_B \mu_B$ 

$$= n_A \left( \mu_A^{\odot} + RT \ln p \right) + n_B \left( \mu_B^{\odot} + RT \ln p \right)$$
 $G_f = n_A \mu_A + n_B \mu_B$ 



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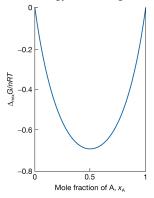
$$G_f = n_A \mu_A + n_B \mu_B$$

$$= n_A \left( \mu_A^{\odot} + RT \ln p_A \right) + n_B \left( \mu_B^{\odot} + RT \ln p_B \right)$$

$$\therefore \Delta_{\text{mix}} G = G_f - G_i$$

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$$= n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$



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$$= nRT (x_A \ln x_A + x_B \ln x_B)$$

Ex.: initial pressures not the same:

3.0 mol H<sub>2</sub> 1.0 mol N<sub>2</sub>

$$p$$
3.0 mol H<sub>2</sub> 1.0 mol N<sub>2</sub>

$$p(H_2) = 3p/2 \qquad p(N_2) = p/2$$

2p

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$$3.0 \text{ mol H}_2$$
  $1.0 \text{ mol N}_2$   
 $3p$   $p$   $1.0 \text{ mol N}_2$   
 $p(H_2) = 3p/2$   $p(N_2) = p/2$ 

2p

$$G_i = 3 \left( \mu_{H_2}^{\odot} + RT \ln 3p \right) + 1 \left( \mu_{N_2}^{\odot} + RT \ln p \right)$$

2p

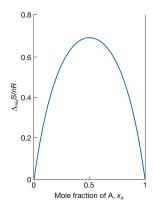
$$G_{i}=3 \left(\mu_{H_{2}}^{\odot}+RT \ln 3\rho\right)+1 \left(\mu_{N_{2}}^{\odot}+RT \ln \rho\right)$$

$$G_{f}=3 \left(\mu_{H_{2}}^{\odot}+RT \ln \frac{3}{2}\rho\right)+n_{B} \left(\mu_{N_{2}}^{\odot}+RT \ln \frac{\rho}{2}\right)$$

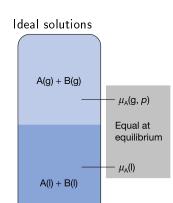
$$\therefore \Delta_{\text{mix}}G=G_{f}-G_{i}$$

$$=-4RT \ln 2 \stackrel{T=298}{=} -6.9 \text{kJ}$$

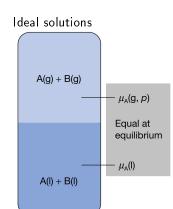
for a mixture of perfect gases initially at the same pressure,  $\Delta_{\text{mix}} S = -\left(\frac{\partial \Delta_{\text{mix}} G}{\partial T}\right)_{p,n_{A},n_{B}} = -nR\left(x_{A} \ln x_{A} + x_{B} \ln x_{B}\right)$ 



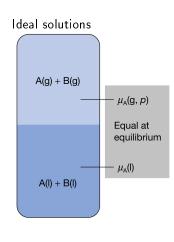
Ideal solutions A(g) + B(g) $\mu_A(g, p)$ Equal at equilibrium  $-\mu_{A}(I)$ A(I) + B(I)



```
*\equiv pure substance \mu_A^*=\text{chemical potential of pure A} \mu_A^*(\mathbf{I})=\text{chemical potential of pure liquid A}
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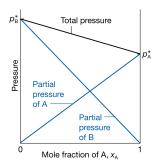


 $*\equiv$  pure substance  $\mu_A^*=\text{chemical potential of pure A}$   $\mu_A^*(\mathbf{I})=\text{chemical potential of pure liquid A}$   $\mu_A^*=\mu_A^\odot+RT\ln p_A^*$ 

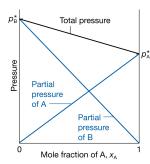


\* 
$$\equiv$$
 pure substance  $\mu_A^* =$  chemical potential of pure A  $\mu_A^*(\mathbf{I}) =$  chemical potential of pure liquid A  $\mu_A^* = \mu_A^{\odot} + RT \ln p_A^*$  soln. :  $\mu_A = \mu_A^{\odot} + RT \ln p_A$  or,  $\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$ 

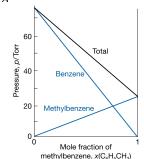
Ideal solutions - Raoult's law:  $p_A = x_A p_A^* \Longrightarrow \mu_A = \mu_A^* + RT \ln x_A$ 

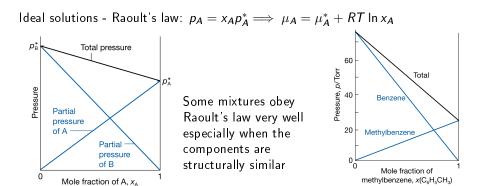


Ideal solutions - Raoult's law:  $p_A = x_A p_A^* \Longrightarrow \mu_A = \mu_A^* + RT \ln x_A$ 



Some mixtures obey Raoult's law very well especially when the components are structurally similar

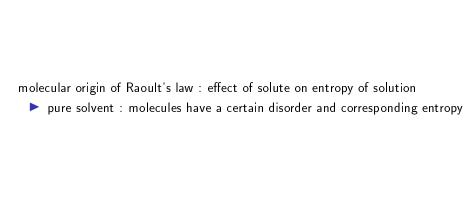


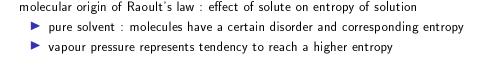


Mixtures that obey the law throughout from pure A to pure B are called ideal solutions

molecular origin of Raoult's law:

molecular origin of Raoult's law : effect of solute on entropy of solution	





molecular origin of Raoult's law: effect of solute on entropy of solution

vapour pressure represents tendency to reach a higher entropy

that a molecule chosen at random will be a solvent molecule

pure solvent: molecules have a certain disorder and corresponding entropy

solution : has a greater disorder than pure solvent because we cannot be sure

molecular origin of Raoult's law: effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy
   solution: has a greater disorder than pure solvent because we cannot be sure
- that a molecule chosen at random will be a solvent molecule  $S_{\text{soln}} > S_{\text{pure solvent}} \quad \therefore \text{ solution has lower tendency to acquire an even}$

higher entropy by solvent vaporizing

molecular origin of Raoult's law: effect of solute on entropy of solution

- pure solvent : molecules have a certain disorder and corresponding entropy
- vapour pressure represents tendency to reach a higher entropy
   solution: has a greater disorder than pure solvent because we cannot be sure
- that a molecule chosen at random will be a solvent molecule  $\ \ \, :: S_{\mathsf{soln.}} > S_{\mathsf{pure}\,\mathsf{solvent}} \quad \ \, :: \mathsf{solution} \,\,\mathsf{has} \,\,\mathsf{lower} \,\,\mathsf{tendency} \,\,\mathsf{to} \,\,\mathsf{acquire} \,\,\mathsf{an} \,\,\mathsf{even} \,\,\mathsf{higher} \,\,\mathsf{entropy} \,\,\mathsf{by} \,\,\mathsf{solvent} \,\,\mathsf{vaporizing}$
- > vapour pressure of solvent in solution < that of pure solvent



#### Ideal-dilute solutions

although vapour pressure of solute  $\propto$  mole fraction constant of proportionality

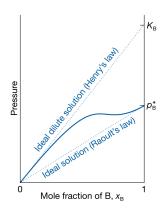
≠ vapour pressure of pure substance

#### Ideal-dilute solutions

although vapour pressure of solute  $\infty$  mole fraction constant of proportionality  $\neq$  vapour pressure of pure substance Henry's law:  $p_B = x_B K_B$ 

#### Ideal-dilute solutions

although vapour pressure of solute  $\infty$  mole fraction constant of proportionality  $\neq$  vapour pressure of pure substance Henry's law:  $p_B = x_B \, K_B$  For practical applications, expressed in terms of molality, b,  $p_B = b_B \, K_B$ 



Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are

called ideal-dilute solutions

Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are

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and solvent at low concentrations?

why this difference in behaviour of solute

Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

why this difference in behaviour of solute and solvent at low concentrations?

solute molecules are surrounded by solvent molecules, which is entirely different from

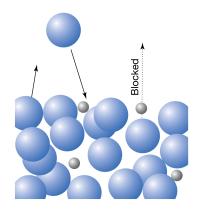
their environment when pure

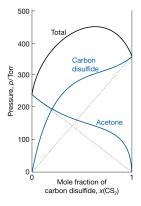
Mixtures for which solute obeys Henry's law and solvent obeys Raoult's law are called ideal-dilute solutions

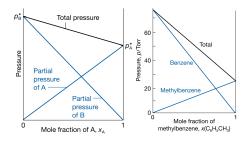
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solute molecules are surrounded by solvent molecules, which is entirely different from their environment when pure

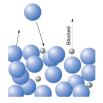
solvent behaves like a slightly modified pure liquid, but the solute behaves entirely differently from its pure state unless the solvent and solute molecules happen to be very similar

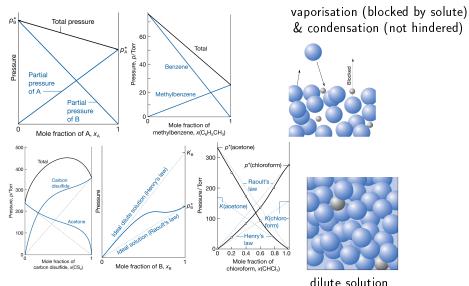






vaporisation (blocked by solute) & condensation (not hindered)





solvent mols - similar environ as pure liq. solute mols - very different environ

