Mass transfer and separation

Lecture 2

Course work

- Mark
- Deadline
- Task

Recap – physical equilibria and phase diagrams

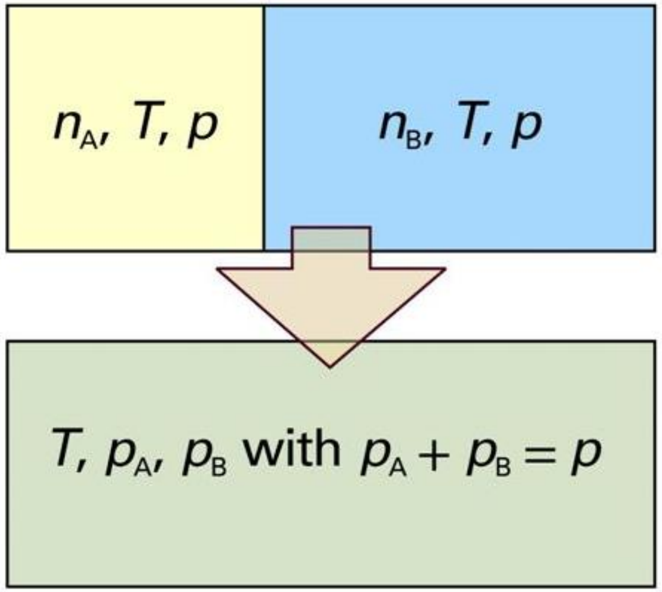
Objectives

- Ideal mixtures
- Raoult’s law
- Henry’s law
- Colligative properties
- Real solutions

Ideal mixtures

- Mixtures are a hugely important aspect of chemical processes
  - Chemical reactions start when reactants are mixed and products are also typically mixtures.
  - Even mixtures of unreactive substances are important, *cf.* the presence of a solute may affect their physical properties (example?)
- The key idea is that changes in the TD properties on mixing of substances are established through the consideration of how μ of each component changes with composition.
- You need to know what μ is, and how G varies with T and p.

Mixing perfect gases



n_A, T, p

n_B, T, p

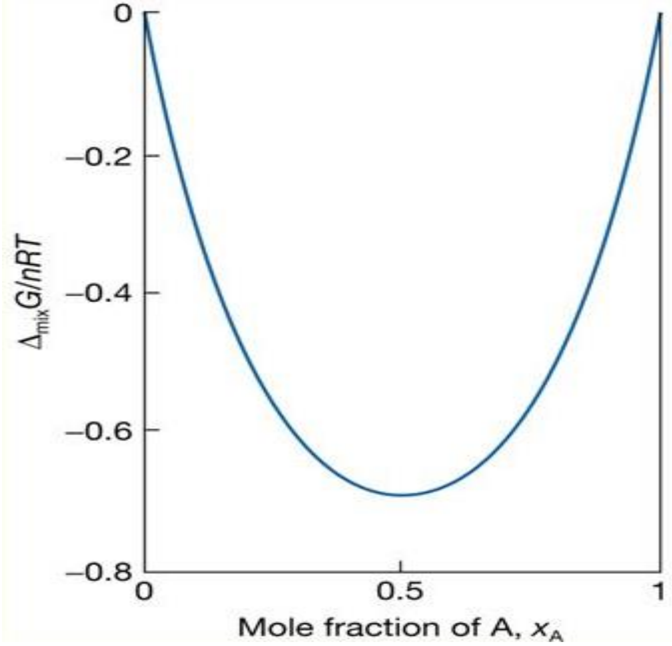
T, p_A, p_B with $p_A + p_B = p$

- Gibbs energy of mixing:
  - Amounts of 2 perfect gases in 2 containers: n_A & n_B
  - They both are at T & p.
  - Their μ have their 'pure' values, $G_m(p) = G_m^{\emptyset} + RT\ln(p/p^{\emptyset})$ (perfect gas) and μ_J=$G_m(J)$
  - For each J gas: $\mu_J = \mu_J^{\emptyset} + RT\ln p/p^{\emptyset}$, $\mu_J^{\emptyset}$ - std chemical potential, *i.e.* μ of pure gas J at 1 bar.
  - The initial total G for the total system is given by $G=n_A\mu_A+n_B\mu_B$ as $G_i = n_A\left(\mu_A^{\emptyset} + RT\ln p/p^{\emptyset}\right) + n_B\left(\mu_B^{\emptyset} + RT\ln p/p^{\emptyset}\right)$.
  - After mixing, the partial pressure of gases are p_A and p_B with $p_A+p_B=p$, the total G changes to $G_f = n_A\left(\mu_A^{\emptyset} + RT\ln p_A/p^{\emptyset}\right) + n_B\left(\mu_B^{\emptyset} + RT\ln p_B/p^{\emptyset}\right)$.
- The difference of G_f and G_i is the Gibbs energy of mixing;

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

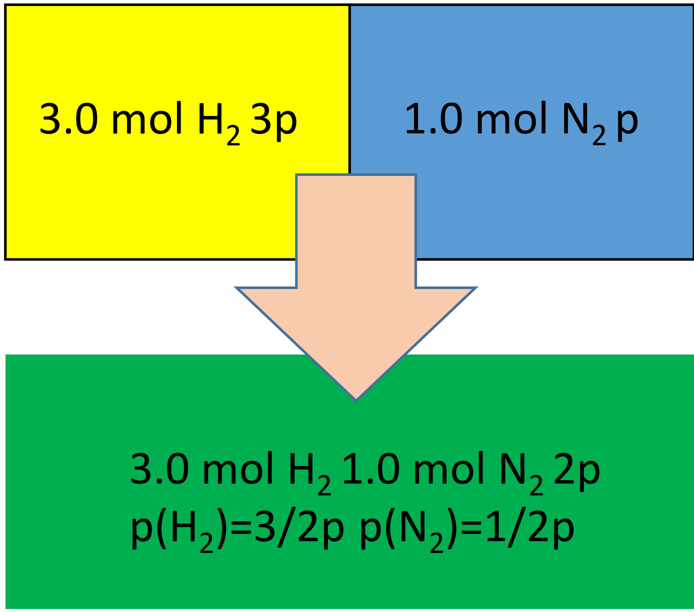
$\Delta_{mix}G$

- $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$, *x*-mole fraction
- $x \le 1$ → logs are negative → $\Delta_{mix}G<0$, *i.e*. mixing of perfect gases is always spontaneous.



Calculating the Gibbs energy of mixing

- Container at 25 °C divided into 2 equal parts contains:
- Calculate the Gibbs energy of the mixing
  - assuming perfect behaviour
- Hint: Note that initial pressures are different.
- Calculate μs then G for the system
- Use $G = n_A\left(\mu_A^{\ominus} + RT \ln p/p^{\ominus}\right) + n_B\left(\mu_B^{\ominus} + RT \ln p/p^{\ominus}\right)$



3.0 mol H_2 3p

1.0 mol N_2 p

3.0 mol H_2 1.0 mol N_2 2p

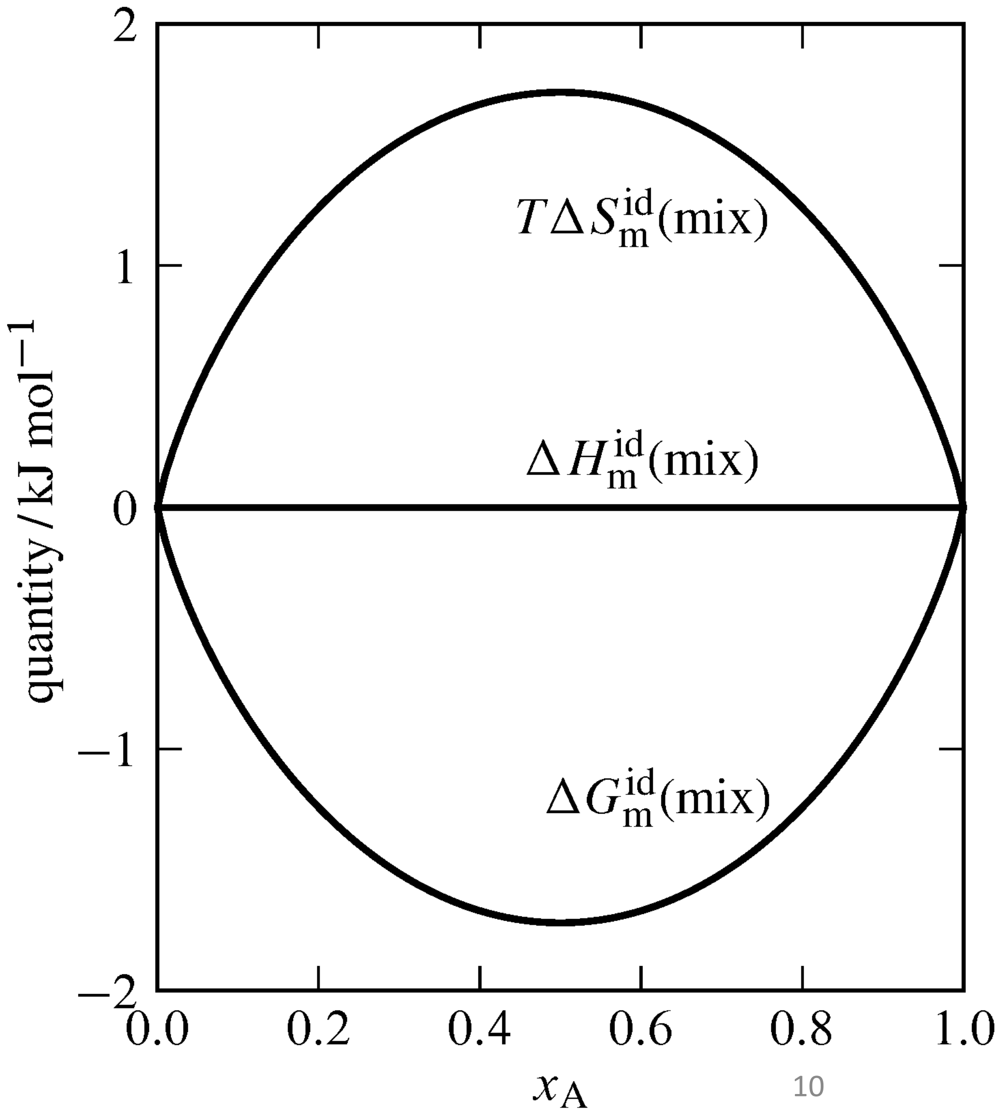
p(H_2)=3/2p p(N_2)=1/2p

Calculating the Gibbs energy of mixing

- $G_i = (3.0\ \text{mol})\left(\mu^{\emptyset}(\text{H}_2) + RT\ln\left(\frac{3p}{p^{\emptyset}}\right)\right) + (1.0\ \text{mol})\left(\mu^{\emptyset}(\text{N}_2) + RT\ln\left(\frac{p}{p^{\emptyset}}\right)\right)$
- When the partition is removed the partial pressure of H_2 falls to 3/2 *p* and that of N_2 to 1/2 *p*
- $G_f = (3.0\ \text{mol})\left(\mu^{\emptyset}(\text{H}_2) + RT\ln\left(\frac{3p}{2p^{\emptyset}}\right)\right) + (1.0\ \text{mol})\left(\mu^{\emptyset}(\text{N}_2) + RT\ln\left(\frac{p}{2p^{\emptyset}}\right)\right)$
- $\Delta_{mix}G = (3.0\ \text{mol})\text{RT}\ln\left(\frac{\frac{3}{2}p}{3p}\right) + (1.0\ \text{mol})\text{RT}\ln\left(\frac{\frac{1}{2}p}{p}\right) = -(3.0\ \text{mol})\text{RT}\ln 2 - (1.0\ \text{mol})\text{RT}\ln 2 = -(4.0\ \text{mol})\text{RT}\ln 2 = -6.9\ \text{kJ}$
- The mixing energy is the sum of two contributions; mixing itself and the changes in pressure.

Entropy and enthalpy of mixing

- $\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)$, sub $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$
- $\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$, it follows that $\Delta_{mix}S>0$.
- $\Delta G = \Delta H - T\Delta S$.
- $\Delta_{mix}H = 0$.
  - This should be expected from a system in which there are no interactions between the MQs.
  - The driving force therefore is the entropy.

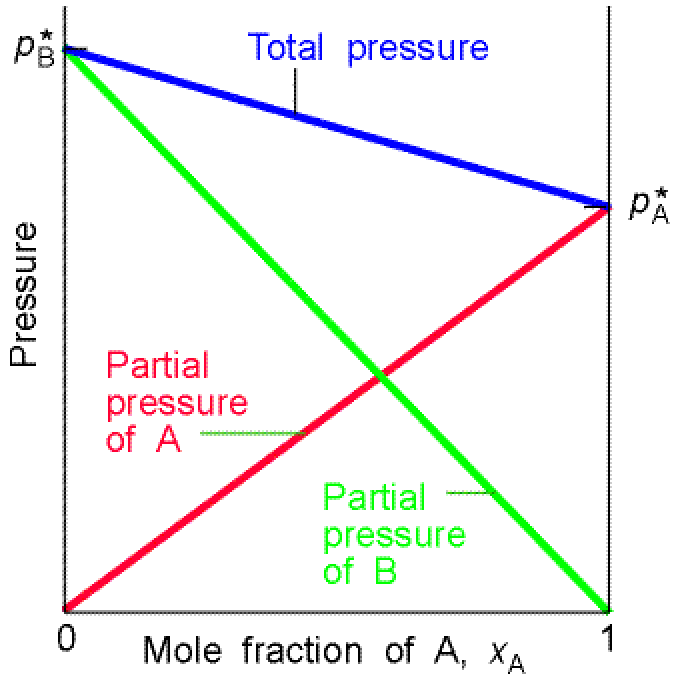


Mixing of liquids

- How *G* varies w composition. To calculate its value we make use of μ of a substance present as a vapour being the same as that as a liquid in equilibrium.
- Chemical potential of pure A: $\mu_A{}^*$ and $\mu_A{}^*(\mathrm{l})$ for a liquid; vapour pressure of pure liquid is $p^*{}_A$.
- $G_m(p) = G_m^\emptyset + RT\ln p/p^\emptyset$, with $\mu = G_m$
- $\mu_A^*(l) = \mu_A^\emptyset + RT\ln p_A^*/p^\emptyset$. If another substances is added A is no longer pure, *i.e.* $\mu_A(l) = \mu_A^\emptyset + RT\ln p_A/p^\emptyset$, as the vapour and solvent are still in equilibrium.
- To eliminate $\mu_A^\emptyset$ we combine them as $\mu_A(l) = \mu_A^*(l) - RT\ln\frac{p_A^*}{p^\emptyset} + RT\ln\frac{p_A}{p^\emptyset} = \mu_A^*(l) + RT\ln\frac{p_A}{p_A^*}$.

Raoult’s law

- $\mu_A(l) = \mu_A^*(l) + RT \ln \frac{p_A}{p_A^*}$
- Considering that the ratio of vapour pressures and the composition of the liquid, François Raoult found that $\frac{p_A(g)}{p_A^*} \approx x_A(l)$.
- Raoult’s law: $p_A = x_A * p_A^*$.
- Mixtures that obey Raoult’s law are ideal solutions.
- It is a good estimate for dilute solutions.



Raoult's law

- The vapour pressure of benzene at 20 °C is 75 Torr (9999.18 Pa) and that of methylbenzene is 21 Torr (2799.77 Pa) at the same T.
- In an equimolar mixture, *i.e.* $x_{\mathrm{benzene}}=x_{\mathrm{methylbenzene}}=1/2$, calculate the partial pressures of the two components.

Answer

- p_{benzene}=1/2*75 Torr = 38 Torr
- $p_{\text{methylbenzene}}$=1/2*21 Torr = 11 Torr.
- The total vapour pressure of the mixture is 49 Torr.
- The mole fractions of the in the vapour are $x_{\text{vap,benzene}}$=38 Torr/49 Torr
- As the partial pressure of a gas J is defined as $p_J=x_Jp$, $x_{\text{vap,benzene}}$=(38 Torr)/(49 Torr)=0.78, and $x_{\text{vap,methylbenzene}}$=(11 Torr)/(49 Torr)=0.22.
- i.e. $x_A+x_B=1$.

Origin of Raoult's law

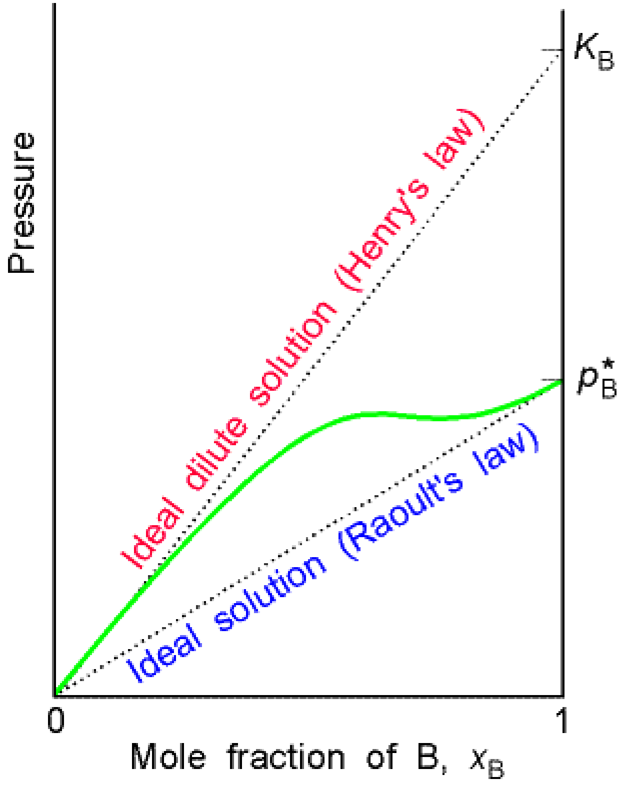
- Effect of the solute on the entropy of the solution.
- In a pure solvent the MQs have a certain disorder and corresponding S, with p_{vap} representing the tendency of the system and its surroundings to reach higher S.
- When a solute is present, the solution has a greater disorder, *i.e.* ↑S (vis-à-vis pure solvent), the solution has a lower tendency to acquire an even higher S by vaporisation, *i.e.* its p_{vap}↓.

Henry's law

- In an ideal solution both solute and solvent obey Raoult's law.
- However, for real solutions at low *c*, William Henry found that although p_{vap}(solute) α *x*(solute), the constant of proportionality is not the p_{vap} of the pure substance p^*.
- Henry's law: $p_B = x_B K_B$, where K_B is an empirical constant.
  - In practice polynomial data fitting is applied.
- In terms of molality: $p_B = b_B K_B$.

Origin of Henry's law

- Mixtures in which the solvent obeys Raoult's law and the solute Henry's law are called ideal-dilute solutions.
- The difference in behaviour between of the solute and solvent arises from the fact that in a dilute solution the solvent MQs are very much in a surrounding as in the pure liquid, whereas the solute MQs are surrounded by solvent MQs.
- The solvent behaves like a slightly modified pure solvent but the solute behaves entirely differently from its pure state.



Thermodynamics of ideal solutions

- *G* of mixing 2 liquids to form an ideal solution is calculated in the same way as for 2 gases; $G_i = n_A \mu_A^* + n_B \mu_B^*$ before mixing and $G_f = n_A(\mu_A^* +$

Colligative properties

- Colligative properties of solutions depend only on the number of solute particles, result from the effect of the solute on the μ of the solvent.
- Remember the concept of μ and its role as a criterion of equilibrium between phases.
- The presence of a solute modifies the physical properties of the solvent, *cf.* p_{vap}, T_{boil}, T_{melt}.
- It also introduces a new property; the osmotic pressure.
- In dilute solutions these properties only depend on he # of solute particles, not their nature, whence the name colligative properties.

The origin of colligative properties

- Stem from the reduction of μ(l) as a result of the presence of solute.
- For an ideal-dilute solution the reduction is from μ_A^* of the pure solvent to $\mu_A^* + RT\ln x_A$ when a solute is present
  (N.B. $RT\ln x_A < 0$ as $x_A < 1$).
- Solute is assumed to be non-volatile and insoluble in the solid solvent so it is only present in the liquid phase, *i.e.* no direct influence on μ.
- $\downarrow\mu$ implies that liquid-vapour equilibrium occurs at $\uparrow T$ and the solid-liquid equilibrium at $\downarrow T$.

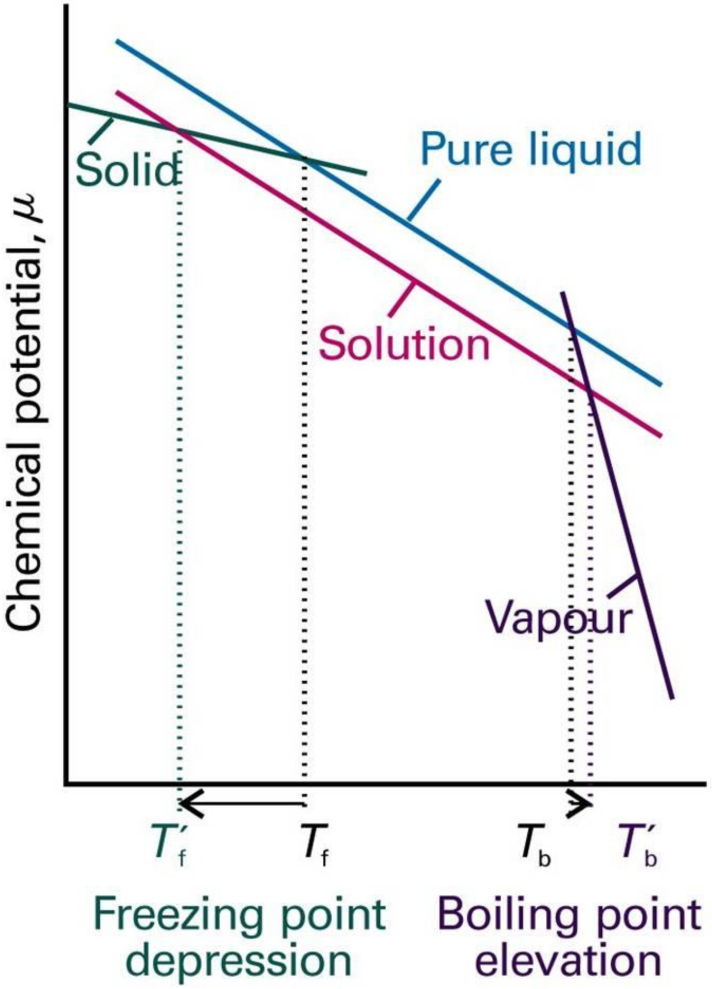


Figure 5-21
Atkins Physical Chemistry, Eighth Edition
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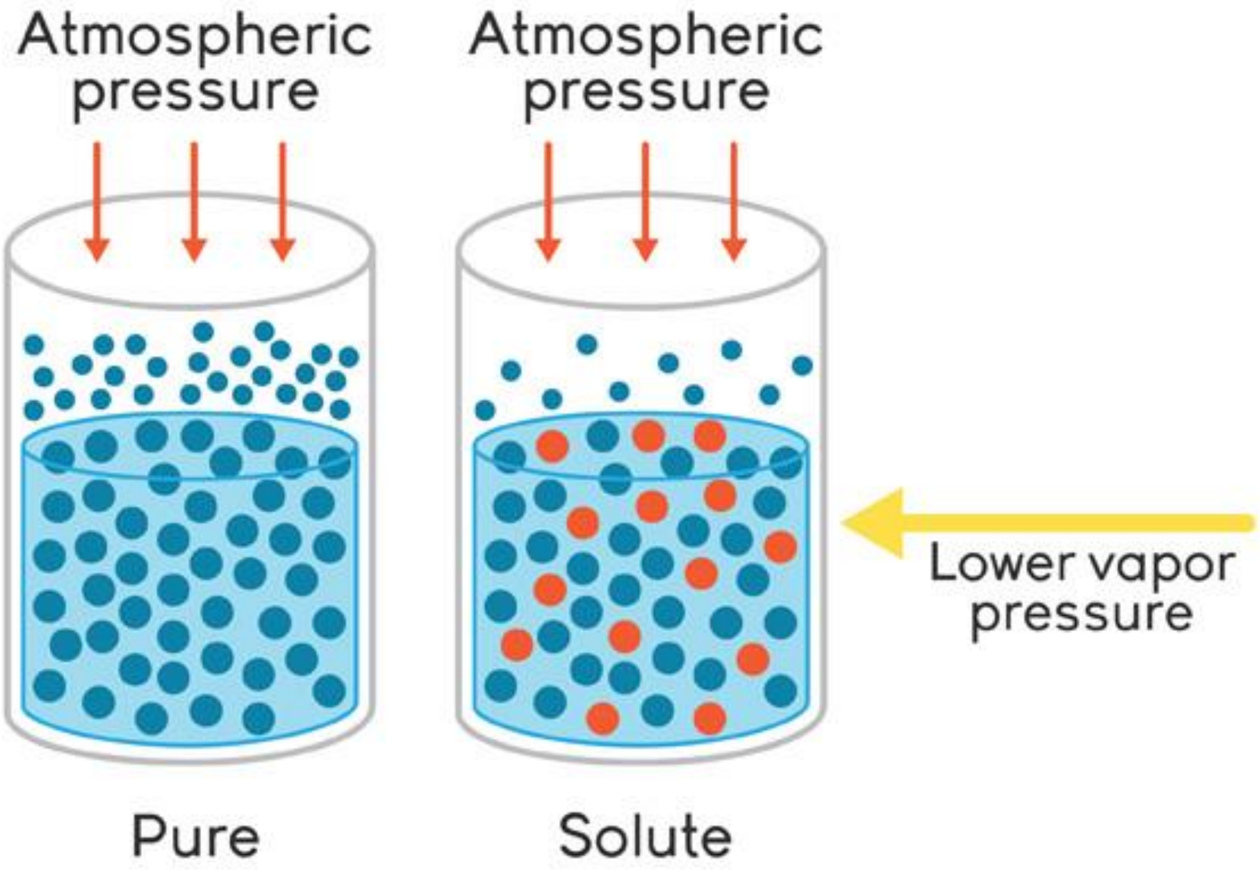
The molecular origin of colligative properties

- ↓μ - effect of the solute on the entropy of the solution.
- Pure liquid solvent has a characteristic S and its p_{vap} reflects the tendency of the system towards greater S, which may be achieved through the vaporisation of the liquid.
- When a solute is present the additional contribution to the S of the liquid results in a weaker tendency for vaporisation.
- ↓p_{vap}(solvent) and ↑T_{boil}.
- Similarly, the enhanced MQlar randomness of the solution opposes the tendency to freeze →↓T_{melt}.

Illustration of the vapour pressure change in solutions



If vessel closed: $p_A{}^*$ p_A

TD analysis of the depression of the freezing point and elevation of the boiling point

- $\Delta T_f = K_f b$, b – molality of the solute, K_f - cryoscopic constant
- $\Delta T_b = K_b b$, K_b - ebullioscopic constant
- Importance is rather small.
- When assessing colligative properties we focus on the solute particles present, not their identity.
- When solute is ionic it gives rise to both cationic and anionic solutes.

Cryoscopic and ebullioscopic effects

- For water as solvent K_f=1.86 K kg mol^{-1} and K_b=0.513 K kg mol^{-1}.
- Therefore in solution in which the molality of a non-electrolyte (*cf.* glucose) is 0.10 mol kg^{-1}.
- Determine the extent of freezing point depression and boiling point elevation in the above system.

Answer

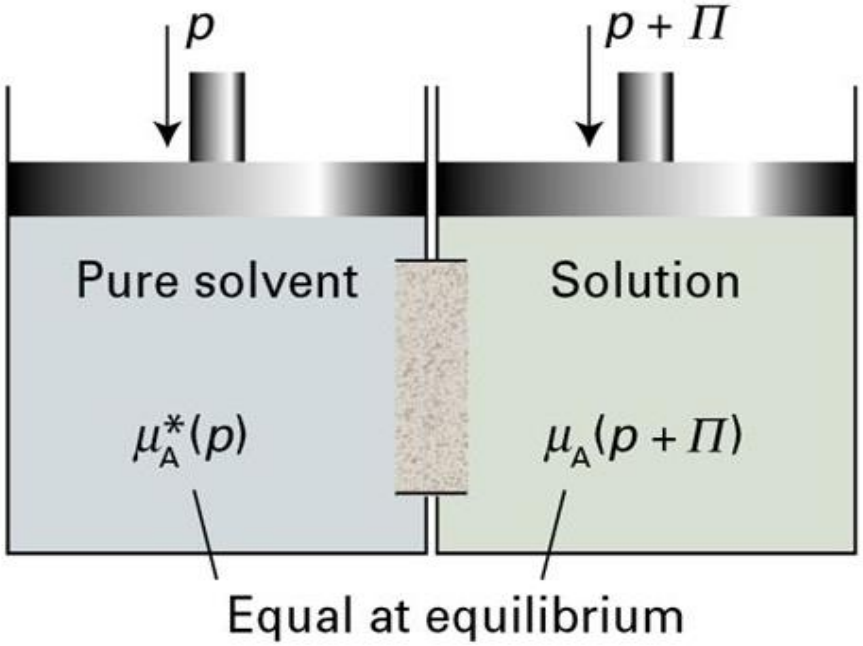
- ΔT_f=(1.86 K kg mol^{-1})*(0.10 mol kg^{-1}) = 0.19 K
- ΔT_b=(0.513 K kg mol^{-1})*(0.10 mol kg^{-1})= 0.051 K.

Application: freezing point depression

- Antifreeze in engines
- Antifreeze is used in much higher concentration that can justify its effect as a colligative property.
    - Use of salt on highways
- Its effect is to interfere with the solidification of water MQs.

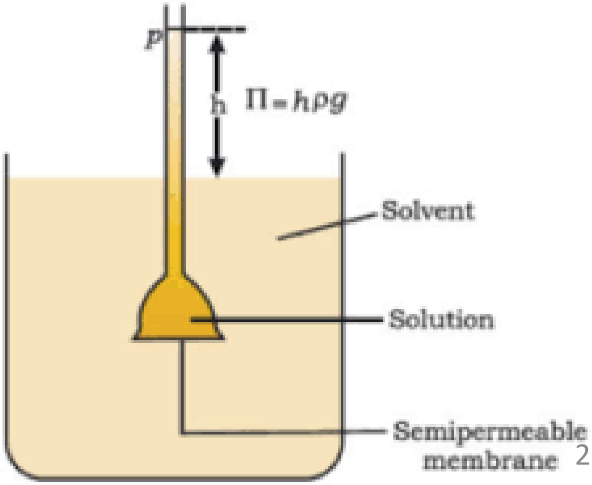
Osmosis

- The only colligative property of real importance is osmosis, the spontaneous passage of a pure solvent into a solution separated from it by a semipermeable membrane.
- The osmotic pressure, Π, is the pressure that must be applied to the solution to stop the influx of solvent.
- Important examples of osmosis include the transport of fluids through cell membranes, dialysis, osmometry (determination of molar mass by Π measurement), and energy generation.



Osmotic pressure

- In measuring Π, opposing pressure arises from the column of the solution that the osmosis itself produces.
- Equilibrium is reached when the hydrostatic pressure of the column of solution matches Π.
- Complication arises from the solvent entering the solution results in its dilution.



TD treatment of osmosis: The van’t Hoff equation

- At equilibrium, μ(solvent) must be the same on each side of the membrane.
- ↓ μ(solvent) by the solute but it is restored to its ‘pure’ value by the application of *p*.
- On the pure solvent side, at *p* pressure the μ is $\mu_A^*(p)$.
- On the solution side, μ is lowered by the presence of the solute, which reduces the molar fraction of the solvent from 1 to x_A.
- The chemical potential of A is raised on account of the greater pressure, $p+\Pi$, that the solution experiences.
- At equilibrium, μ of A is the same on both sides: $\mu_A^*(p) = \mu_A(x_A, p+\pi)$
- The presence of solute is taken into account as: $\mu_A(x_A, p+\pi) = \mu_A^*(p+\pi) + RT \ln x_A$.

The van’t Hoff equation

- As $\left(\frac{\partial \mu_A}{\partial p}\right)_T = V_{A,m}$ for pure A we can write dμ_A=$V_{A,m}$dp, and on integration we obtain: $\mu_A^*(p+\pi) = \mu_A^*(p) + \int_p^{p+\pi} V_m \, \mathrm{d}p$, where V_m is the molar volume of the pure solvent A.
- We can assume this to be negligibly different from its partial volume, $V_{A,m}$ and combine the above equations to $-RT \ln x_A = \int_p^{p+\pi} V_m \, \mathrm{d}p$.
- This enables the calculation of the additional pressure, Π, that must be applied to restore μ of the solvent to its pure value and thus restore the equilibrium across the membrane.
- For dilute solutions $\ln x_A = \ln(1 - x_B) \approx -x_B$.
- We may also assume that the pressure range on integration is so small that V_m is constant, so it may be taken outside of the integral giving $RTx_B = \pi V_m$.
- When solution is dilute, $x_B \approx n_B/n_A$ and as $n_A V_m = V$, we get
- Π=[B]RT, the van’t Hoff equation, where [B]=n_B/V, is the molar concentration of the solute.

The van’t Hoff equation

- We saw previously that 0.10 mol kg^{-1} non-electrolyte solution only has tiny effects on the freezing and boiling points of water.

- Calculate the osmotic pressure of the same solution at 25 °C, assuming that the molar concentration is 0.10 mol dm-3, corresponding to $1.0*10^2$ mol m^{-3}. [1 J m^{-3}=1 Pa]

- What height would this osmotic pressure drive water?

Answer

- Π=(1.0*10^2 mol m^{-3})*(8.3145 J K-1 mol^{-1})*(298 K)=2.5*10^5 J m^{-3}.
- i.e. 2.5 bar
- This would drive water to a height of 25 m.

Real solutions

- In real solutions the intermolecular and interionic interactions need to be taken into account to describe their TD properties accurately.
- In ideal solutions A-A, A-B and B-B interactions, where A denotes the solvent and B the solute, were all considered to be the same.
- In the case of real solutions however these interactions may differ, *cf*. ΔH and ΔV on mixing, S contribution.
- If ΔH is large and +ve, or if ΔS is adverse (*i.e.* the re-organisation of the MQs results in an orderly mix, any ideas what this may look like?), ΔG will be +ve, *i.e.* the separation of the mix will be spontaneous and the liquids are immiscible.
- Liquids may be partially miscible, i.e. miscible over a certain range of compositions.

Activities

- Real solutions differ from ideal solutions as a result of differences in the intermolecular interactions between their components and how the MQs aggregate.
- These differences are taken into account by replacing the concentrations in expression for μ by effective concentrations known as activities.

Solvent activity

- Consider $\mu_A(l) = \mu_A^* + RT \ln p_A/p_A^*$, where p_A^* is the vapour pressure of pure A and p_A is the vapour pressure of A when it is a component of the solution.
- For an ideal solution the solvent obeys Raoult’s law at all concentrations and we can express this as $\mu_A = \mu_A^* + RT \ln x_A$.
- Even if the solution does not obey Raoult’s law the above formalism may be preserved as $\mu_A = \mu_A^* + RT \ln a_A$, where a_A denotes the solvent activity, a kind of an ‘effective’ mole fraction.
- As equation is true both for ideal and non-ideal solutions $a_A = p_A/p_A^*$.
- It follows that the activity of a pure substance is 1.

Solvent activity

- The vapour pressure of 0.500 M KNO_3 (aq) at 100 °C (when the vapour pressure of water is 1 atm, *i.e.* 101.3 kPa) is 99.95 kPa.
- What is the activity of water in the above solution at this temperature?

Answer

- a_A=(99.95 kPa)/(101.3 kPa) = 0.9867

Solvent activity

- Because all solvents obey Raoult's law ($p_A/p_A^* = x_A$) increasingly closely as the concentration of solute →0, the $a_A \rightarrow x_A$ as $x_A \rightarrow 1$.
- To express this we introduce the activity coefficient, γ: $a_A = \gamma_A x_A$; $\gamma_A \rightarrow 1$ as $x_A \rightarrow 1$ at all T and p.
- μ of the solvent is: $\mu_A = \mu_A^* + RT \ln a_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$, and all deviation from ideal may be expressed in the term.
- The std state of the solvent, the pure liquid solvent at 1 bar, is established when x_A=1.

Solute activity

- The problem with defining activity coefficients & std states for solutes is that they approach ideal—dilute behaviour (Henry's law) as $x_B \rightarrow 0$, not 1.
- The vapour pressure of a solute B that satisfies Henry's law is given by $p_B = K_B x_B$, where K_B is an empirical constant.
- From the general expression $\mu_B = \mu_B^* + RT \ln p_B / p_B^*$, we get $\mu_B = \mu_B^* + RT \ln \frac{K_B x_B}{p_B^*} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B$.
- Both K_B and p_B^* are characteristics of the solute independent of its abundance, so term may be combined with term to give a new std μ, $\mu_B^\emptyset = \mu_B^* + RT \ln \frac{K_B}{p_B^*}$, *i.e.* the std chemical potential of the solute.

Solute activity

- If the solution is ideal $K_B = p_B^*$ so $\mu_B^\emptyset = \mu_B^*$. μ_B in an ideal dilute solution therefore is $\mu_B = \mu_B^\emptyset + RT \ln x_B$.
- If we deviate from the ideal-dilute behaviour we get $\mu_B = \mu_B^\emptyset + RT \ln a_B$.
- As the std state remains unchanged, all deviations from 'ideal' are captured in a_B, obtained as $a_B = p_B / K_B$.
- We introduce the activity coefficient: $a_B = \gamma_B x_B$, so all deviations from 'ideal' to be captured in γ_B. ($\mu_B = \mu_B^\emptyset + RT \ln x_B + RT \ln \gamma_B$)
- Because all solute obeys Henry's law as its concentration $x_B \rightarrow 0$, $a_B \rightarrow x_B$ and $\gamma_B \rightarrow 1$ as $x_B \rightarrow 0$.

Model system: regular solutions

- TD properties of real solutions are normally expressed in terms of excess function, X^{E}, *i.e.* the difference between the observed TD function of mixing & the function for an ideal solution;

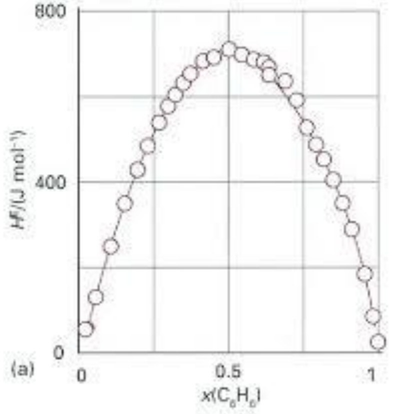
$S^{\mathrm{E}}=\Delta_{\mathrm{mix}}S-\Delta_{\mathrm{mix}}S^{\mathrm{ideal}}$, where $\Delta_{\mathrm{mix}}S^{\mathrm{ideal}}=-nR(x_{\mathrm{A}}\ln x_{\mathrm{A}}+x_{\mathrm{B}}\ln x_{\mathrm{B}})$.

- H^{E} & V_{mix}^{E} both = observed H & V_{mix}, as the ideal values are 0. Deviations from 0 indicate the extent to which the solutions are not ideal.
- In this connection a useful model system is the regular solution, for which $H^{\mathrm{E}}\neq 0$ and $S^{\mathrm{E}}=0$.
  - 2 kinds of MQs are distributed randomly, as in an ideal solution, but have different interaction energies.

Regular solutions

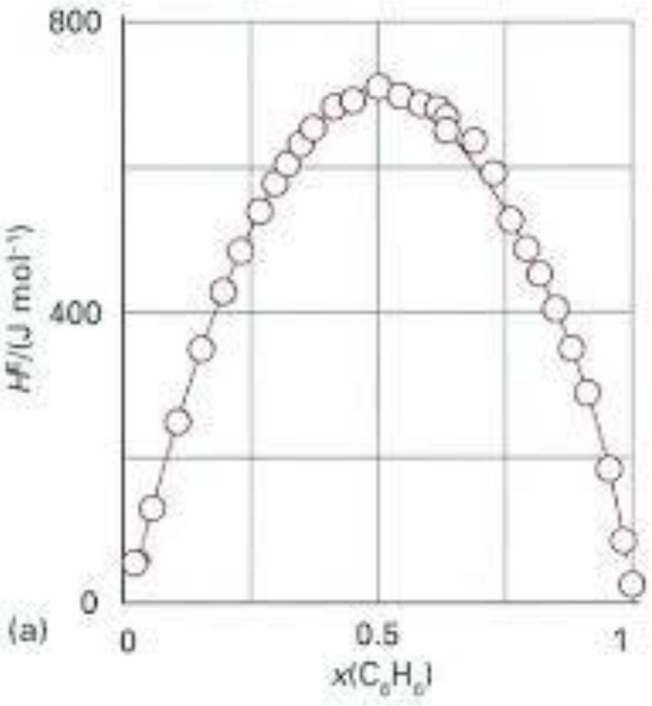
- Quantitative expression of regular solution model: $H^E = n\xi RT x_A x_B$, where ξ is a dimensionless parameter that is a measure of the energy of the A-B interactions relative to the A-A and B-B interactions. For an ideal solution $\xi=0$.
- If $\xi<0$: mixing is exothermic
  - solute-solvent are more favourable than solvent-solvent and solute-solute ones
- if $\xi>0$: mixing is endothermic.
- As, for a regular solution, the ΔS_{mix} has its ideal value, excess Gibbs energy=excess enthalpy; $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B)$, with $x_B = 1 - x_A$.

Benzene-cyclohexane



Regular solutions

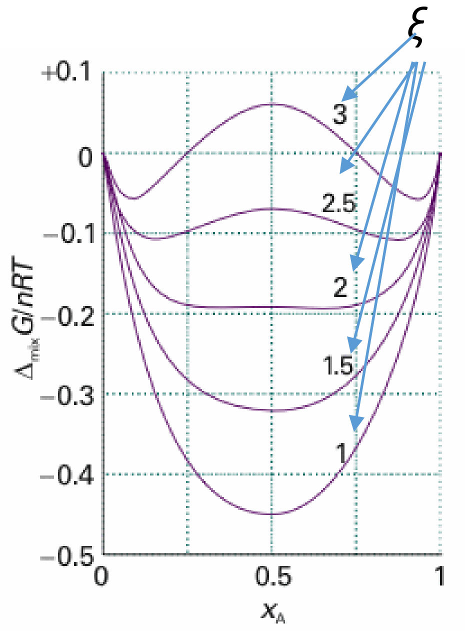
- When $x_A=x_B=1/2$, the excess enthalpy is $H^{E/n}=1/4\xi RT$ (molar).
- Determine ξ for the benzene-cyclohexane mixture.



Answer

- As H^E is *ca.* 700 J (from the graph), using $H^E=1/4\xi RT$ we can express $\xi= 4*H^E/(RT)$=(4*700 J mol-1)/(8.314 J K^{-1} mol^{-1} * 298 K)=1.13

Regular solutions



- $\Delta_{mix}G$ varies with composition for different ξ.
  - For $\xi>2$ ∃ 2 minima separated by a maximum. This implies that for $\xi>2$ the system will spontaneously separate into 2 phases with compositions corresponding to the 2 minima.
  - The concentration of the 2 phases are given by using the expression $\ln\frac{x_A}{1-x_A}+\xi(1-2x_A)=0$. (This can also be extended to determine T_{uc}).
- We will see how the concept of a regular solution gives further insight into the origin of deviations from Raoult's law and its relation to γ.
- For a regular solution modelled by the parameter ξ the activity coefficients are given by the Margules equations:

$$\ln\gamma_a=\xi x_B^2 \text{ and } \ln\gamma_B=\xi x_A^2$$

Margules equations

- $\Delta_{mix}G = nRT(x_A \ln a_A + x_B \ln a_B)$ for non-ideal solutions
- As $a_i = x_i\gamma_i$: $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B)$
- Using the Margules equations and as $x_A + x_B = 1$:

$\ln \gamma_a = \xi x_B^2$ and $\ln \gamma_B = \xi x_A^2$

$$\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B + \xi x_A x_B^2 + \xi x_B x_A^2) =$$
$$nRT\{x_A \ln x_A + x_B \ln x_B + \xi x_A x_B (x_B + x_A)\} = nRT(x_A \ln x_A +$$

Vapour pressure of regular solutions

- As a_A is the ratio for the vapour pressure of A in the solution to the vapour pressure of pure A: $p_A = a_A p_A^* = \{e^{\xi(1-x_A)^2} x_A\} p_A^*$.
  - ξ=0, *i.e.* ideal solution, this corresponds to a linear function.
  - ξ>0 (endothermic mixture): vapour pressure>ideal
  - ξ<0 (exothermic mixture): vapour pressure<ideal
  - As $x_A \rightarrow 1$ (pure substance) the functions also become more linear, in accordance with Raoult's law.
  - When $x_A \ll 1$ $p_A \rightarrow x_A e^{\xi} p_A^*$. This expression has the form of Henry's law when $K = e^{\xi} p_A^*$, which is different to each solute-solvent system.

Vapour pressure of regular solutions

- The vapour pressure of benzene at 25 °C is 13.8 kPa.
- For a mixture of benzene and cyclohexane at the above temperature we know that ξ=1.13.
- Calculate the value of Henry's law constant for benzene in this mixture.

Answer

- $K = e^{1.13} * 13.8$ kPa = 42.7 kPa

Model system: ionic solutions

- Solutions of ionic compounds are central to much of the chemical industry.
- The Coulombic interactions are so strong that the approximation of replacing activities by mole fractions or molalities is only valid in very dilute solutions.
- We need to pay attention to the activities of ions in solution.
- !μ_+ - μ of cation M^+ and μ_- - μ of anion X^-
- $G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$
- For a real solution in which M^+ and X^- are the same molality (think of NaCl).
- $G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT\ln\gamma_+ + RT\ln\gamma_- = G_m^{ideal} + RT\ln\gamma_+\gamma_-$, all the deviations from 'ideal' are in the term.

Mean activity coefficient

- Experimentally $\gamma_+\gamma_-$ cannot be separated into cationic and anionic contributions. Therefore, for an electrolyte of MX we can introduce the mean activity coefficient, $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$.
- $\mu_+ = \mu_+^{ideal} + \mathrm{RT}\ln\gamma_\pm$ and $\mu_- = \mu_-^{ideal} + \mathrm{RT}\ln\gamma_\pm$
- In general, for a compound of M_pX_q: $G_m = p\mu_+ + q\mu_- = G_m^{ideal} + pRT\ln\gamma_+ + qRT\ln\gamma_-$
- With the introduction of the mean activity coefficient: $\gamma_\pm = (\gamma_+^p\gamma_-^q)^{1/s}$; $s = p + q$
- $\mu_i = \mu_i^{ideal} + \mathrm{RT}\ln\gamma_\pm$, mean ionic chemical potential

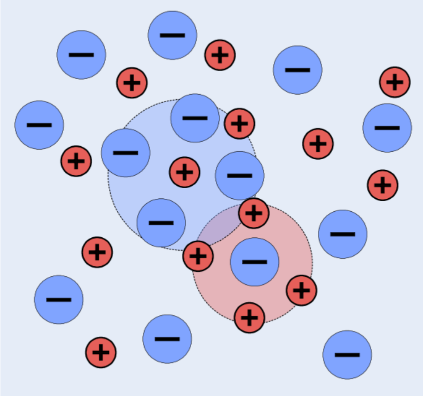
Mean activity coefficient

- In a certain solution of $CaCl_2$, the activity coefficient of the Ca^{2+} and Cl^- ions were calculated as 0.874 and 0.981, respectively.
- What are p, q and s for this solute?
- What is the mean activity coefficient?

Answer

- $p=1$; $q=2$ and $s=3$.
- $\gamma_{\pm}=\{(0.874)(0.981)^2\}^{1/3} = 0.944$

The Debye-Hückel theory



- The long range and strength of Coulombic interactions between ions mean that this is likely to be the primary reason for any departure from ‘ideal’ in ionic solutions and to dominate all further contributions to ‘non-ideal’.
- This domination is the basis of the Debye-Hückel theory.
  - Oppositely charged ions attract each other → anions are more likely found near cations and vice versa.
  - Overall, the solution is neutral but near any ion there is an excess of counter-ions, so averaged on time, counter-ions are likely to be found around any given ion.
  - This time averaged spherical haze around the central ion has a magnitude equal but of opposite charge to the central ion’s, and it is called ionic atmosphere.
  - G & μ therefore ↓ because of these interactions
    - We look at the departure of G_{m} from G_m^{ideal}, which is identified with $\mathrm{RT}\ln\gamma_\pm$.

Debye-Hückel limiting law

- At very low concentrations the activity may be therefore calculated from the Debye-Hückel limiting law: $\log \gamma_{\pm} = -|z_+ z_-| A I^{\frac{1}{2}}$, where A=0.509 for aqueous solutions at 25 °C and *I* is the dimensionless ionic strength of the solution, $I = \frac{1}{2} \sum_i z_i^2 b_i / b^{\emptyset}$, z_i – charge # of ion *i*, b_i – molality of ion *i*, and $b^{\emptyset} = 1$ mol kg^{-1}.
- The sum extends over all the ions present in the solution.
- For a solution of 2 types of ions at molalities of b_+ and b_-, $I = \frac{1}{2}(b_+ z_+^2 + b_- z_-^2)/b^{\emptyset}$.

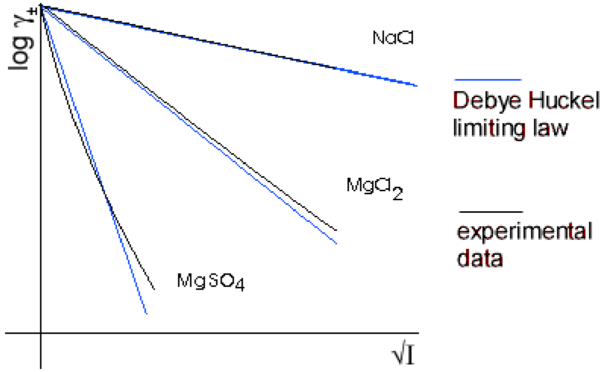
Ionic strength

- Calculate the mean activity coefficient of 5.0 mmol kg^{-1} KCl(aq) at 25 °C.

Answer

- $I = \frac{1}{2}(b_+ z_+^2 + b_- z_-^2)/b^{\emptyset}$; $z_+ = z_- = 1$
- $I = 1/2(b_+ + b_-)/b° = b/b°$, where b is the molality of the solution (and $b_+ + b_- = b$).
- log $\gamma_{\pm} = -0.509 * (5.0 * 10^{-3})^{1/2} = -0.036$
- $\gamma_{\pm} = 0.92$.

Davies equation

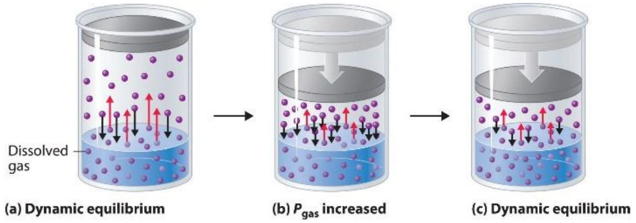


- Ionic solutions of moderate molalities may have coefficients that differ from the values given by $\log \gamma_{\pm} = -|z_{+}z_{-}|AI^{\frac{1}{2}}$, yet all solutions are expected to conform as *b*→0.
- When *I* of the solution is too high for the limiting law to be valid, the activity coefficient may be estimated by the Davies eq.:

$\log \gamma_{\pm} = -\frac{A|z_{+}z_{-}|I^{\frac{1}{2}}}{1+BI^{\frac{1}{2}}} + CI$, where *A*, *B* and *C* are dimensionless constants.

Summary of phase equilibria in gas-liquid systems

- As the upper limit of mass transfer is restricted by the relevant phase equilibrium and the dependence of the rate of mass transfer on the phase equilibrium – must be familiar with phase equilibria of systems.
- Solubility of gases in liquids: ↑ w *p*↑ and ↓ w *T*↑
  - $p_i = Kix_i$ (K_i – Henry's constant)
  - Think of entropy!
- Vapour pressure of pure liquids: function only of *T*
  - $\log p^* = A - \frac{B}{T+C}$, where *A*, *B* and *C* are constants
- Vapour pressure of solutions
  - Raoult's law: $p_i = p_i^* x_i$ - ideal solutions
  - Non-ideal solutions: $p_i = p_i^* \gamma_i x_i$, where γ_i – activity coefficient of species *i*.
    - The estimation of γ_i is one of the important subjects in chemical engineering.



Any questions?