CHEM 206 section 01

LECTURE #9 Fri. Feb.01, 2008

ASSIGNED READINGS:

TODAY'S CLASS: Ch.14 section 14.4

NEXT CLASS: finish 14.4
start Ch.15

(1)

14.4: Colligative Properties

= Physical properties of a solution that depend only on the number of solute particles dissolved in the solvent

1. Elevation of boiling point
2. Depression of freezing point
3. Osmotic pressure

IMPORTANT:

- Independent of solute's identity !
- Assumes "ideal" solution behaviour

(2)

Example: a closer look at wine

Consider a red wine with ~12% alcohol (C_2H_5OH) by mass.
Assume that the rest is water (but thankfully there is other stuff too).

a) What is the vapour pressure in a closed wine bottle at around room temperature, say 20°C?

b) If the wine is forgotten in the trunk of your car overnight in the winter, and the temperature is -15°C, will it freeze ?
& expand…& possibly make a big mess…

Image from:
http://www.artevino.co.uk/images/bigphoto2.jpg

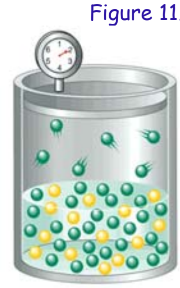
(3)

Vapour pressures of SOLUTIONS

- **PURE volatile liquid**: vapour pressure = "$P°$"

  To vaporize: molecules from bulk liquid must
  a) reach surface
  b) overcome intermolecular interactions & escape liquid

Zumdahl's Figure 11.10



- **SOLUTION** = solute + solvent

  If **solute** is **nonvolatile**:
  - not all molecules at surface CAN vaporize
  - **solvent molecules access to surface blocked…**
  - **but: nothing blocks the vapour condensing.**

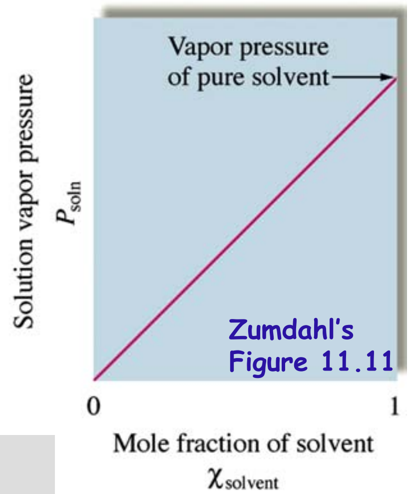
  ⇨ **lowers solvent's vapour pressure**
  ⇨ at any given temperature, vapour P_{soln} < for pure liquid $P°$

To predict P_{soln}: What fraction of molecules in solution ARE volatile?

Raoult's Law: The presence of a nonvolatile solute lowers the vapor pressure of a solvent.

$$P_{soln} = \chi_{solvent} P^\circ_{solvent}$$

P_{soln} = solution's vapour pressure
$\chi_{solvent}$ = mole fraction of solvent
$P^\circ_{solvent}$ = vapour pressure of pure solvent



Zumdahl's Figure 11.11

➔ Linear plot: P_{soln} *vs.* $\chi_{solvent}$

If Raoult's law is OBEYED, the solution is considered "IDEAL"

More solute ⇨ lower mole fraction solvent ⇨ less vapour

(5)

Example: a closer look at wine

Consider a red wine with ~12% alcohol (C_2H_5OH) by volume.
Assume that the rest is water (but thankfully there is other stuff too).
What is the vapour pressure in a closed wine bottle at 20°C?

Useful data:

Ethanol (C_2H_5OH)
MM = 46.07 g/mol
d = 0.785 g/mL
m.p.= -130°C
b.p.= 78°C
P° = 43.89 mm Hg at 20°C

Water (H_2O)
MM = 18.02 g/mol
d = 1.000 g/mL
m.p.= 0°C
b.p.= 100°C
P° = 17.535 mm Hg at 20°C

Problem: water is also volatile !

http://berkshirepublishing.com/assets/images/blogimages/Bottledwater.jpg
http://images.google.ca/imgres?imgurl=http://farm1.static.flickr.com/76/168461428_aed5c5c40a.jpg&imgrefurl=http://www.flickr.com/photos/amery/168461428/&h=399&w=500&sz=296&hl=en&start=6&um=1&tbnid=dQadkWEbYunoZM:&tbnh=104&tbnw=130&prev=/images%3Fq%3Dwater%2Bbottle%2Bcondensation%26svnum%3D10%26um%3D1%26hl%3Den%26client%3Dfirefox-a%26rls%3Dorg.mozilla:en-US:official%26sa%3DN

(6)

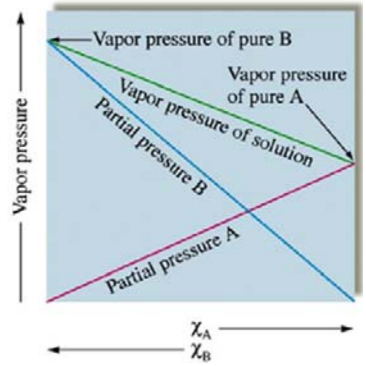
When a solution contains <u>two volatile components</u>, **both** contribute to the total vapour pressure P_{soln}.

Zumdahl's Fig. 11.13

If "ideal": Raoult's law applies to EACH component separately:

Zumdahl's Fig. 11.12

$$P_{soln} = \underbrace{(\chi_A P^\circ_A)}_{\text{Partial P of A}} + \underbrace{(\chi_B P^\circ_B)}_{\text{Partial P of B}}$$

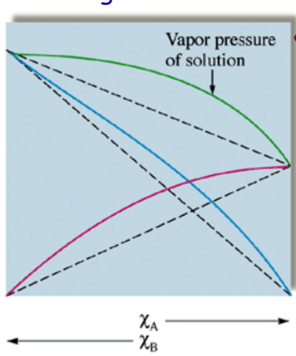


A 2-volatile component solutions <u>will</u> be ideal if:
intermolecular interactions A↔B are equally strong as A↔A and B↔B

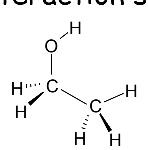
e.g., hexane (C_6H_{14}) and octane (C_8H_{18}) → both have only C-C and C-H bonds
long, nonpolar molecules
id-id (dispersion) forces similar for both
⇨ no "preference" for one over the other

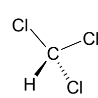
Z's Fig. 11.13

NONIDEAL mixtures of 2 volatile liquids

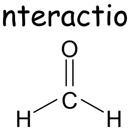


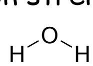
POSITIVE deviation from Raoult's law
= P_{soln} higher than expected
"unmixing" is favoured
⇨ interaction strengths: A↔B << A↔A, B↔B

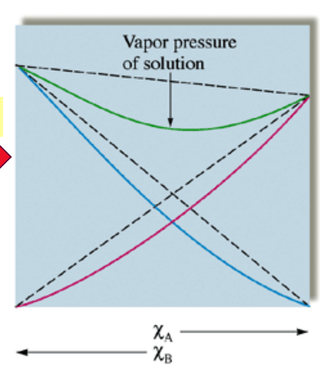




NEGATIVE deviation from Raoult's law
= P_{soln} lower than expected
mixing is highly favoured
⇨interaction strengths: A↔B >> A↔A, B↔B







What is our wine's vapour pressure…

Wine with ~12% C_2H_5OH *by volume* *(error-prone unit, but we'll use it)*

a) Find P_{soln} at 20°C

a) Vapour pressure: two volatile components

$$P_{soln} = P_{ethanol} + P_{water} = \chi_{eth} P^{o}_{eth} + \chi_{water} P^{o}_{water}$$

if have 1L: 0.12 x 1L = 0.12L ethanol and 0.88L water

$$n_{eth} = \frac{(120 \text{ mL} \times 0.785 \text{ g/mL})}{46.07 \text{ g/mol}} = 2.048 \text{ mol}$$

$$n_{water} = \frac{(880 \text{ mL} \times 1.000 \text{ g/mL})}{18.02 \text{ g/mol}} = 48.83 \text{ mol}$$

$$\chi_{eth} = \frac{2.048 \text{ mol}}{(2.048 + 48.83 \text{ mol})} = 0.04025$$

$$\chi_{water} = \frac{48.83 \text{ mol}}{50.88 \text{ mol total}} = 0.9597$$

THUS:

$$P_{soln} = P_{ethanol} + P_{water}$$

$$= (0.04025 \times 43.89 \text{ mm Hg}) + (0.9597 \times 17.535 \text{ mm Hg})$$

$$= 1.767 + 16.83 \text{ mm Hg}$$

$$= 19 \text{ mm Hg total}$$ *to 2 SF* *= 0.025 atm for comparison*

(9)

By lowering vapour pressure, solutes cause "Elevation of the Boiling Point"

Back to simple situations:

A nonvolatile solute raises the boiling point of the solvent.

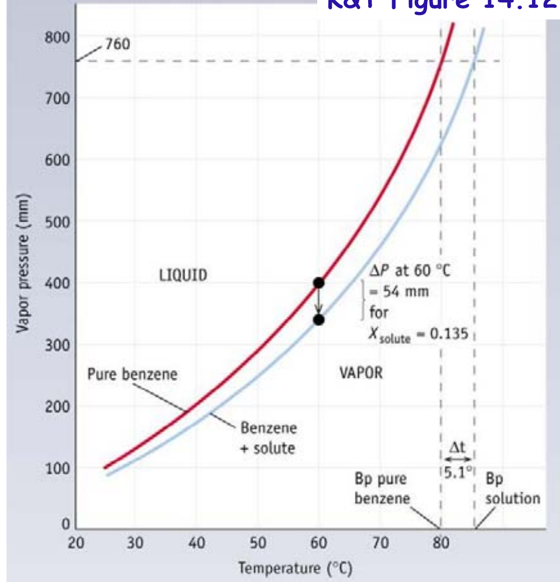
WHY?

- boiling point
= temperature at which vapour pressure matches external P…
i.e., $P_{soln} = P_{ext}$

- **add SOLUTE: ↓ P_{soln}**
⇨ **higher T required for P_{soln} to reach P_{ext}**

***i.e.,* need higher T for $rate_{evap} = rate_{condens}$**

K&T Figure 14.12



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Quantitative changes in bp (& mp) easily calculated

Degree of bp elevation / fp depression depends only on:
(1) total [dissolved particles] & (2) the solvent used

$\Delta T_b = K_b m_{solute}$ AND $\Delta T_f = K_f m_{solute}$

ΔT_b = increase in bp
K_b = bp elevation constant

ΔT_f = decrease in mp (=fp)
K_f = fp depression constant

m = molality of solute (total # molecules / dissociated ions…)

Important: for ionic compounds, the ions are individually solvated
→ every one of them acts as a solute particle…

Zumdahl's Table 11.5

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	−22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	−63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79

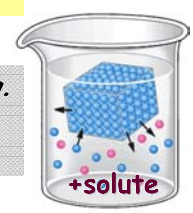
(11)

Why do solutes also cause Depression of the Freezing Point?

Z's Fig.11.15

Solutes hinder freezing & facilitate melting.

- freezing point = melting point = Temp. with EQUAL RATES of forming solid & melting solid



- **Consider solidification (freezing):**
  - Solvent molecules interact & enter crystal
  - Solutes block access ⇨ ↓ rate of solvent entering crystal
    ⇨ less freezing at any T
  - Solutes: lower probability to enter crystal than solvent
- **Consider fusion (melting) of impure crystal:**
  - Impure crystal has defects ⇨ weaker interactions
    ⇨ less thermal E required for molecules to leave crystal
  - ↑ rate of molecules leaving crystal (⇨ more melting at any T)

Result: $rate_{freezing}$ = $rate_{melting}$ at lower T than in pure solvent

(12)

Will our wine freeze if left overnight at -15°C?

Wine with ~12% C_2H_5OH by volume
b) Find m.p. If m.p. < -15°C: won't be frozen at -15°C
If m.p. > -15°C: will be frozen at -15°C

b) Find temperature where wine will freeze: relative to pure water

$\Delta T_f = i\, m\, K_f$ *with solute concentration in* ***molality;***
solute is molecular, so i = 1

If have 1L: have 2.048 mol ethanol & 0.88 L water = 0.88 kg H_2O

$$molality = \frac{2.048 \text{ mol ethanol}}{0.88 \text{ kg water}} = 2.327\ m \quad \text{(extra SFs)}$$

m_{water} = 0.88L x 1.000kg/L
= 0.88 kg

$\Delta T_f = m\, K_f$
= (2.327 mol/kg) x (1.86°C·kg/mol)
= 4.328°C
= 4.3°C depression of freezing point relative to water

THUS:
the wine will freeze at -4.3°C
⇨ definitely frozen at -15°C

(13)

ANOTHER APPLICATION of F.P. depression & B.P. elevation
Used to help characterize unidentified molecular solutes

Don't forget the definition of molality: $m = n_{solute}/kg_{solvent}$

and the definition of a mole: n = m/MM

Combine them: Molality $(m) = \left(\frac{\text{mass solute}}{\text{MM solute}}\right) \cdot (\text{kg solvent})^{-1}$

So: $\Delta T_f = m \cdot K_f$

$$= \frac{\text{mass solute} \cdot K_f}{\text{MM solute} \cdot \text{kg solvent}}$$

$$\text{MM solute} = \frac{\text{mass solute}}{\text{1kg solvent}} \cdot \frac{K_f}{\Delta T_f}$$

What if solute is ionic? ⇨ not so simple (…need to know ion ratio…)

- remember, colligative properties yield total conc. dissolved particles

(14)

How many solute particles are in there??

van't Hoff factor, i, relates to the number of particles released when a substance dissolves:

IONIC COMPOUNDS: NaCl $i = 2$ K_2SO_4 $i = 3$
MOLECULAR COMPOUNDS: $C_6H_{12}O_6$ $i = 1$

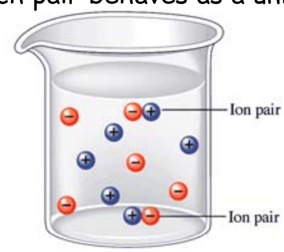
Compensate for this when calculating colligative properties:
$\Delta T_b = i K_b m$ *and* $\Delta T_f = i K_f m$ (using $i_{expected}$ unless told i_{obs})

Zumdahl's

TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	*i* (expected)	*i* (observed)
NaCl	2.0	1.9
$MgCl_2$	3.0	2.7
$MgSO_4$	2.0	1.3
$FeCl_3$	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

Zum.Fig.11.22: $i_{obs} < i_{expected}$
→ small proportion of ions remain paired up
(each pair behaves as a unit)



Predicting properties of solutions…

Solute	Conc.	Species in solution	van't Hoff factor, i	Total [particles]
KCl	0.25 M			
$C_6H_{12}O_6$	0.40 M			
$(NH_4)_2SO_4$	0.20 M			

Rank these solutions from lowest → highest:

a) Vapour pressure
b) Boiling point
c) Freezing point
d) Osmotic pressure *(next class…)*

On your own: briefly explain these on molecular level…

Example: freezing point of battery acid…

The electrolyte in car batteries (12 V lead storage batteries) is a 3.75 M sulfuric acid solution with a density of 1.230 g/mL. Calculate the mass percent and molality of the sulfuric acid. *Hint: solvent is water…* H_2SO_4 MM=98.07 g/mol

What is the battery acid's freezing point?
(…car won't start if battery is frozen…)

From last class…

- Molality = $\frac{3.75 \text{ mol } H_2SO_4}{0.8623 \text{ kg } H_2O}$ = 4.35 mol/kg = 4.35 m of "sulfuric acid"

How to determine its freezing point?

- Must know TOTAL molality of solute particles in the solution.
- ***Hint:*** ***what is the solute's predicted van't Hoff factor ?***

ANS: -24.3 °C (using overestimated ***i***)

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: rest of Ch.14

Practice: solving colligative properties problems

Next class: finish Ch.14, start Ch.15…

A sample exam question: regulating humidity

Cigars are best stored in a "humidor" at 18°C and 55% relative humidity. This means the pressure of water vapour should be 55% of the vapour pressure of pure water at the same temperature. The proper humidity can be maintained by placing an aqueous solution of glycerol, $C_3H_5(OH)_3$, inside the humidor. **Calculate the concentration of glycerol (in mass %) required to lower the vapour pressure of water to the desired value.**

[Assume ideal behaviour, with glycerol as a nonvolatile component.]

Approach:
1. Determine the desired value of water's vapour pressure in humidor
2. Relate vapour pressure to composition of solution using Raoult's law

Cigars are best stored in a "humidor" at 18°C and 55% relative humidity. The proper humidity can be maintained by placing an aqueous solution of glycerol, $C_3H_5(OH)_3$, inside the humidor. **Calculate the mass % glycerol required to lower the vapour pressure of water to the desired value.**
[Because glycerol is relatively nonvolatile, water is considered as the solvent.]

Relate vapour pressure to composition of solution:

- $P_{soln} = 0.55\ P°_{water}$ ⇨ $\chi_{water} = 0.55 = \dfrac{n_{water}}{n_{water} + n_{glyc}}$

solvent (n_{water}); solute (n_{glyc})

Convert into mass percent:

- Consider an arbitrary amount of this solution: *e.g.,* 1 mole total
  $n_{water} + n_{glycerol} = 1$ mol ⇨ $n_{water} = 0.55$ mol
  $n_{glycerol} = 0.45$ mol
- Mass of water: $m_{water} = (0.55\text{ mol})(18.02\text{ g/mol}) = 9.91\text{ g}$
- Mass glycerol: $m_{glyc} = (0.45\text{ mol})(97.14\text{ g/mol}) = 43.71\text{ g}$
- Mass % glycerol = $100 \times (43.71\text{g} / (9.91 + 43.71\text{g})) = 81.5\%$