Salts

Salts are solid crystalline substances at room temperature that contains the cation of a base and the anion of an acid, e.g.:

NaCl	$Mg_3(PO_4)_2$	$Al_2(SO_4)_3$
NaOCl	LiBr	KNO_3

Some common salts are summarized in the table, below:

Salt	Name
$CaSO_4 \cdot \frac{1}{2}H_2O$	Plaster of Paris
$MgSO_4 \cdot 7H_2O$	Epsom salts
$Na_2B_4O_7 \cdot 10H_2O$	Borax
$NaHCO_3$	Baking soda
$NaNO_2$	Preservative
$AgNO_3$	Antiseptic/germicide

The formation of salts necessarily depend on their solubility -- or the lack thereof -- in water. Solubility rules that actually help make chemical reactions make sense are tabulated, following slide:

Rule	Exceptions
Alkali metal and NH_4^+ salts are all soluble.	Some cations in analytical group 5 are moderately insoluble
Nitrates and acetates are all soluble.	AgOAc is moderately insoluble
Chlorides, bromides and iodides are all soluble.	Those salts of Pb^{2+}, Ag^+, Hg_2^{2+} ; BiOCl and SbOCl
Sulfates are soluble.	Those salts of Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Pb^{2+}, Hg_2^{2+}
Carbonate and sulfite salts are generally insoluble.	Those of the alkali metals and NH_4^+
Sulfides are generally insoluble.	Those of the alkali metals and NH_4^+; alkaline earth sulfides and Cr_2S_3 and Al_2S_3 are decomposed by water
Hydroxides are generally insoluble.	Alkali metals and NH_4^+; Barium, strontium and calcium hydroxides are moderately soluble.
All other salts are insoluble.	

As a general rule, solubility is defined as being dissolved in aqueous solution to about 3-5%.

Soluble salts are electrolytes, i.e., they will conduct an electrical current. The rules of electrolytes are summarized in the table, next slide, as well:

Summary of Strong and Weak Electrolytes	
Rule	**Exception**
Most acids are weak electrolytes.	**The common strong acids: hydrochloric, hydrobromic, hydroiodic, nitric, sulfuric, chloric and perchloric**
Most bases are weak electrolytes.	**The strong basic hydroxides: Li, Na, K, Rb, Cs, Ca, Sr, Ba hydroxides**
Most salts are strong electrolytes	**The most importantly weakly ionized salt is $HgCl_2$; occasionally, the following are listed without general agreement: $Hg(CN)_2$, $CdCl_2$, $CdBr_2$, CdI_2 and $Pb(OAc)_2$**

Preparation of Salts

Mechanism	Representative Reactions
Direct union of their elements.	$2Na + Cl_2 \rightarrow 2NaCl$ $Fe + S \rightarrow FeS$
Reactions of acids with metals, metal hydroxides or metal oxides.	$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$ $Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O$ $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$
Reactions of basic anhydrides with acid anhydrides.	$BaO + SO_3 \rightarrow BaSO_4$ $CaO + CO_2 \rightarrow CaCO_3$
Reaction of acids with salts.	$BaCO_3 + 2HCl \rightarrow BaCl_2 + H_2O + CO_2\uparrow$ $BaCl_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HCl$
Reaction of salts with other salts.	$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$ $ZnCl_2 + Na_2S \rightarrow ZnS + 2NaCl$

MO_yX Synthesis. - Synthesis of the Oxyhalides

- $Cl_2(g) + 2NaOH(aq) + cold \rightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$
- The chlorine is bubbled through the lye; NaOCl is used for bleach, e.g., Clorox.
- $3Cl_2(g) + 6NaOH(aq) + heat \rightarrow NaClO_3(aq) + 5NaCl(aq) + 3H_2O(l)$
- $NaClO_3$ is used to bleach paper pulp.
- $NaClO_3$ +oxygen + electrolytic conditions $\rightarrow NaClO_4$
- $NaClO_4$ is an oxidizer, e.g.,
- $3NH_4ClO_4(s) + 3Al(s; powder) \rightarrow Al_2O_3(s) + AlCl_3(g) + 3NO + 6H_2O$
- $1.4*10^6$ pounds of ammonium perchlorate are used per launch to get the space shuttle off the ground.

Ionic Reactions and Ionic Equations

- When reactions between ions occur, at least one kind of ion is removed from the "field of action".
- Simply put, its concentration decreases as the reaction proceeds.
- There are three ways to remove ions:

1. Formation of an insoluble precipitate
2. Formation of a weakly ionized substance, and
3. Oxidation or reduction of an ion

Let's examine each way individually:

1: Formation of An Insoluble Precipitate

$$Overall\ \mathrm{Re}action: AgNO_3 + HCl \rightarrow AgCl\downarrow + HNO_3$$

$$Ionic\ \mathrm{Re}action: Ag^+ + NO_3^- + H_3O^+ + Cl^- \rightarrow AgCl\downarrow + NO_3^- + H_3O^+$$

$$Net\ Ionic\ \mathrm{Re}action: Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Excess chloride ion "drives" this reaction to the right.

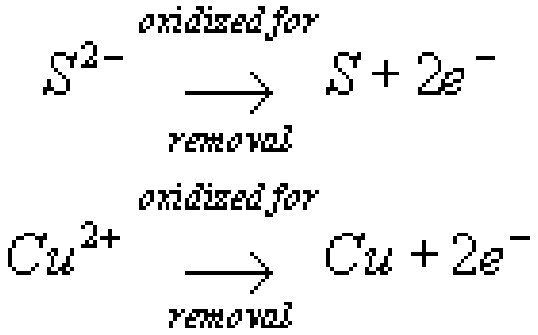
2: Formation of A Weakly Ionized Substance

$$Overall\ \mathrm{Re}action: NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$

$$Ionic\ \mathrm{Re}action: NH_4^+ + Cl^- + Na^+ + OH^- \rightarrow NH_3 + H_2O + Na^+ + Cl^-$$

$$Net\ Ionic\ \mathrm{Re}action: NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

3: Oxidation or Reduction of An Ion



Note, also, that most of these reactions, one way or another, follow the solubility rules discussed previously in both CHEM 121 and 122.

Rules for Writing Ionic Equations

1: Ionic formulas are written for a strong electrolyte in solution (review Electrolyte Rules, previously in 121 and 122), e.g.:

$$Na^+ + Cl^- \ for \ NaCl$$

$$2Na^+ + SO_4^{2-} \ for Na_2SO_4$$

$$2H^+ + SO_4^{2-} \ for \ H_2SO_4$$

$$Na^+ + HCO_3^- \ for \ NaHCO_3$$

$$3Na^+ + PO_4^{3-} \ for \ Na_3PO_4$$

2: Molecular formulas are written for:

a) Elements, gases, solids and non-electrolytes, e.g.:

Cl_2 SO_2 Cu $HCl(g)$

CH_3CSNH_2 CCl_4 C_2H_5OH

b) Weak electrolytes in solution, e.g.:

H_2O $HOAc$ NH_3

c) Solid strong electrolytes or precipitates, e.g.:

$\underline{AgCl}$ or $AgCl\downarrow$

$\underline{BaSO_4}$ or $BaSO_4\downarrow$

$\underline{CaCO_3}$ or $CaCO_3\downarrow$

Writing Ionic Equations

When writing these equations, do so to answer the following three (3) questions:

1. What kind of reaction is it? Double decomposition? Redox?
2. What are the possible products of the reaction?
3. Are any of the possible products or reactants insoluble or weakly ionized?

Double Decomposition Reactions (Precipitate and Weak Electrolyte Reactions) -- Examples

a) KCl + Na(NO_3) → NR

Even the products would be soluble and, hence, no reaction occurs.

b) Silver nitrate and hydrochloric acid -- precipitate formation

$$Overall\ \mathrm{Re}action: AgNO_3 + HCl \rightarrow AgCl + HNO_3$$

$$Ionic\ \mathrm{Re}action: Ag^+ + NO_3^- + H^+ + Cl^- \rightarrow AgCl\downarrow + H^+ + NO_3^-$$

$$Net\ Ionic\ \mathrm{Re}action: Ag^+ + Cl^- \rightarrow \underline{AgCl}$$

Since the hydrogen ion and the nitrate ion are spectators, the net ionic reaction is the result.

c) Hydrochloric acid and calcium acetate -- weak electrolyte formation

$$Overall\ \mathrm{Re}action: HCl + Ca(OAc)_2 \rightarrow 2HOAc + CaCl_2$$

$$Ionic\ \mathrm{Re}action: 2H^+ + 2Cl^- + Ca^{2+} + 2OAc^- \rightarrow 2HOAc + Ca^{2+} + 2Cl^-$$

$$Net\ Ionic\ \mathrm{Re}action: H^+ + OAc^- \rightarrow HOAc$$

d) Acetic acid and sodium hydroxide -- conversion of one weak electrolyte to another

$$\textit{Overall Reaction}: \; HOAc + NaOH \rightarrow NaOAc + H_2O$$

$$\textit{Ionic Reaction}: \; H^+ + OAc^- + Na^+ + OH^- \rightarrow OAc^- + H_2O + Na^+$$

$$\textit{Net Ionic Reaction}: \; HOAc + OH^- \rightarrow OAc^- + H_2O$$

e) Lead chloride and sodium sulfate -- conversion of one precipitate to another

$$\textit{Overall Reaction}: \; PbCl_2 + Na_2SO_4 \rightarrow PbSO_4 + 2NaCl$$

$$\textit{Ionic Reaction}: \; \underline{PbCl_2} + 2Na^+ + SO_4^{2-} \rightarrow \underline{PbSO_4} + 2Na^+ + 2Cl^-$$

$$\textit{Net Ionic Reaction}: \; \underline{PbCl_2} + SO_4^{2-} \rightarrow \underline{PbSO_4} + 2Cl^-$$

f) Hydrogen sulfide and copper (II) nitrate in acidic solution – competition between a weak electrolyte and a precipitate

$$\textit{Overall Reaction}: \; H_2S + Cu(NO_3)_2 \xrightarrow{H^+} \underline{CuS} + 2HNO_3$$

$$\textit{Ionic Reaction}: \; 2H^+ + S^{2-} + Cu^{2+} + 2NO_3^- \xrightarrow{H^+} \underline{CuS} + 2H^+ + 2NO_3^-$$

$$\textit{Net Ionic Reaction}: \; Cu^{2+} + H_2S \rightarrow \underline{CuS} + 2H^+$$

Double Decomposition Reactions (by Proton Transfer)

In this type of reaction, there must be a proton donor (D_1) and a proton acceptor (A_1). Donors dissociate as follows:

$$D1 \rightarrow A_1 + H^+$$

Acceptors accept the proton as follows:

$$H^+ + A_2 \rightarrow D_2$$

The overall reaction, then, is obtained by adding the two up (similarly to adding half reactions in redox:

$$D_1 + A_2 \rightarrow A_1 + D_2 –$$

remember conjugate acid-base pairs from CHEM 121?

Keeping with this form of these reactions, in the reactions, following slide, are examples of protolytic reactions -- Donors on the left of both reactants and products and Acceptors on the right of both reactants and products.

$$D_1 + A_2 \Leftrightarrow D_2 + A_1$$

$$HCO_2H + H_2O \Leftrightarrow H_3O^+ + HCO_2^- \quad (Ionization)$$

$$H_2O + NH_3 \Leftrightarrow NH_4^+ + OH^- \quad (Ionization)$$

$$HSO_4^- + CH_3NH_2 \Leftrightarrow CH_3NH_3^+ + SO_4^{2-} \quad (Neutralization)$$

$$NH_4^+ + CO_3^- \Leftrightarrow HCO_3^- + NH_3 \quad (Equilibrium)$$

$$H_2O + S^{2-} \Leftrightarrow HS^- + OH^- \quad (Hydrolysis)$$

Double Decomposition Reactions (by Reactions Involving Precipitates and Complex Ions)

a) Silver chloride and ammonia -- Solution by Complex Ion Formation

$$\underline{AgCl} + NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$$

b) Diamino silver chloride and potassium iodide – Dissociation of A Complex Ion to Form a Precipitate

$$Overall\ \text{Re}action: Ag(NH_3)_2Cl + KI \rightarrow \underline{AgI} + 2NH_3 + KCl$$

$$Net\ Ionic\ \text{Re}action: Ag(NH_3)_2^+ + I^- \rightarrow AgI + 2NH_3$$

c) Tetra-amino cadmium sulfate and potassium cyanide – Conversion of One Complex to Another

$$Net\ Ionic\ \text{Re}action: Cd(NH_3)_4^{2+} + 4CN^- \rightarrow Cd(CN)_4^{2-} + 4NH_3$$

d) Diamino silver chloride and nitric acid – Decomposition of A Complex with Precipitate Formation

$$Net\ Ionic\ \text{Re}action: Ag(NH_3)_2^+ + Cl^- + 2H^+ \rightarrow \underline{AgCl} + 2NH_4^+$$

Redox Equations/Reactions

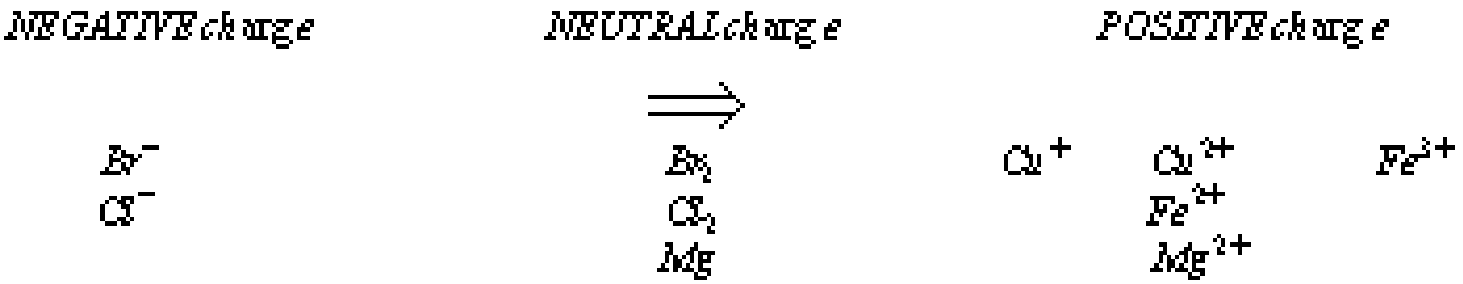
Examples:

$Fe^{3+} + V^{2+} \rightarrow V^{3+} + Fe^{2+}$

$Cl_2 + 2Br^- \rightarrow Br_2 + 2Cl^-$

Remember: an increase in the oxidation number is oxidation; a reduction in the oxidation number is a reduction reaction.

The graphic, below, helps put this in the proper perspective:



The negatively charged end is the reduced end and the positively charged end is the oxidized end of the above graphic.

The Table, Below, Summarizes Typical Reducing Agents:

Typical Reducing Agents			
Reducing Agents	**Conditions**	**Oxidized Form**	**Change in Oxidation Number**
Zn	**Acidic**	**Zn^{2+}**	**0 to 2+**
Al	**Alkaline**	**$Al(OH)_4^-$**	**0 to 3+**
H_2S	**Acidic**	**S**	**-2 to 0**
Sn^{2+}	**HCl**	**$SnCl_6^{2-}$**	**+2 to +4**
$S_2O_4^{2-}$	**Alkaline**	**SO_3^{2-}**	**+3 to +4 (S)**
HNO_2	**Acidic**	**NO_3^-**	**+3 to +5 (N)**
H_2O_2	**Acidic**	**O_2**	**-1 to 0 (O)**

The table, below, summarizes typical oxidizing agents:

Typical Oxidizing Agents			
Oxidizing Agent	**Conditions**	**Reduced Form**	**Change in Oxidation Number**
Cu^{2+}		Cu	+2 to 0
Fe^{3+}		Fe^{2+}	+3 to +2
Br_2	Acidic	Br^-	0 to -1
$Cr_2O_7^{2-}$	Acidic	Cr^{3+}	+6 to +3 (Cr)
MnO_4^-	Acidic	Mn^{2+}	+7 to +2 (Mn)
MnO_4^-	Alkaline	MnO_2	+7 to +4 (Mn)
NO_3^-	16 M HNO_3	NO_2	+5 to +4 (N)
NO_3^-	Alkaline	NH_3	+5 to -3 (N)
ClO_3^-	HNO_3	ClO_2	+5 to +4 (Cl)
H_2O_2	Acidic	H_2O	-1 to -2 (O)
H_2O_2	Alkaline	OH^-	-1 to -2 (O)

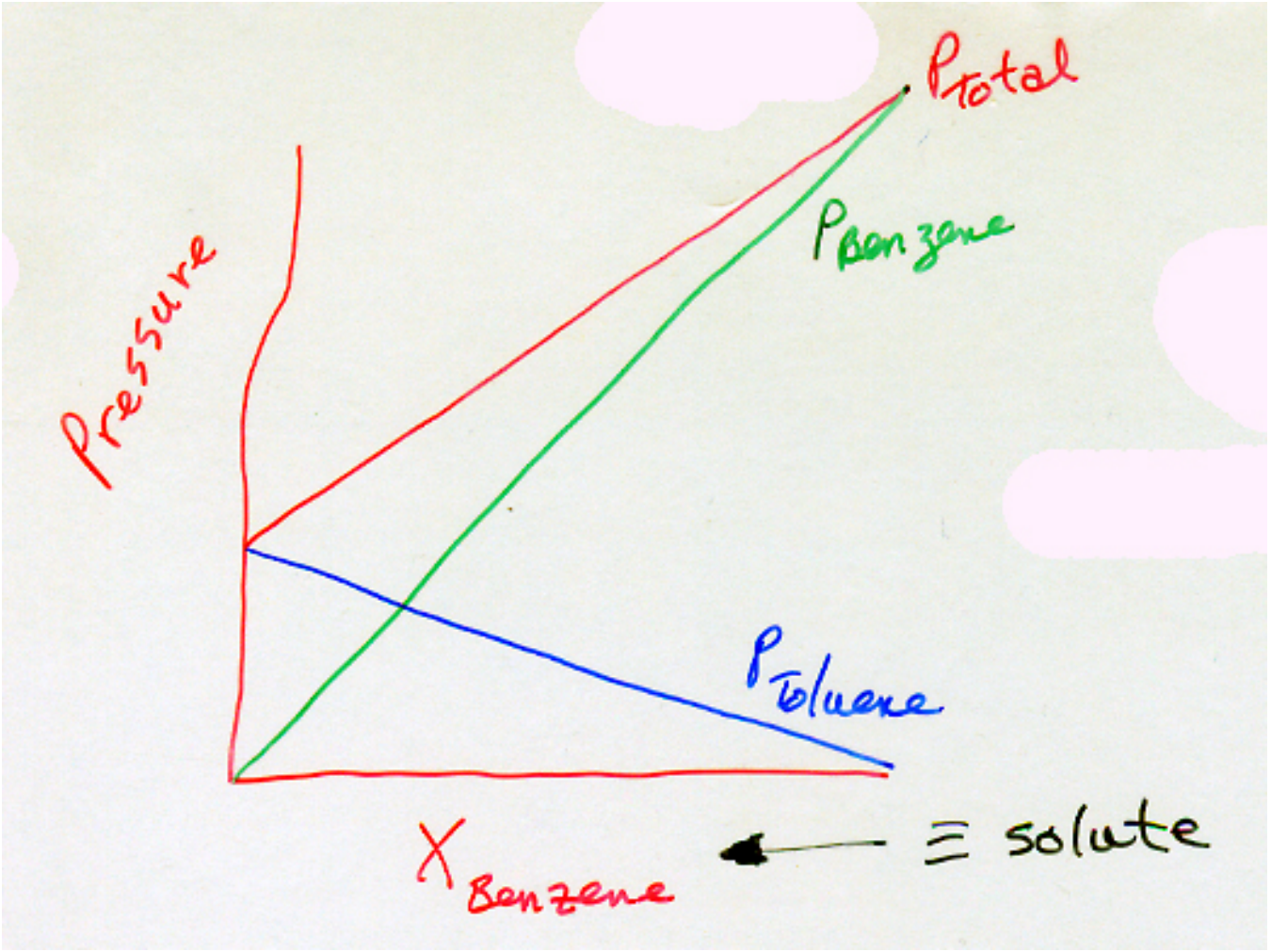
Colligative Properties

- Aka collective properties because they are bound together through their common origin.
- Each of these properties is proportional to ONLY the number of solute molecules present – NOT on the size or molar mass of the molecules.

For The Time Being, The Following Assumptions are Necessary

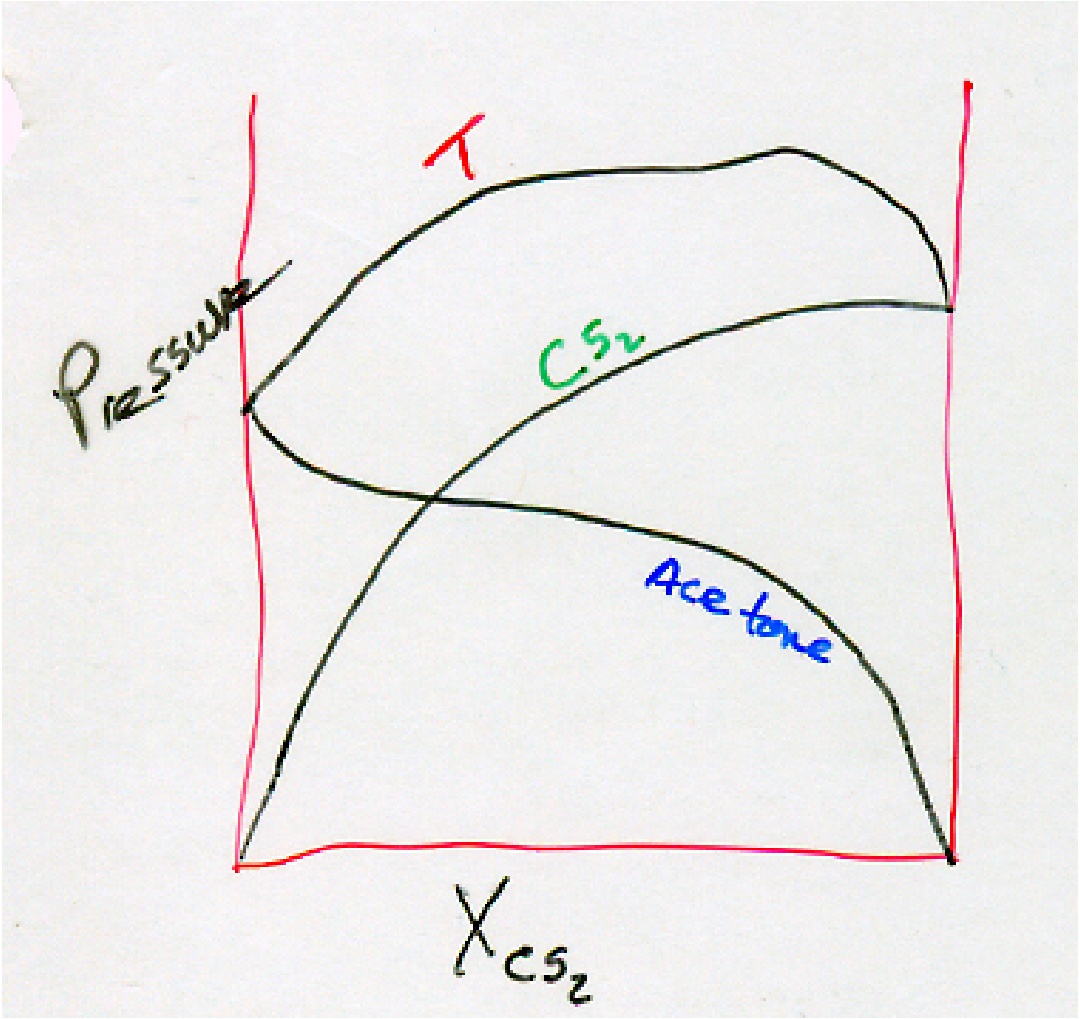
1. The solutions are IDEAL,
    1. i.e., the vapor pressure of a solution of liquids is equal to the sum of each individual liquid's vapor pressure and
    2. the vapor pressure of the defined solute varies with its concentration in a linear manner: $P_1 = k X_1$

Ideal Solution -- Graphically



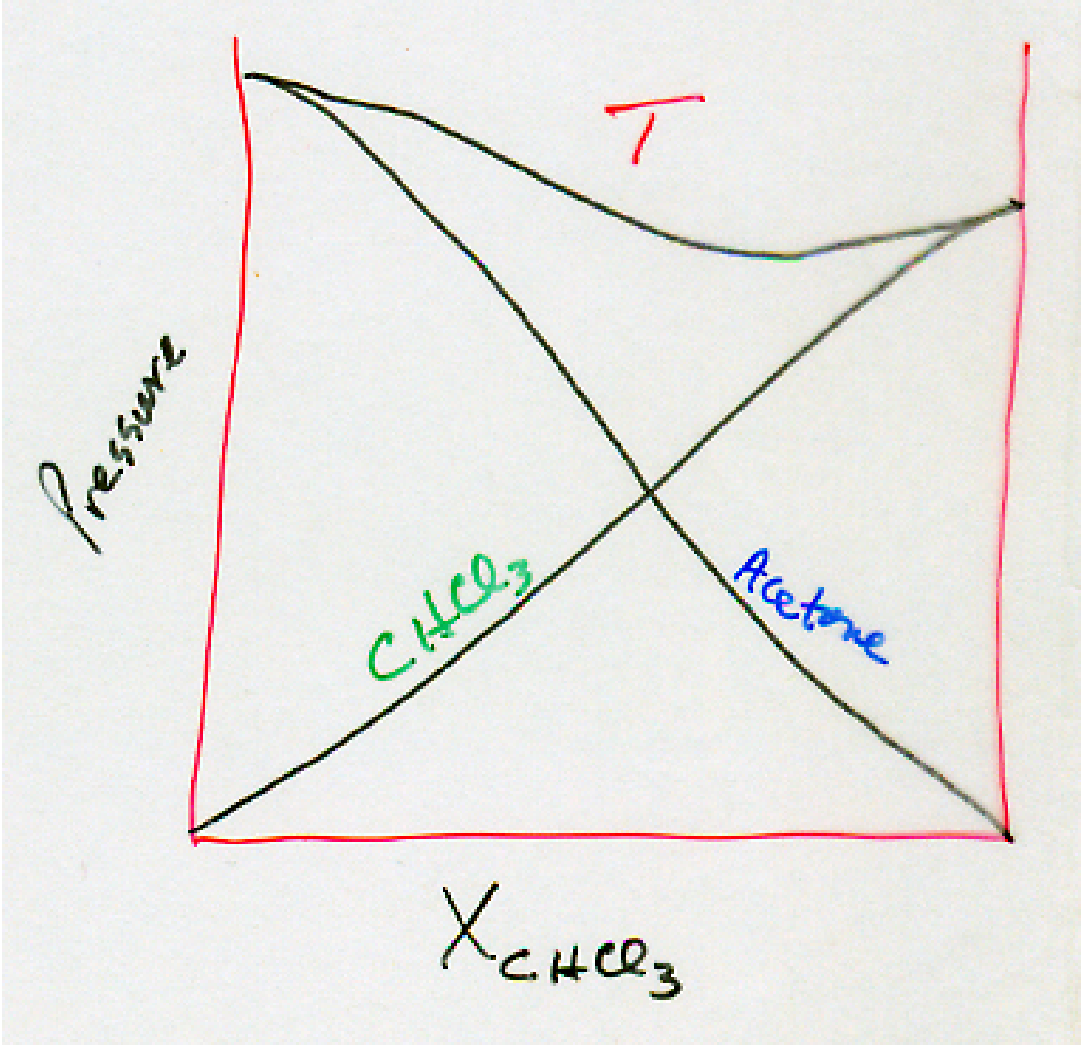
Non-Ideal Solution

- Positive deviation from NON-Ideal solution of CS_2 with acetone.



NON-Ideal Solution

- Negative Deviation from NON-Ideal solution of $CHCl_3$ with Acetone



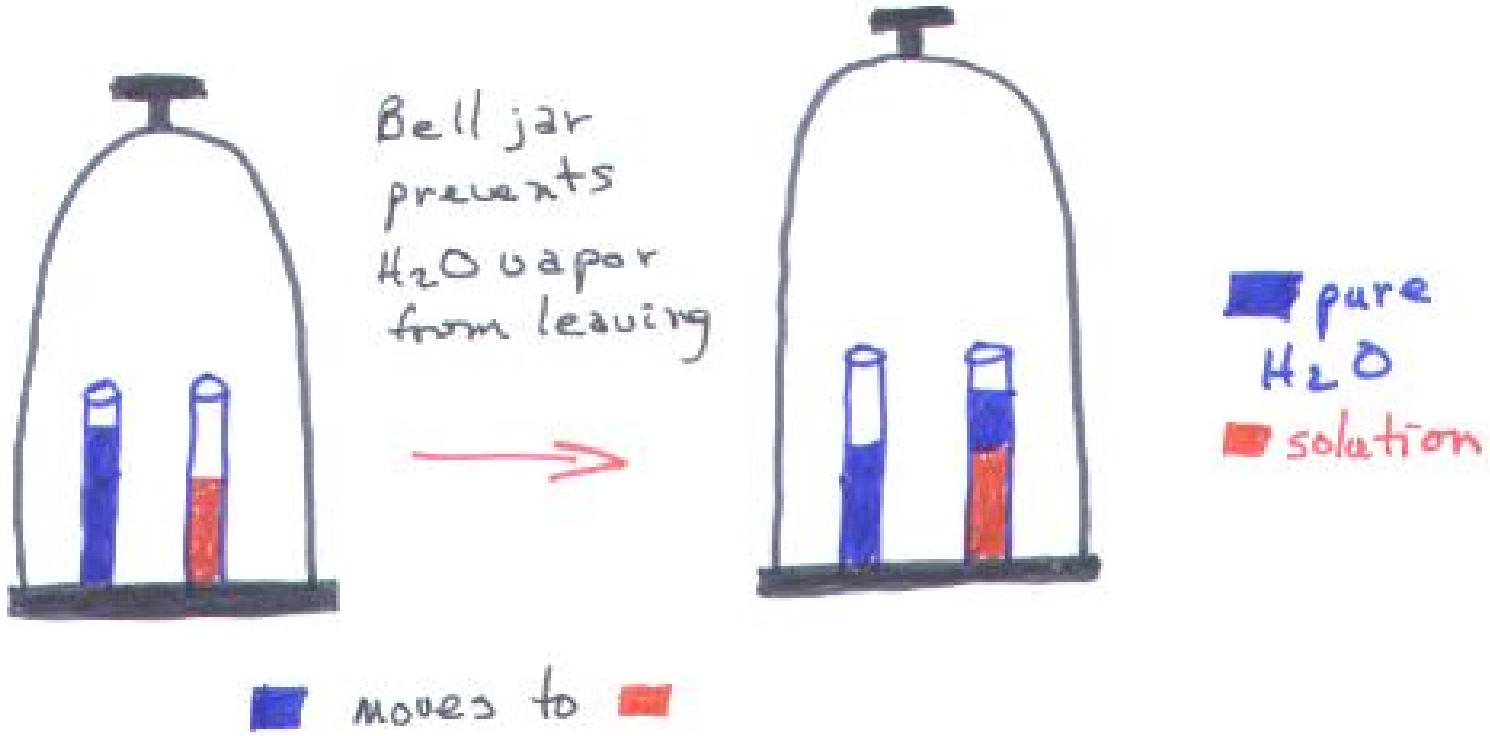
Assumptions

2. The solutions are dilute – concentrations less than 0.2 m
3. We will consider ONLY (at this time) non-electrolyte solutions

Summary of Colligative Properties

1. Lower of the Vapor Pressure of the Solvent
2. Boiling Point Elevation
3. Freezing Point Depression
4. Osmotic Pressure

Vapor Pressure Lowering -- Graphically



Vapor Pressure -- Arithmetic

- An IDEAL solution, i.e., one that contains a solvent 1 and a NON-volatile solute 2 (e.g., sucrose in water) follows Raoult's Law:

- The vapor pressure of a component of a solution is equal to the product of its mole fraction and the vapor pressure of the pure liquid.

Vapor Pressure -- Example

- $P_1 = X_1 P_1^*$
- P_1^* = vapor pressure of the pure liquid 1
- X_1 = mol fraction of 1
- P_1 = experimentally obtained pressure

- $P_2 = X_2 P_2^*$
- P_2^* = vapor pressure of the pure liquid 2
- X_2 = mol fraction of 2
- P_2 = experimentally obtained pressure

How to Calculate Mol Fraction

- Calculate the mole fraction of each component in an ideal solution of glycerine (92.1 g; MW 92.1 g/mol) and ethanol (184 g; MW 46 g/mol) at 40°C.

$$(92.1\,g\ glycerine)\left(\frac{1\,mol}{92.1\,g\ glycerine}\right)=1\,mol\ glycerine$$

$$(184\,g\ EtOH)\left(\frac{1\,mol}{46\,g\ EtOH}\right)=4\,mol\ EtOH$$

$$X_{glycerine}=\frac{1\,mol}{(1+4)\,mol}=0.2$$

$$X_{EtOH}=\frac{4\,mol}{(1+4)\,mol}=0.8$$

Example, Cont'd

- Determine the vapor pressure of the EtOH component of the solution if the vapor pressure of pure EtOH at 40°C is 135.3 torr.

$$P_{EtOH} = X_{EtOH} P^*_{EtOH}$$

$$P_{EtOH} = (0.8)(135.3\,torr)$$

$$P_{EtOH} = 108.2\,torr$$

Cont'd

- The reduction in vapor pressure is
  - 135.3 – 108.2 = 27.1 torr and is calculated also as follows:

$$\Delta P = X_{glycerine}\, P^{*}_{EtOH}$$

$$\Delta P = (0.2)(135.3 torr)$$

$$\Delta P = 27.1 torr$$

- In other words, the glycerine molecules in this solution lower the frequency of escape of EtOH molecules from the surface of the liquid

- The greater the number of molecules of SOLUTE, the less the vapor pressure exerted by the SOLUTION

Boiling Point Elevation

- Boiling point ≡ the temperature at which a pure solvent's or solution's vapor pressure = atmospheric pressure
  - NOTE: with reduction in vapor pressure comes an increase in boiling point (BP)
- Arithmetically:

$$\Delta T = K_b\, m$$

- ΔT = rise in BP in °C

- K_b = boiling point elevation constant
  = 0.51 °C/m -- ALWAYS

- m = molality of the solution

Molarity vs Molality

- M
- Molarity
- Dependent upon temperature

$$M = \frac{mol\ of\ solute}{L\ of\ solution}$$

- m
- molality
- Independent of temperature

$$m = \frac{mol\ of\ solute}{kg\ of\ solution}$$

Example

- 500 mL water are mixed with 5.85 g NaCl. Calculate the M and m of this solution. ρ_{H_2O} at this temperature is 0.985 g/mol.

$$5.85\,g\ NaCl\left(\frac{1\,mol\ NaCl}{23\,g\ Na+35.5\,g\ Cl}\right)=\frac{5.85}{58.5}=0.1\,mol\ NaCl$$

$$(500\,mL\ water)\left(\frac{0.985\,g}{mL}\right)\left(\frac{1\,kg}{1000\,g}\right)=\frac{0.985}{2}=0.493\,kg\ water$$

Cont'd

$$M = \frac{mol}{L} = \frac{0.1\,mol}{0.5\,L} = 0.2\,M$$

$$m = \frac{mol}{kg} = \frac{0.1\,mol}{0.493\,kg} = 0.203\,m$$

Example

- Determine the boiling point of a solution of 15 g ethylene glycol ($C_2H_4(OH)_2$) in 1 kg water.

$$(15\,g\ ethylene\ glycol)\left(\frac{1\,mol}{62\,g\ Ethylene\ glycol}\right)=0.24\,mol$$

$$m=\frac{0.24\,mol}{1\,kg}=0.24\,m$$

$$\Delta T=K_b\,m=(0.51)(0.24)=0.123\,^{\circ}C$$

$$\therefore T_{BP}=100^{\circ}C+0.123^{\circ}C=100.123^{\circ}C$$

Another Example

- Determine the boiling point of a solution of 186 g ethylene glycol in 1 kg water.

$$(186\,g\ Ethylene\ glycol)\left(\frac{1\,mol\ Ethylene\ glycol}{62\,g\ Ethylene\ glycol}\right)=3\,mol$$

$$m=\frac{3\,mol}{1\,kg}=3\,m$$

$$\Delta T=K_b\,m=(0.51)(3)=1.53^{\circ}C$$

$$\therefore T_{BP}=100+1.53=101.53^{\circ}C$$

Another Example

- The boiling point of a solution of water and ethylene glycol is 105°C. How much ethylene glycol is present in 1 kg of water?

$$\Delta T = K_B\, m$$

$$5^\circ C = \frac{0.51^\circ C}{m}(X)$$

$$\frac{5^\circ C\, m}{0.51^\circ C} = 9.8\, m$$

$$\frac{9.8\, mol}{kg} * 1 kg = 9.8\, mol\ Ethylene\ glycol$$

$$(9.8\, mol\ Ethylene\ glycol)\left(\frac{62\, g\ Ethylene\ glycol}{1 mol}\right) = 607.6\, g\ Ethylene\ glycol$$

Freezing Point Depression

- $\Delta T = K_f\, m$
- ΔT= change in temperature – the freezing point depression
- K_f = freezing point constant = 1.86 °C/m
- m = molality of the solution

Example

- Determine the freezing point of a solution of 50 g NaCl in 0.5 kg water.

$$(50\,g\ NaCl)\left(\frac{1\,mol}{23\,g\ Na+35.5\,g\ Cl}\right)=0.855\,mol$$

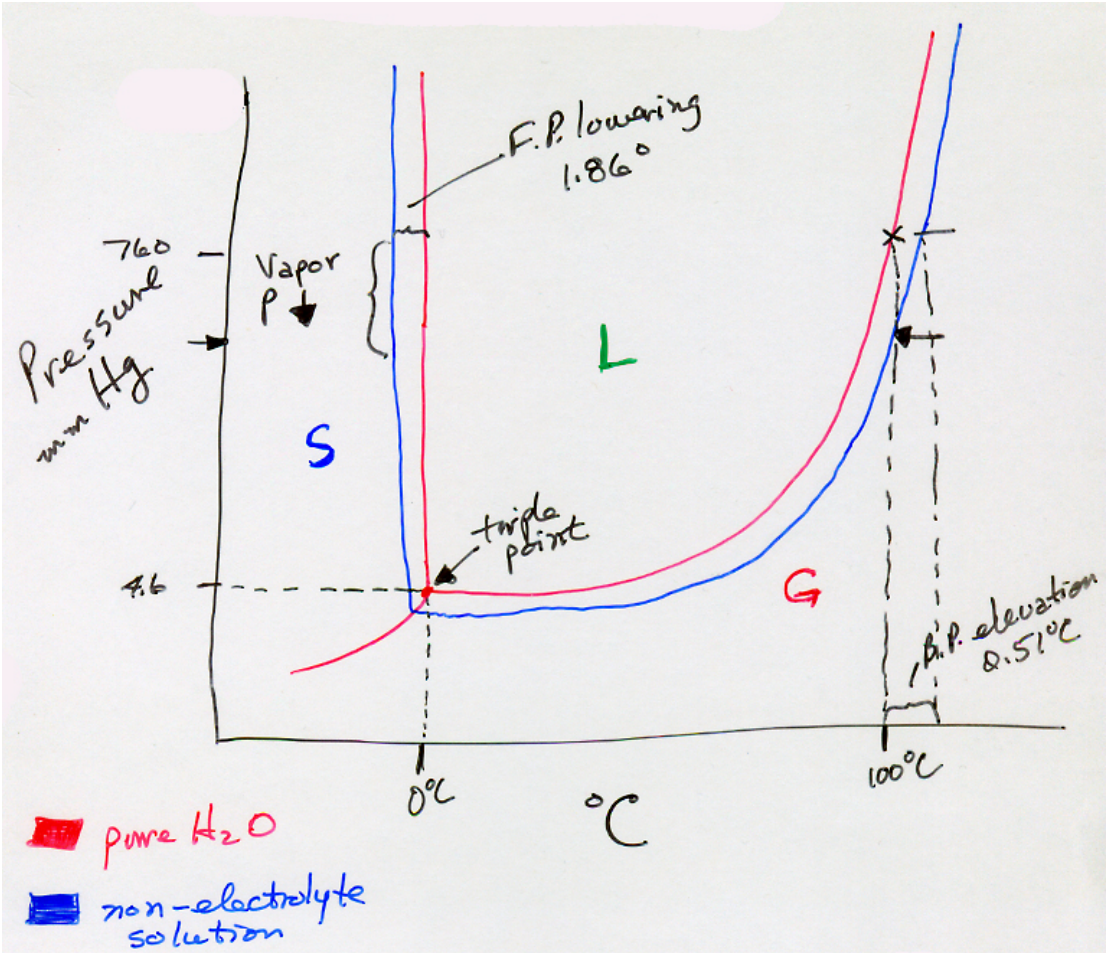
$$m=\frac{0.855\,mol}{0.5\,kg}=1.71m$$

$$\Delta T=(1.86)(1.71)=3.18^{\circ}C$$

$$100^{\circ}C-3.18^{\circ}C=96.8^{\circ}C$$

What is Origin of BP and FP constants? Phase Diagram

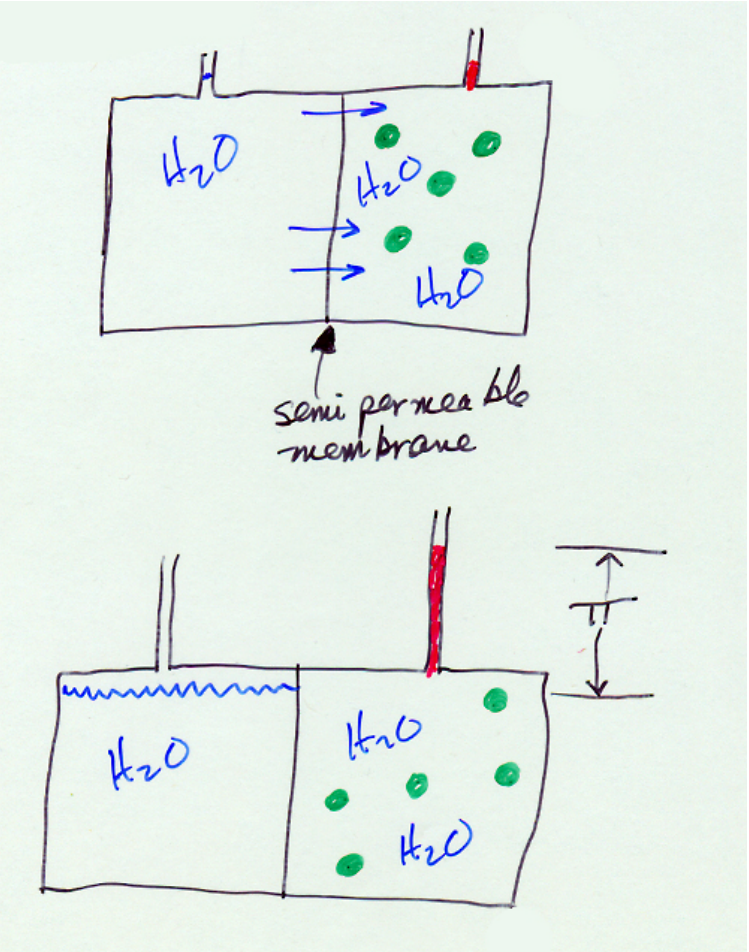
- Left shift for FP depression
- Right shift for BP elevation
- When compared against **pure water** and **non-electrolyte solution**



Osmosis/Osmotic Pressure

- Osmosis ≡ the movement of water from a region of [higher] to [lower]

- Osmotic pressure ≡ the force causing the movement of water



$$\Pi = M\ R\ T$$

- Π = osmotic pressure in atm
- M = molarity of the solution
- R = gas constant = 0.08206 L-atm/mol-K
- T = temperature in K (absolute temperature)

Example

- What is the osmotic pressure of a 0.4 M solution of albumin at 40°C?

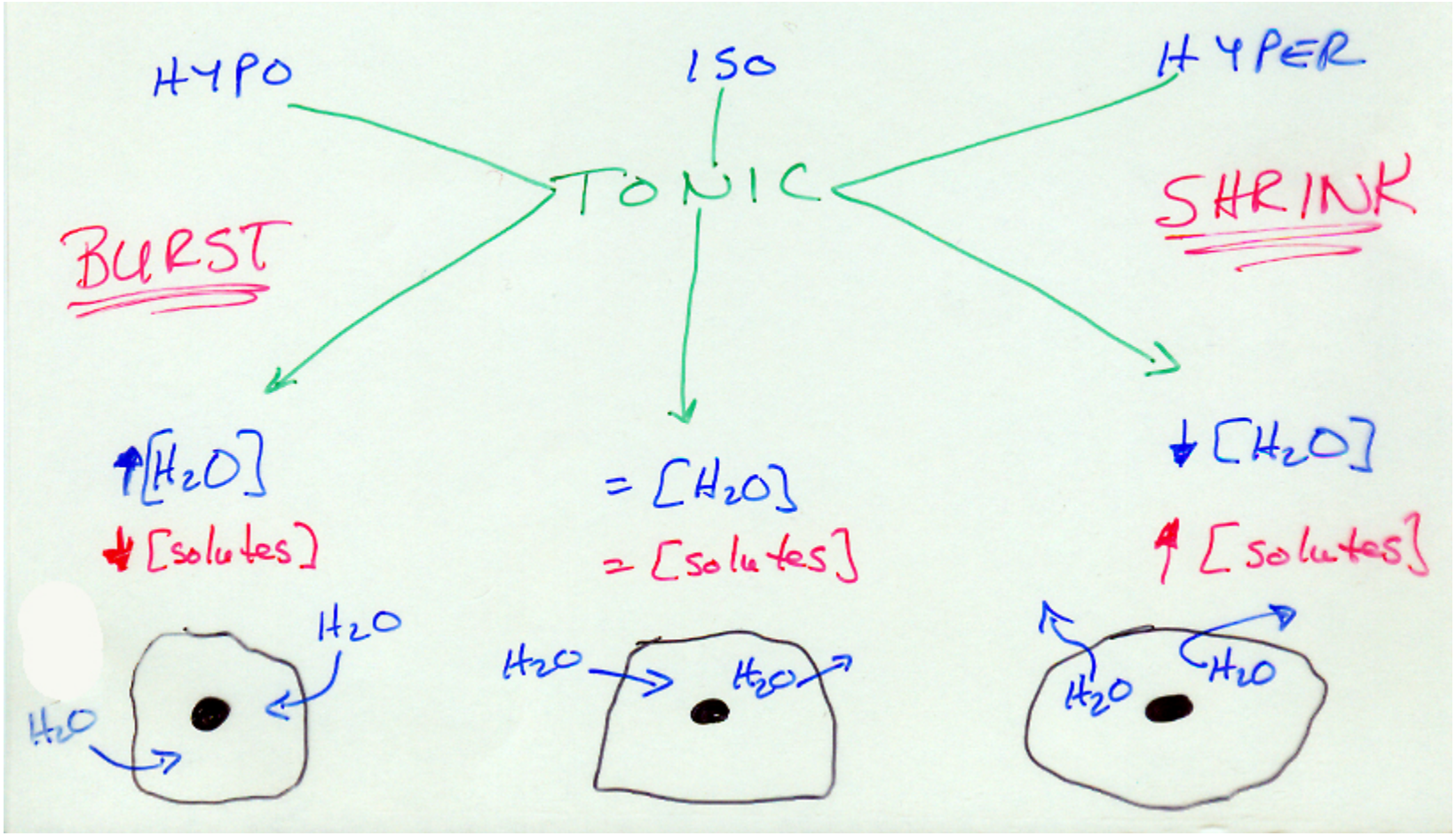
$$\Pi = M\ R\ T$$

$$T = 40 + 273 = 313\,K$$

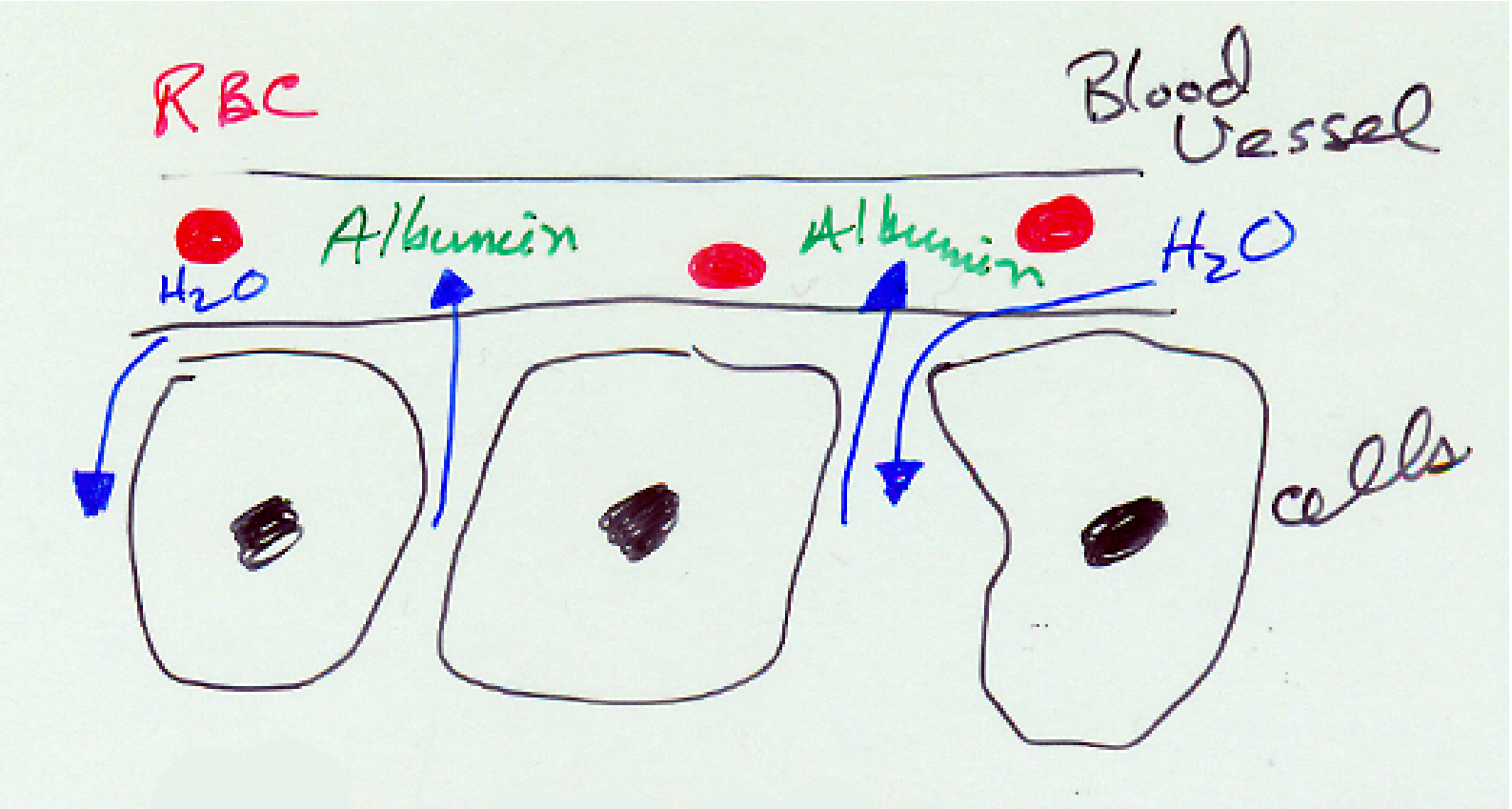
$$\Pi = (0.4)(0.08206)(313)$$

$$\Pi = 10.3\,atm$$

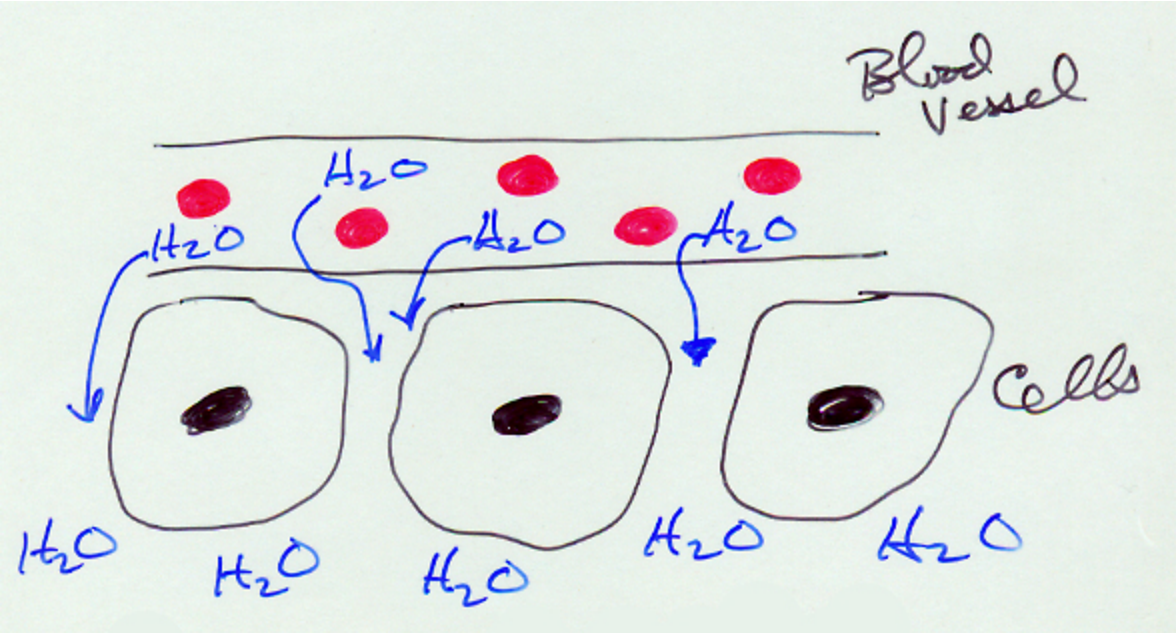
Osmotic Pressure Significance



Physiological Application – Iso-Osmotic



Physiological Application -- Starvation



Blood is hypo-osmotic (hypo-albuminemia) which leads to increased tissue water retention = edema

Arithmetic Application – Step 1

- The following data was obtained during an osmotic pressure experiment: 20 g Hb/L; height of column = 77.8 mm; T = 298K. From this data, determine the MW of Hemoglobin.

$$\text{Pressure} = \frac{Force}{Area}$$

$$P = \frac{A h \rho g}{A} = h \rho g$$

- A = cross-sectional area of the tube
- h = height of the column
- ρ = density of the solution
- g = acceleration due to gravity

Arithmetic Application – Step 2

$$h = 7.78 \underline{c}m$$

$$g = 980.7 \frac{cm}{s^2}$$

$$\rho \approx 1 \frac{g}{cm^3} \approx pure\ water$$

$$\Pi = (7.78)\ (980.7)\ (1) = 7629.85 \frac{g}{cm \bullet s^2}$$

$$\sin ce 1 \frac{g}{cm \bullet s^2} = 1 \frac{dyne}{cm^2}$$

$$7629.85 \frac{g}{cm \bullet s^2} = 7629.85 \frac{dyne}{cm^2}$$

$$1 atm = 1.0133 \times 10^6 \frac{dyne}{cm^2}$$

$$\therefore$$

$$\Pi = \left(7629.85 \frac{dyne}{cm^2} \right) \left(\frac{cm^2}{1.0133 \times 10^6\ dyne} \right) = 7.53 \times 10^{-3}\ atm$$

Arithmetic Application – Step 3

$$\Pi = M\ R\ T$$

$$M = \frac{c}{MW}$$

$$c = \frac{g}{L}$$

$$MW = molecular\ weight\ in\ g/mol$$

$$\therefore$$

$$\Pi = \frac{c\,R\,T}{MW}$$

$$\wedge MW = \frac{c\,R\,T}{\Pi}$$

$$MW = \frac{(20)(0.08206)(298)}{7.53\times10^{-3}} = 64950.5\ g/mol \approx 65{,}000\ g\ Hb/mol$$

Uncommon Colligative Properties -- 1

- Atomic Weight Determination in Solution
- From Specific Heats: the product of the specific heat and atomic weight of solid elements is very nearly a constant, i.e., about 6.4
- This approximately valid for all solid elements with atomic weights > 40 and for most metallic elements
- It does NOT hold for such elements as C, Si, P, S

Example

- Determine the approximate atomic weight of Fe. Its specific heat is 0.115 cal/g/°.

$$atomic\,mass \times specific\,heat = 6.4$$

$$atomic\,mass = \frac{6.4}{specific\,heat} = \frac{6.4}{0.115} = 56\,g/mol$$

•Actual molecular weight of Fe is 55.85 g/mol

•Gives us an approximation, however.

•Called the Law of Dulong and Petit

Uncommon Colligative Properties -- 2

- From Equivalent Weights
- Exact atomic weights come from experimental determination of
  - Exact equivalent weight
  - Approximate atomic weight

Example

- Approximate atomic weight of C = 12.071 g
- Exact equivalent weight of C = 3.0027

$$\frac{12.071}{3.0027} = 4.02 \leftarrow \textit{oxidation state of } C$$

$$\textit{ought to be } 4 - - \textit{it's not because } 12.071 \textit{ is incorrect}$$

$$\therefore \textit{ for exact atomic wt}: \; 4 \times 3.0027 = 12.011 \frac{g}{mol}$$

Colligative Properties of Electrolyte Solutions

- These properties are influenced by the # of ions present in solution, therefore:

ΔT_f of 0.01 m NaCl ought to be 2X ΔT_f of 0.01 m sucrose

($NaCl \Leftrightarrow Na^+ + Cl^-$)

van't Hoff factor -- #1

$$i = \frac{\textit{actual \# of particles in solution}}{\textit{\# of particles in solution BEFORE dissociation}}$$

$$\textit{E.g., NaCl}$$

$$i = \frac{2}{1} = \frac{1\ \textit{from}\ Na^{+}\ \textit{and}\ 1\ \textit{from}\ Cl^{-}}{1\ \textit{from NaCl}}$$

$$i = 2$$

van’t Hoff Factor -- #2

- Given N units of an electrolyte and if
- α = the degree of dissociation, then for

$$MX \Leftrightarrow \#M^{+} + \#X^{-}$$

- There will be N(1-α) undissociated units and N(#M^{+} + #X^{-}) α ions in solution at equilibrium

van't Hoff Factor Re-Written

$$i = \frac{N(1-\alpha) + N(\#M^{+} + \#X^{-})\alpha}{N}$$

$$i = 1 - \alpha + (\#M^{+} + \#X^{-})\alpha$$

$$and\ \alpha = \frac{i-1}{(\#M^{+} + \#X^{-}) - 1}$$

i is also calculable from Π

- For two solutions, 0.01 m $CaCl_2$ with an osmotic pressure of 0.605 atm and 0.01 m sucrose with an osmotic pressure of 0.224 atm, at 298K, **calculate the van't Hoff factor and α for $CaCl_2$**. Assume ideal behavior.
- Remember that Π is directly proportional to the # of particles present.

$$\therefore$$

$$i = \frac{0.605\,atm}{0.224\,atm} = 2.70$$

$$CaCl_2 \Leftrightarrow Ca^{2+} + 2Cl^-$$

$$\therefore \#M^+ + \#X^- = 3 = 1+2$$

$$\alpha = \frac{i-1}{(\#M^+ + \#X^-)-1} = \frac{2.70-1}{3-14} = 0.85$$

$$\therefore CaCl_2 \text{ is only } 85\% \text{ dissociated}$$

Modifications of Equations for Electrolytes

$$\Delta T = K_b \; i \; m$$

$$\Delta T = K_f \; i \; m$$

$$\Pi = M \; i \; R \; T$$

Where i *= van't Hoff factor*!