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Colligative properties

PHYSICAL CHEMISTRY, 2nd course

Degree in Pharmacy

2018-2019

COLLIGATIVE PROPERTIES

- Definition of Colligative Property
- Vapour Pressure Lowering
- Freezing Point Depression (Cryoscopy)
- Boiling Point Elevation (Ebullioscopy)
- Osmotic Pressure
- Colligative Properties of Electrolyte Solutions

COLLIGATIVE PROPERTIES

- The word comes from the Latin "*colligatus*" that means together.
- These properties :
  - depend ONLY on the number of solute particles.
  - do NOT depend on the nature of the solute.

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COLLIGATIVE PROPERTIES

- The solutions have certain characteristics:
  - the solute is NOT VOLATILE.
  - the solid solute does NOT dissolve into the solid solvent.

COLLIGATIVE PROPERTIES

- These properties are studied in :

  A. **NON- ELECTROLYTE** Solutions.

  B. **ELECTROLYTE** Solutions.

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COLLIGATIVE PROPERTIES

- VAPOUR PRESSURE LOWERING
- FREEZING POINT DEPRESSION (CRYOSCOPY)
- BOILING POINT ELEVATION (EBULLIOSCOPY)
- OSMOTIC PRESSURE

COLLIGATIVE PROPERTIES

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- Applications
- Summary and Conclusions

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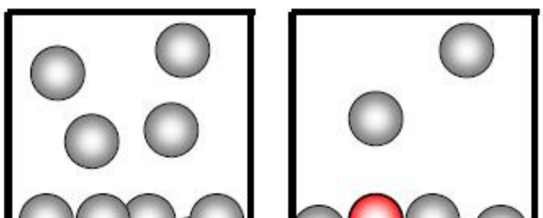
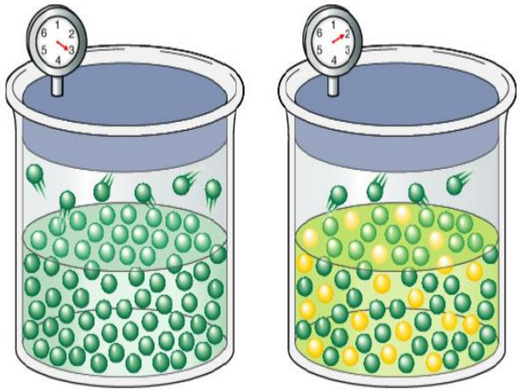
VAPOUR PRESSURE LOWERING

- The presence of the solute reduce the solvent tendency to go to the vapour phase.



VAPOUR PRESSURE LOWERING



Pure solvent

Solution of a non-volatile solute

VAPOUR PRESSURE LOWERING

$$\Delta P = P_A^* - P = P_A^* - P_A$$

Ideal and ideal dilute solutions

$$\Delta P = x_B^1 \, P_A^*$$

Real solutions

VAPOUR PRESSURE LOWERING

$$\Delta P_{rel} = \frac{P_A^* - P}{P_A^*} = \frac{P_A^* - P_A}{P_A^*}$$

Ideal and ideal dilute solutions

$$\Delta P_{rel} = x_B^l$$

Real solutions

$$\Delta P_{rel} = 1 - a_A = 1 - \gamma_A x_A^l$$

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COLLIGATIVE PROPERTIES

VAPOUR Phase
Pure solvent (A)

↑↓

SOLUTION
Non-Volatile Solute
Volatile Solvent (A)

SOLUTION
Non-Volatile Solute
Volatile Solvent (A)

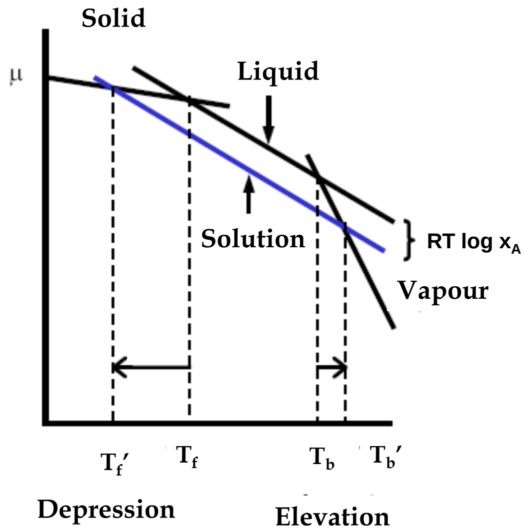
↑↓

SOLID Phase
Pure solvent (A)

Non-volatile solute

The solute does not dissolve in the solid solvent

COLLIGATIVE PROPERTIES



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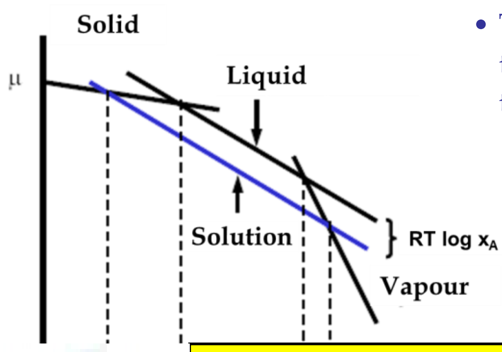
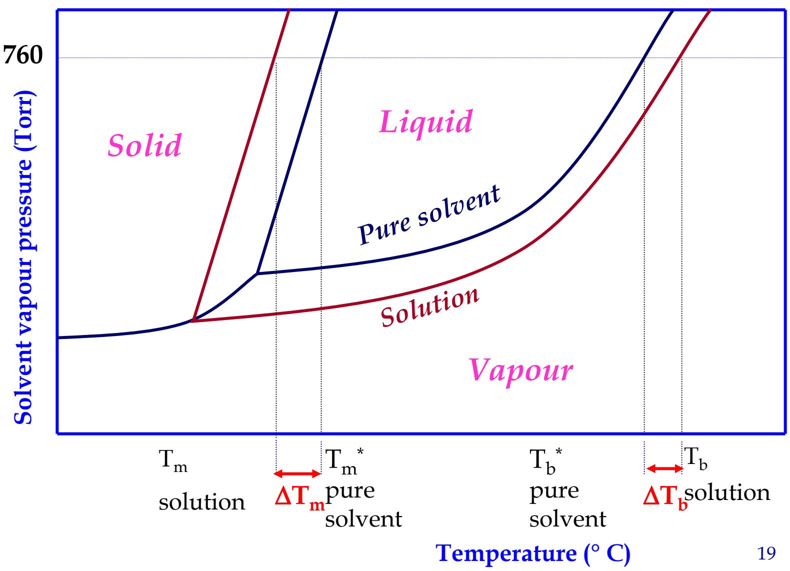
COLLIGATIVE PROPERTIES



- The change in μ affects the freezing point and the boiling point

$$\left(\frac{\partial \mu}{\;}\right) = \left(\frac{\partial \overline{G}}{\;}\right) = -\overline{S}$$

COLLIGATIVE PROPERTIES



COLLIGATIVE PROPERTIES

- **Definition of Colligative Property**
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- **Osmotic Pressure**
- **Colligative Properties of Electrolyte Solutions**

FREEZING POINT DEPRESSION

SOLUTION
Non-Volatile Solute
Volatile Solvent (A)

SOLID Phas
Pure solvent (A)

This property appears when there is phase equilibrium

⇓ between

solution and the pure solvent in solid state

⇓

pure A solidifies from the solution when it is cooled

FREEZING POINT DEPRESSION

- **IDEAL SOLUTION**

$$\mu_A^{*(s)} = \mu_A^{sol}$$

$$\mu_A^{*(s)} = \mu_A^{o(l)} + R\,T\,\log x_A^{l}$$

FREEZING POINT DEPRESSION

• **IDEAL SOLUTION**

$$-RT\log x_A^l = \mu_A^{*(l)} - \mu_A^{*(s)}$$

$$-RT\log x_A^l = \overline{\Delta G}_{m,A}$$

$$\log x_A^l = \frac{-\overline{\Delta G}_{m,A}}{RT}$$

FREEZING POINT DEPRESSION

• **IDEAL SOLUTION**

$$\left(\frac{\partial \log x_A^l}{\partial T}\right)_P = \left(\frac{\partial \dfrac{-\overline{\Delta G}_{m,A}}{RT}}{\partial T}\right)_P$$

FREEZING POINT DEPRESSION

- **IDEAL SOLUTION**

$$\left(\frac{\partial \log x_A^1}{\partial T}\right)_P = -\frac{\left(\frac{\partial \overline{\Delta G}_{m,A}}{\partial T}\right)_P R\,T - \left(\frac{\partial R\,T}{\partial T}\right)_P \overline{\Delta G}_{m,A}}{R^2\,T^2}$$

$$\left(\frac{\partial \log x_A^1}{\partial T}\right)_P = -\frac{-\overline{\Delta S}_{m,A}\,T - \overline{\Delta G}_{m,A}}{R\,T^2}$$

$$\left(\frac{\partial \log x_A^1}{\partial T}\right)_P = \frac{\overline{\Delta H}_{m,A}}{R\,T^2}$$

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FREEZING POINT DEPRESSION

- **IDEAL SOLUTION**

$$\int_{\log 1}^{\log x_A^1} d\log x_A^1 = \int_{T_{m,A}^*}^{T_m} \frac{\overline{\Delta H}_{m,A}}{R\,T^2}\,dT$$

$$\log x_A^1 = \frac{-\overline{\Delta H}_{m,A}}{R}\left(\frac{1}{T_m} - \frac{1}{T_{m,A}^*}\right)$$

FREEZING POINT DEPRESSION

- **IDEAL SOLUTION**

$$\log x_A^l = \frac{-\overline{\Delta H}_{m,A}}{R}\left(\frac{T_{m,A}^{*} - T_m}{T_{m,A}^{*}\, T_m}\right)$$

$$\Delta T_m = T_{m,A}^{*} - T_m$$

$$\log x_A^l = \frac{-\overline{\Delta H}_{m,A}}{R}\left(\frac{\Delta T_m}{T_{m,A}^{*}\, T_m}\right)$$

$$\log x_A^l \cong \frac{-\overline{\Delta H}_{fus,A}}{R}\left(\frac{\Delta T_{fus}}{T_{fus,A}^{*\,2}}\right)$$

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FREEZING POINT DEPRESSION

- **IDEAL DILUTE SOLUTIONS**

$$\log(1-x) = -x + \frac{1}{2!}x^2 - \frac{2}{3!}x^3 + \frac{6}{4!}x^4 - \ldots\ldots$$

$$\log(1-x_B^l) \cong -x_B^l$$

$$x_B^l \cong \frac{\overline{\Delta H}_{m,A}}{R}\left(\frac{\Delta T_m}{T^{*\,2}}\right)$$

FREEZING POINT DEPRESSION

• IDEAL DILUTE SOLUTION

$$\Delta T_m = \frac{M_A\ 10^{-3}\ R\ T^{*2}_{m,A}}{\overline{\overline{\Delta H}}_{m,A}}\ m_B$$

$$\boxed{\Delta T_m = K_c\ m_B}$$

$$K_c = \frac{M_A\ R\ T^{*2}_{m,A}}{\overline{\overline{\Delta H}}_{m,A}\ 10^3}$$

FREEZING POINT DEPRESSION

• REAL SOLUTION

$$\mu_A^{*(s)} = \mu_A^{sol}$$

$$\mu_A^{*(s)} = \mu_A^{o(l)} + R\ T \log a_A$$

$$- R\ T \log a_A = \mu_A^{o(l)} - \mu_A^{*(s)}$$

FREEZING POINT DEPRESSION

• REAL SOLUTION

$$-R\,T\log a_A = \mu_A^{*(l)} - \mu_A^{*(s)}$$

$$-R\,T\log a_A = \overline{\Delta G}_{m,A}$$

$$\left(\frac{\partial \log a_A}{\partial T}\right)_P = \frac{\overline{\Delta H}_{m,A}}{R\,T^2}$$

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FREEZING POINT DEPRESSION

• REAL SOLUTION

$$\int_{\log 1}^{\log a_A} d\log a_A = \int_{T_{m,A}^*}^{T_m} \frac{\overline{\Delta H}_{m,A}}{R\,T^2}\,dT$$

$$\log a_A = \frac{-\overline{\Delta H}_{m,A}}{R}\left(\frac{\Delta T_m}{T_{m,A}^*\,T_m}\right)$$

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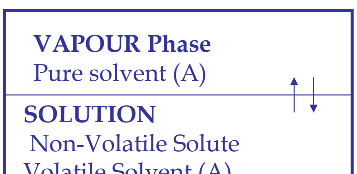
- **Applications**
- **Summary and Conclusions**

BOILING POINT ELEVATION

This property appears when there is phase equilibrium

⇩ between

solution and the pure solvent in the vapour state



BOILING POINT ELEVATION

- IDEAL SOLUTION

$$\mu_A^{*(v)} = \mu_A^{sol}$$

$$\mu_A^{*(v)} = \mu_A^{o(l)} + R\,T \log x_A^{l}$$

$$\mu_A^{*(v)} - \mu_A^{o(l)} = R\,T \log x_A^{l}$$

$$\mu_A^{*(v)} - \mu_A^{*(l)} = R\,T \log x_A^{l}$$

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BOILING POINT ELEVATION

- IDEAL SOLUTION

$$\mu_A^{*(v)} - \mu_A^{*(l)} = R\,T \log x_A^{l}$$

$$\overline{\Delta G}_{vap,A} = R\,T \log x_A^{l}$$

BOILING POINT ELEVATION

• IDEAL SOLUTION

$$\int_{\log 1}^{\log x_A^l} d\log x_A^l = \int_{T_{b,A}^*}^{T_b} - \frac{\overline{\Delta H}_{vap,A}}{R\,T^2}\, dT$$

$$\log x_A^l = \frac{-\overline{\Delta H}_{vap,A}}{R}\left(\frac{\Delta T_b}{T_{b,A}^*\ T_b}\right) \qquad \Delta T_b = T_b - T_{b,A}^*$$

$$\boxed{\log x_A^l \cong \frac{-\overline{\Delta H}_{vap,A}}{R}\left(\frac{\Delta T_b}{T_{b,A}^{*\,2}}\right)}$$

BOILING POINT ELEVATION

• IDEAL DILUTE SOLUTION

$$\log(1-x) = -x + \frac{1}{2!}x^2 - \frac{2}{3!}x^3 + \frac{6}{4!}x^4 - ....$$

$$\log(1-x_B^l) \cong -x_B^l$$

$$x_B^l \cong \frac{\overline{\Delta H}_{vap,A}}{R}\left(\frac{\Delta T_b}{T^{*\,2}}\right)$$

BOILING POINT ELEVATION

- **IDEAL DILUTE SOLUTION**

$$\Delta T_b = \frac{M_A\, 10^{-3}\, R\, T^{*2}_{b,A}}{\Delta \overline{\overline{H}}_{vap,A}}\, m_B$$

$$\boxed{\Delta T_b = K_b\, m_B}$$

$$K_b = \frac{M_A\, R\, T^{*2}_{b,A}}{\Delta \overline{\overline{H}}_{vap,A}\, 10^3}$$

BOILING POINT ELEVATION

- **REAL SOLUTION**

$$\mu_A^{*(v)} = \mu_A^{sol}$$

$$\mu_A^{*(v)} = \mu_A^{o(l)} + R\, T \log a_A$$

$$\mu_A^{*(v)} - \mu_A^{o(l)} = R\, T \log a$$

BOILING POINT ELEVATION

- **REAL SOLUTION**

$$\mu_A^{*(v)} - \mu_A^{*(l)} = R\,T \log a_A$$

$$\overline{\Delta G}_{vap,A} = R\,T \log a_A$$

$$\left(\frac{\partial \log a_A}{\partial T}\right)_P = -\frac{\overline{\Delta H}_{vap,A}}{R\,T^2}$$

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BOILING POINT ELEVATION

- **REAL SOLUTION**

$$\int_{\log 1}^{\log a_A} d\log a_A = \int_{T_{b,A}^*}^{T_b} -\frac{\overline{\Delta H}_{vap,A}}{R\,T^2}\, dT$$

$$\log a_A = \frac{-\overline{\Delta H}_{vap,A}}{R}\left(\frac{\Delta T_b}{T_{b,A}^*\, T_b}\right)$$

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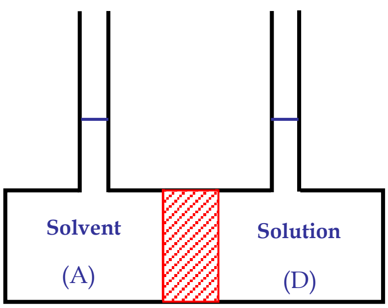
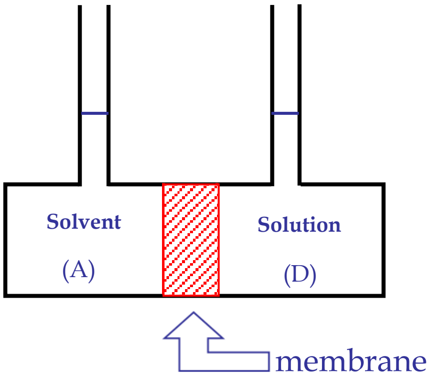
OSMOTIC PRESSURE



This property appears when theres is phase equilibrium

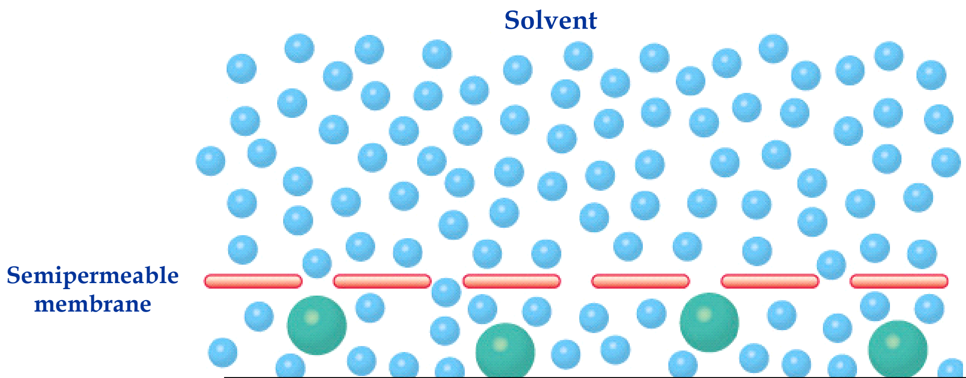
between

OSMOTIC PRESSURE

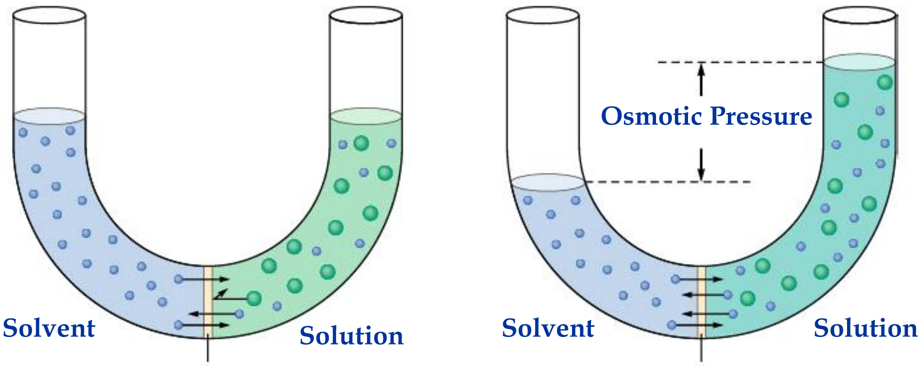


- rigid → V = constant
- diathermy → $T_A = T_D$
- semipermeable → only allows A to pass through

OSMOTIC PRESSURE



OSMOTIC PRESSURE



OSMOTIC PRESSURE

- **IDEAL SOLUTION**

$$\mu_A^{*(l)}(T, P_\alpha) = \mu_A^{(l)}(T, P_\beta)$$

$$\mu_A^{*(l)}(T, P_\alpha) = \mu_A^{*(l)}(T, P_\beta) + R\,T \log x_A^l$$

$$\mu_A^{*(l)}(T, P_\alpha) - \mu_A^{*(l)}(T, P_\beta) = R\,T \log x_A^l$$

OSMOTIC PRESSURE

- **IDEAL SOLUTION**

$$\mu_A^{*(l)}(T, P_\beta) - \mu_A^{*(l)}(T, P_\alpha) = \overline{V}_A^* \, \pi$$

$$\mu_A^{*(l)}(T, P_\alpha) - \mu_A^{*(l)}(T, P_\beta) = R\,T \log x_A^l$$

$$\boxed{-R\,T \log x_A^l = \overline{V}_A^* \, \pi}$$

OSMOTIC PRESSURE

- **IDEAL DILUTE SOLUTION**

$$\log(1 - x_B^l) \cong -x_B^l$$

$$x_B^l \, R\,T \cong \overline{V}_A^* \, \pi$$

$$x_B^l \cong c_B \, \overline{V}_A^*$$

OSMOTIC PRESSURE

- **REAL SOLUTION**

$$\mu_A^{*(l)}(T, P_\alpha) = \mu_A^{(l)}(T, P_\beta)$$

$$\mu_A^{*(l)}(T, P_\alpha) = \mu_A^{*(l)}(T, P_\beta) + R\,T \log a_A$$

$$\mu_A^{*(l)}(T, P_\beta) - \mu_A^{*(l)}(T, P_\alpha) = \overline{V}_A^{*}\,(P_\beta - P_\alpha)$$

$$\mu_A^{*(l)}(T, P_\beta) - \mu_A^{*(l)}(T, P_\alpha) = \overline{V}_A^{*}\,\pi$$

$$\boxed{-R\,T \log a_A = -R\,T \log \gamma_A\, x_A^{l} = \overline{V}_A^{*}\,\pi}$$

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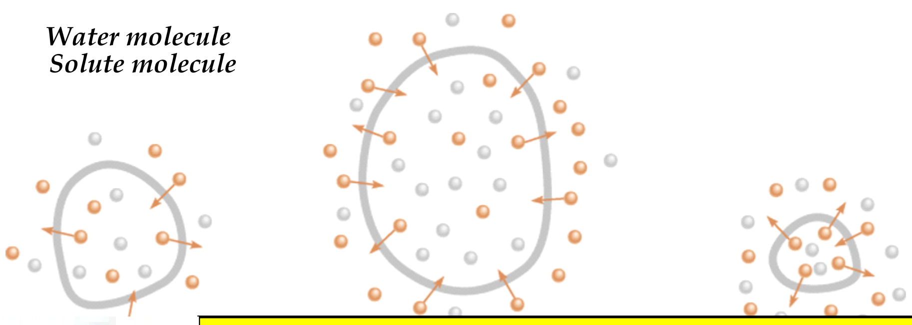
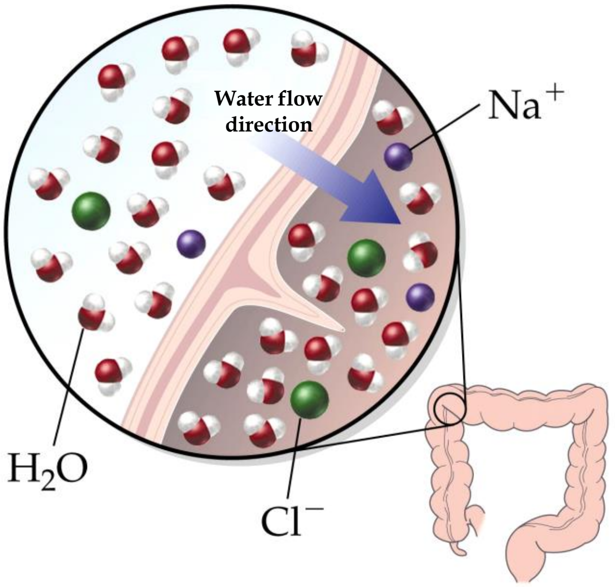
OSMOTIC PRESSURE

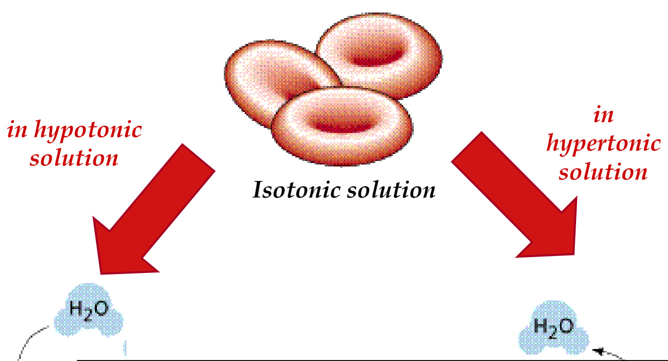


OSMOTIC PRESSURE



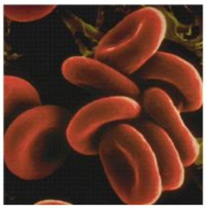
Drinking sea water causes dehydration.

OSMOTIC PRESSURE

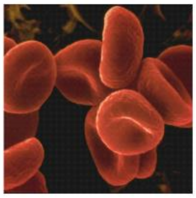


OSMOTIC PRESSURE

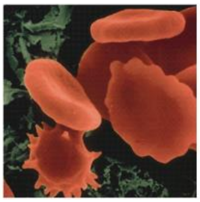
Isotonic solution



Hypotonic solution



Hypertonic solution



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COLLIGATIVE PROPERTIES ELECTROLYTE SOLUTIONS

Colligative properties are proportional to the concentration of ALL solute particles
(ION + MOLECULES)

⇩

The dissociation of electrolytes modify the value of the colligative properties of a solution.

One must distinguish between:

- Ideal dilute solutions of electrolytes
- Real solutions of electrolytes

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COLLIGATIVE PROPERTIES ELECTROLYTE SOLUTIONS

A. IDEAL DILUTE SOLUTION:

- The effective concentration is greater than the real concentration.
- The Van't Hoff factor, i, needs to be introduced.

COLLIGATIVE PROPERTIES
ELECTROLYTE SOLUTIONS

$$M_{\nu_+}X_{\nu_-} \rightleftarrows \nu_+ M^{z_+} + \nu_- X^{z_-}$$

$$t = 0 \quad m \quad 0 \quad 0$$

$$t = t_{eq} \quad m(1-\alpha) \quad \nu_+ m\alpha \quad \nu_- m\alpha$$

$$m_{efect} = m(1-\alpha) + \nu_+ m\alpha + \nu_- m\alpha =$$
$$= m(1-\alpha + \nu\,\alpha) = m(1+\alpha(\nu - 1)) = m\,i$$

$$\boxed{i = 1 + \alpha(\nu - 1)}$$

COLLIGATIVE PROPERTIES
ELECTROLYTE SOLUTIONS

- **Vapour pressure lowering**
  - ✓Ideal dilute solution: $\Delta P = x_B\, i\, P_A^*$
- **Freezing Point Depression (Cryoscopy)**
  - ✓Ideal dilute solution: $\Delta T_m = K_c\, m_B\, i$
- **Boiling point elevation (ebullioscopy)**

COLLIGATIVE PROPERTIES
ELECTROLYTE SOLUTIONS

- For a electrolyte completely dissociated: i = ν

➢ **Vapour pressure lowering**

✓Ideal dilute solution: $$\Delta P = x_B \, \nu \, P_A^*$$

➢ **Freezing Point Depression (Cryoscopy)**

✓Ideal dilute solution: $$\Delta T_m = K_c \, m_B \, \nu$$

➢ **Boiling point elevation (ebullioscopy)**

➢Ideal dilute solution: $$\Delta T_b = K_b \, m_B \, \nu$$

➢ **Osmotic Pressure**

✓Ideal dilute solution: $$\pi = R \, T \, c_B \, \nu$$

COLLIGATIVE PROPERTIES
ELECTROLYTE SOLUTIONS

B. REAL SOLUTION:

- The effective concentration is greater than the real concentration.
- The expressions are the same that the ones for a real solution, but now the values depend on the total

COLLIGATIVE PROPERTIES
ELECTROLYTE SOLUTIONS

B. REAL SOLUTIONS:

$$\Delta P = P_A^* (1 - a_A)$$

$$\log a_A = -\frac{\Delta T_m \, \Delta \overline{H}_{m,A}}{R \, T_{m,A}^2}$$

$$\log a_A = -\frac{\Delta T_b \, \Delta \overline{H}_{vap,A}}{R \, T_{b,A}^2}$$

$$- R \, T \log a_A = \overline{V}_A^* \, \pi$$

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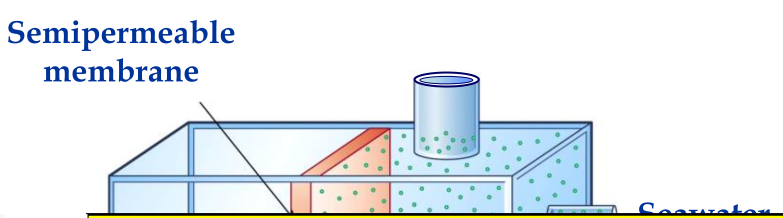
APPLICATIONS

- Determination of solutes molecular weight.
- Antifreeze compounds.
- Ascent of sap.
- Mechanical stability of the plants.
- Use of salt and sugar to preserve food.
- Gherkin in vinegar.
- Reverse osmosis.

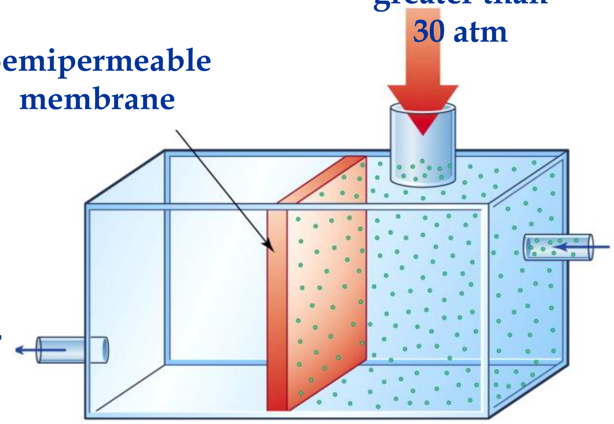
OSMOTIC PRESSURE

Reverse Osmosis: Water Purification



OSMOTIC PRESSURE

Reverse Osmosis: Water Purification



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SUMMARY AND CONCLUSIONS

- **VAPOUR PRESSURE LOWERING:**

  - Ideal and an ideal dilute solution: $\Delta P = x_B \, P_A^*$

  - Real Solution: $\Delta P = P_A^* \, (1 - a_A)$

  - Electrolyte solutions: $\Delta P = x_B \; i \; P_A^*$

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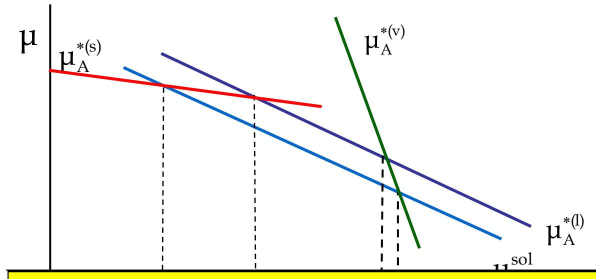
SUMMARY AND CONCLUSIONS

- **FREEZING POINT DEPRESSION AND BOILING POINT ELEVATION**



SUMMARY AND CONCLUSIONS

- **FREEZING POINT DEPRESSION :**

➢Ideal solution: $$\log x^{l}_{A} = -\frac{\Delta T_{m}\,\Delta \overline{H}_{m,A}}{R\,T^{2}_{m,A}}$$

➢Ideal dilute solution: $$\Delta T_{m} = K_{c}\,m_{B}$$

➢Real Solution: $$\log a_{A} = -\frac{\Delta T_{m}\,\Delta \overline{H}_{m,A}}{R\,T^{2}_{m,A}}$$

➢Electrolyte solution: $$\Delta T_{m} = K_{c}\,m_{B}\,i$$

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SUMMARY AND CONCLUSIONS

- **BOILING POINT ELEVATION (EBULLIOSCOPY):**

➢Ideal solution: $$\log x^{l}_{A} = -\frac{\Delta T_{b}\,\Delta \overline{H}_{vap,A}}{R\,T^{2}_{b,A}}$$

➢Ideal dilute solution: $$\Delta T_{b} = K_{b}\,m_{B}$$

➢Real Solution: $$\log a_{A} = -\frac{\Delta T_{b}\,\Delta \overline{H}_{vap,A}}{R\,T^{2}_{b,A}}$$

SUMMARY AND CONCLUSIONS

- **Osmotic PRESSURE:**

  - Ideal solution: $-RT\log x_A^l = \overline{V}_A^* \pi$
  - Ideal dilute solution: $\pi = c_B RT$
  - Real Solution: $-RT\log a_A = \overline{V}_A^* \pi$
  - Electrolyte solution: $\pi = RT c_B i$

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