# 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
- Applications
- Summary and Conclusions

# 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.



# 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.



## COLLIGATIVE PROPERTIES

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

# COLLIGATIVE PROPERTIES

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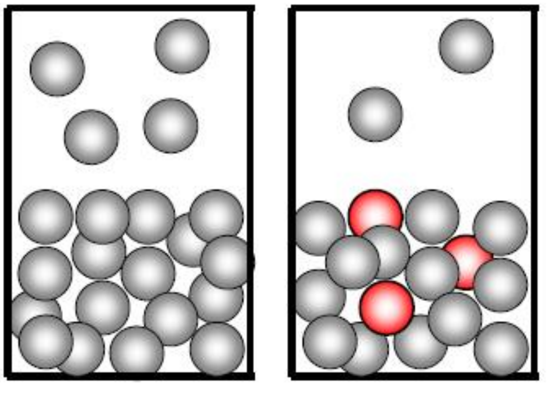
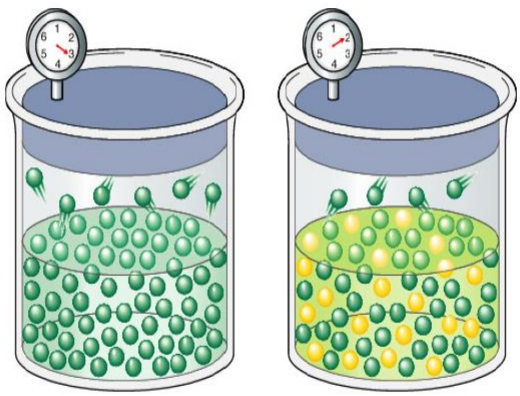
# VAPOUR PRESSURE LOWERING

- 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**

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# VAPOUR PRESSURE LOWERING

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

Ideal and ideal dilute solutions

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

Real solutions

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

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# 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)

Non-volatile solute

⇩

The vapour curve does not change

**SOLUTION**
Non-Volatile Solute
Volatile Solvent (A)

↑↓

**SOLID Phase**
Pure solvent (A)

The solute does not dissolve in the solid solvent

⇩

The solid curve does not change

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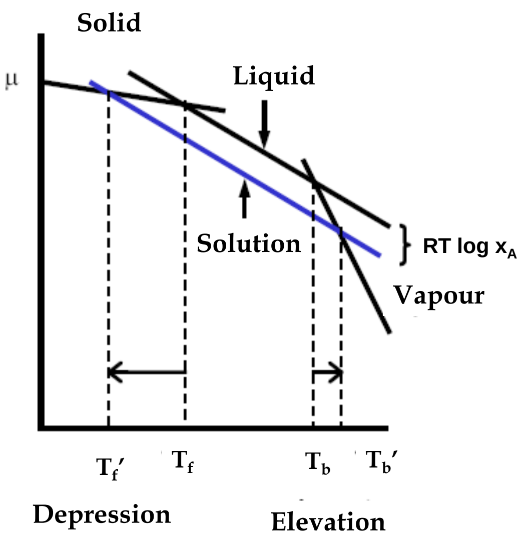
# COLLIGATIVE PROPERTIES

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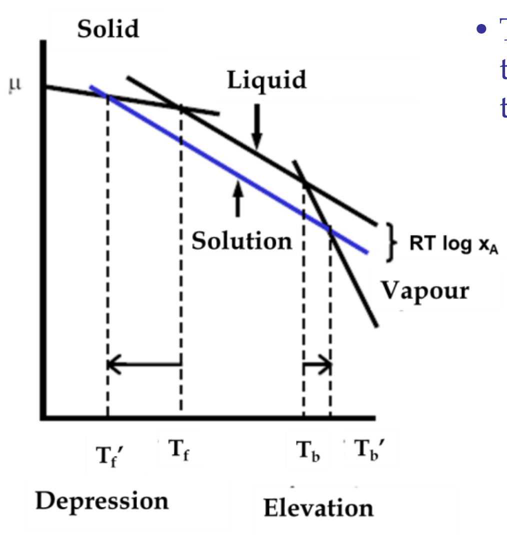
# COLLIGATIVE PROPERTIES




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

$$\left(\frac{\partial \mu}{\partial T}\right)_P = \left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$$

$$\bar{S}_{vapour} >>> \bar{S}_{liquid} > \bar{S}_{solid}$$

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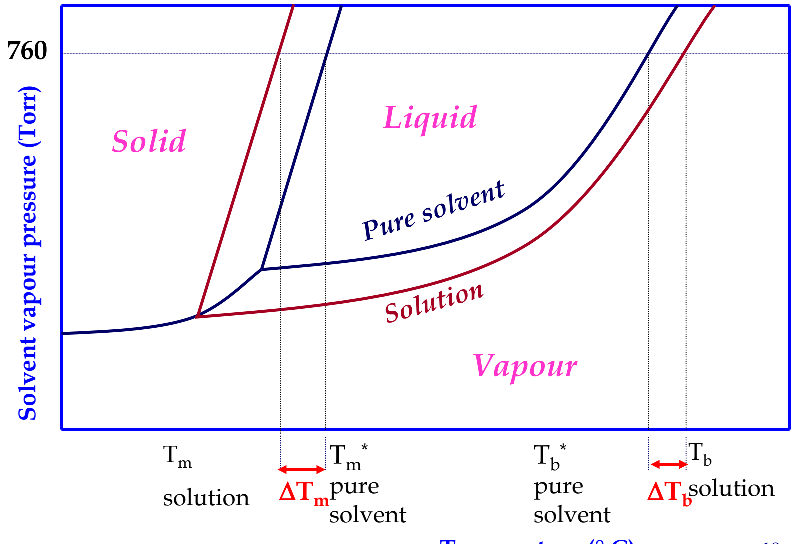
## COLLIGATIVE PROPERTIES

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## COLLIGATIVE PROPERTIES

- **Definition of Colligative Property**
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- **Summary and Conclusions**

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## 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**

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

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

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

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

## FREEZING POINT DEPRESSION

• IDEAL SOLUTION

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

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

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



## FREEZING POINT DEPRESSION

• IDEAL SOLUTION

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

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

## FREEZING POINT DEPRESSION

• IDEAL SOLUTION

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

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

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

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## FREEZING POINT DEPRESSION

• IDEAL SOLUTION

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

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

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

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## FREEZING POINT DEPRESSION

- **IDEAL SOLUTION**

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

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

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

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



## FREEZING POINT DEPRESSION

- **IDEAL DILUTE SOLUTIONS**

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

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

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

$$x_B^l \cong m_B\ M_A\ 10^{-3}$$

## FREEZING POINT DEPRESSION

- IDEAL DILUTE SOLUTION

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

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

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



## FREEZING POINT DEPRESSION

- REAL SOLUTION

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

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

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

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

## 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**

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

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

$$\boxed{\log a_A = \log \gamma_A\, x_A^l \cong \frac{-\overline{\Delta H}_{m,A}}{R}\left(\frac{\Delta T_m}{T_{m,A}^{*\,2}}\right)}$$

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# BOILING POINT ELEVATION

**VAPOUR Phase**
Pure solvent (A)

**SOLUTION**
Non-Volatile Solute
Volatile Solvent (A)

This property appears when there is phase equilibrium

⇩ between

solution and the pure solvent in the vapour state

⇩

**pure A vaporizes** when the solution is heated

# 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

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

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

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

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# BOILING POINT ELEVATION

- **IDEAL SOLUTION**

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

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

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

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# BOILING POINT ELEVATION

- **IDEAL DILUTE SOLUTION**

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

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

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

$$x_B^l \cong m_B\,M_A\,10^{-3}$$

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# BOILING POINT ELEVATION

- IDEAL DILUTE SOLUTION

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

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

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



# BOILING POINT ELEVATION

- REAL SOLUTION

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

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

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

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

## 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**

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

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

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

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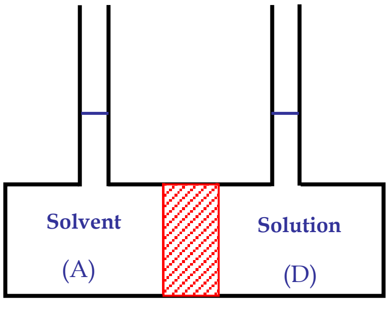
## OSMOTIC PRESSURE

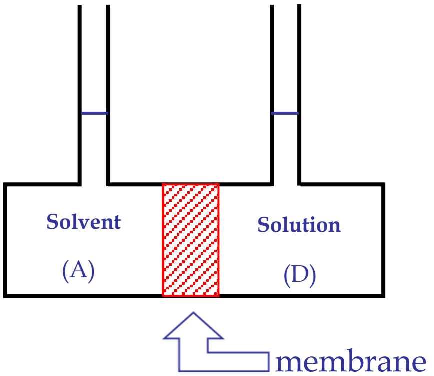



This property appears when theres is phase equilibrium

⇩ between

solution and the pure solvent in liquid phase

# OSMOTIC PRESSURE




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

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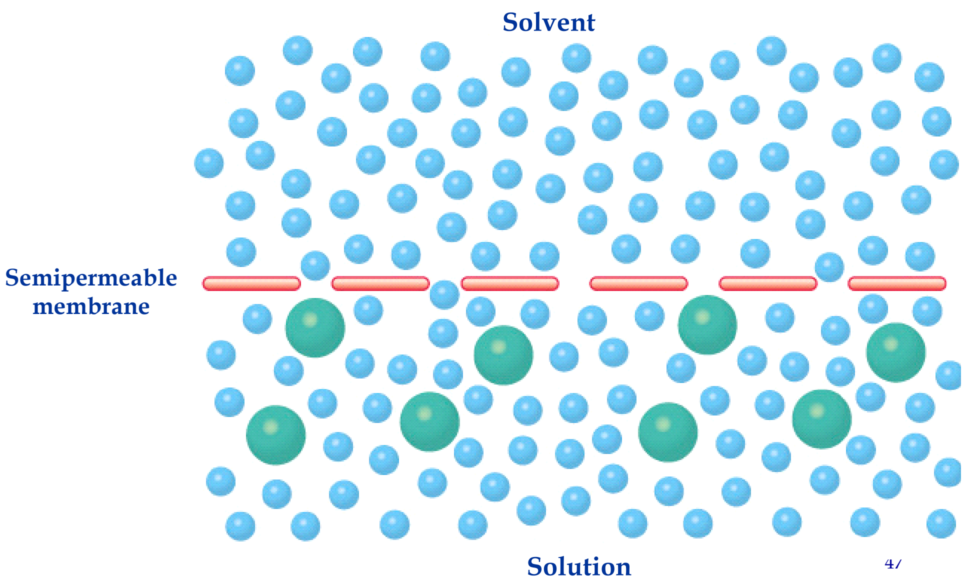
# OSMOTIC PRESSURE

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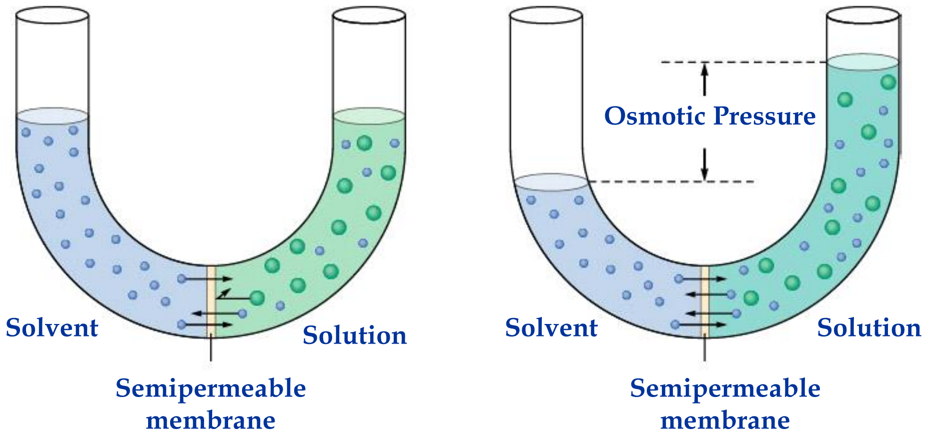
# OSMOTIC PRESSURE






# OSMOTIC PRESSURE

- **IDEAL SOLUTION**

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

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

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

$$\left(\frac{\partial \mu_A^*}{\partial P}\right)_T = \overline{V}_A^*$$

## OSMOTIC PRESSURE

• **IDEAL SOLUTION**

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

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

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

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## OSMOTIC PRESSURE

• **IDEAL DILUTE SOLUTION**

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

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

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

$$\boxed{\pi \cong c_B \, R\,T}$$

Van't Hoff Equation

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## OSMOTIC PRESSURE

- **REAL SOLUTION**

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

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

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

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

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

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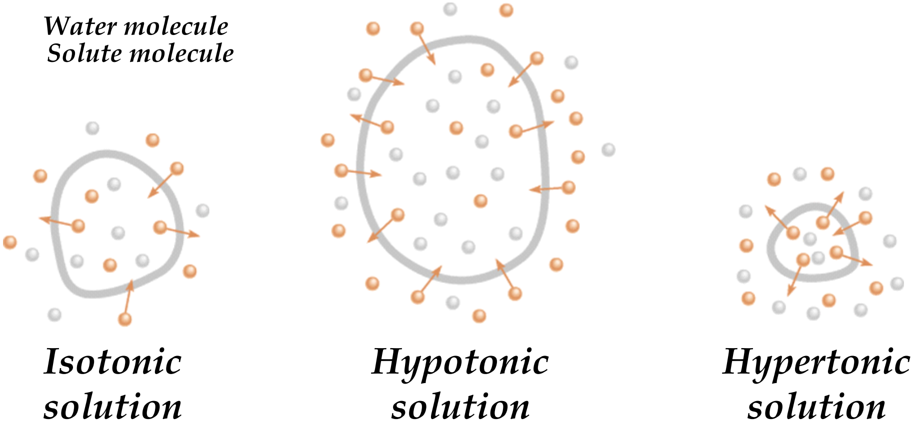
## OSMOTIC PRESSURE

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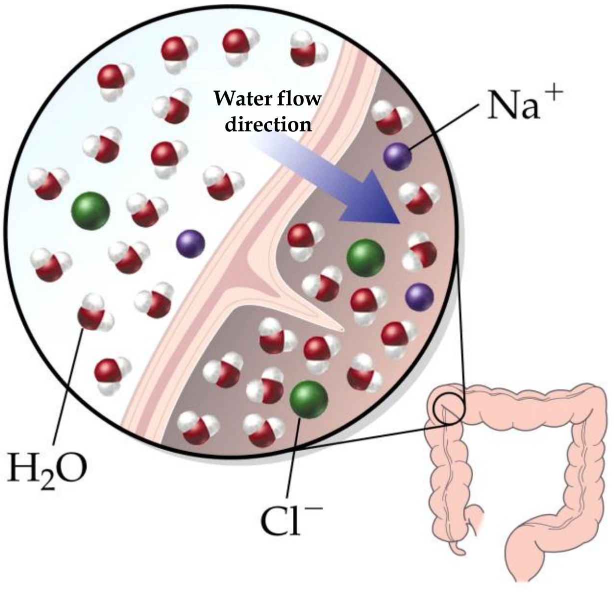
# OSMOTIC PRESSURE




Drinking sea water causes dehydration.

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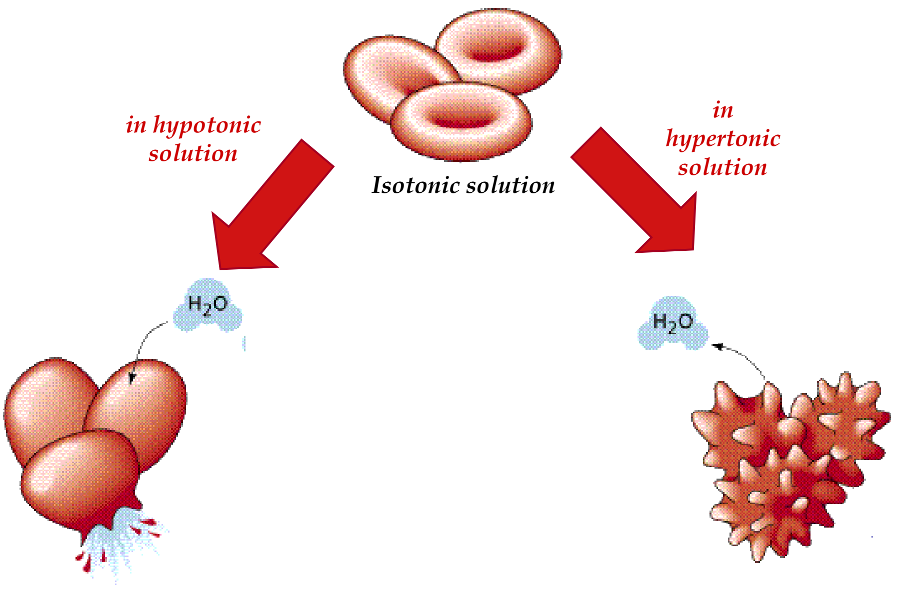
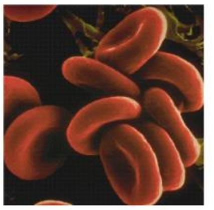
# OSMOTIC PRESSURE

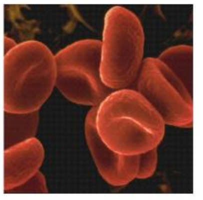


## OSMOTIC PRESSURE

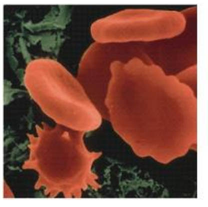
*Isotonic solution*



*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.

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## COLLIGATIVE PROPERTIES
## ELECTROLYTE SOLUTIONS

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

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

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

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

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

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## COLLIGATIVE PROPERTIES
## ELECTROLYTE SOLUTIONS

- **Vapour pressure lowering**
  - ✓Ideal dilute solution: $\boxed{\Delta P = x_B\ i\ P_A^*}$
- **Freezing Point Depression (Cryoscopy)**
  - ✓Ideal dilute solution: $\boxed{\Delta T_m = K_c\ m_B\ i}$
- **Boiling point elevation (ebullioscopy)**
  - ✓Ideal dilute solution: $\boxed{\Delta T_b = K_b\ m_B\ i}$
- **Osmotic Pressure**
  - ✓Ideal dilute solution: $\boxed{\pi = R\ T\ c_B\ i}$

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## 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 number of particles

## 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.

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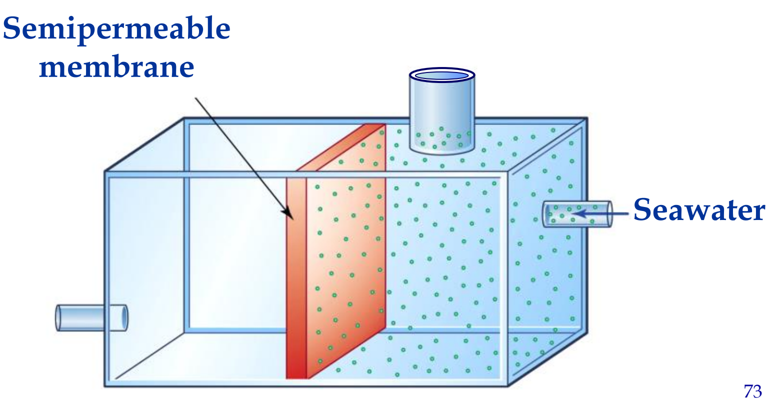
# OSMOTIC PRESSURE

**Reverse Osmosis:** Water Purification

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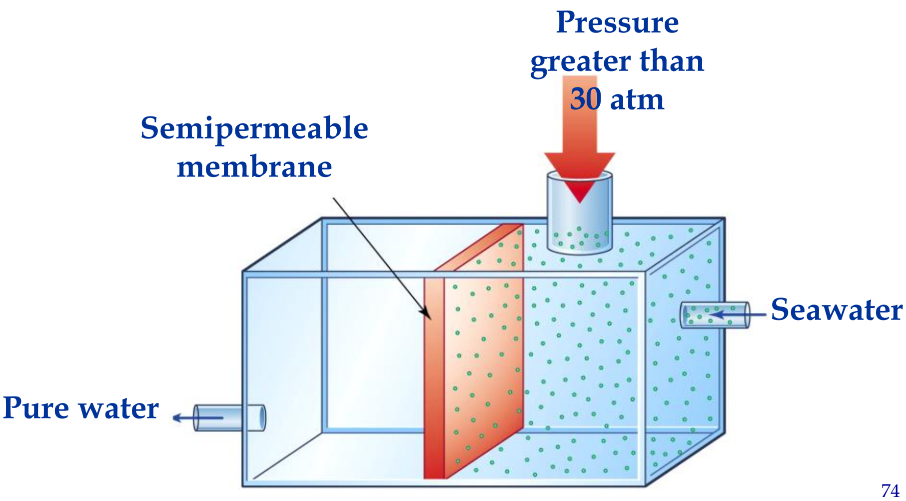
## OSMOTIC PRESSURE

**Reverse Osmosis:** Water Purification

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## COLLIGATIVE PROPERTIES

- **Definition of colligative property**
- **Vapour Pressure Lowering**
- **Freezing Point Depression (Cryoscopy)**
- **Boiling Point Elevation (Ebullioscopy)**
- **Osmotic Pressure**
- **Colligative Properties of Electrolyte Solutions**
- **Applications**
- **Summary and Conclusions**

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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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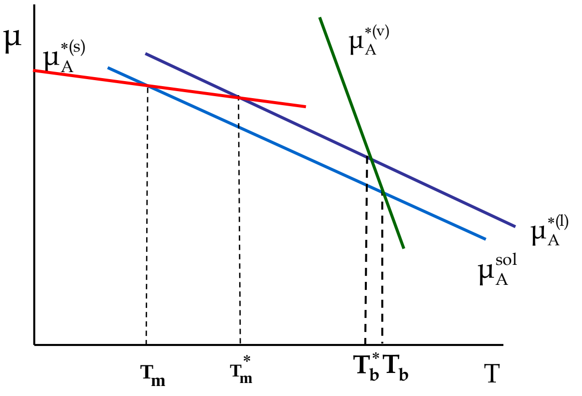
## SUMMARY AND CONCLUSIONS

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

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## SUMMARY AND CONCLUSIONS

• **FREEZING POINT DEPRESSION :**

- Ideal solution: $$\log x_A^l = -\frac{\Delta T_m \, \Delta \overline{H}_{m,A}}{R\, T_{m,A}^2}$$
- Ideal dilute solution: $$\Delta T_m = K_c \, m_B$$
- Real Solution: $$\log a_A = -\frac{\Delta T_m \, \Delta \overline{H}_{m,A}}{R\, T_{m,A}^2}$$
- Electrolyte solution: $$\Delta T_m = K_c \, m_B \, i$$

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## SUMMARY AND CONCLUSIONS

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

- Ideal solution: $$\log x_A^l = -\frac{\Delta T_b \, \Delta \overline{H}_{vap,A}}{R\, T_{b,A}^2}$$
- Ideal dilute solution: $$\Delta T_b = K_b \, m_B$$
- Real Solution: $$\log a_A = -\frac{\Delta T_b \, \Delta \overline{H}_{vap,A}}{R\, T_{b,A}^2}$$
- Electrolyte solution: $$\Delta T_b = K_b \, m_B \, i$$

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# SUMMARY AND CONCLUSIONS

- **Osmotic PRESSURE:**

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

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

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

  - Electrolyte solution: $\pi = R\,T\,c_B\, i$

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