

Physical Pharmacy



Electrolytes 1

Solutions of Electrolytes : Colligative Properties of Electrolytic Solutions

- As stated in the previous chapter, van't Hoff observed that the osmotic pressure, π , of dilute solutions of **nonelectrolytes**, such as sucrose and urea, could be expressed satisfactorily by the equation : $n\pi = RTc$
- Where R is the gas constant, T is the absolute temperature, and c is the concentration in moles/liter.
- Van't Hoff found, however, that solutions of electrolytes (of the same concentration) gave osmotic pressures approximately two, three, and more times larger than expected from this equation, depending on the electrolyte investigated.



Solutions of Electrolytes: Colligative Properties of Electrolytic Solutions

- Introducing a correction factor i to account for the irrational behavior of ionic solutions, and in this case
 : π = iRTc
- By the use of this equation, van't Hoff was able to obtain:
- a. A calculated values that compared favorably with the experimental results of osmotic pressure.
- b. Van't Hoff recognized that i approached the number of ions into which the molecule dissociated as the solution was made increasingly dilute.





Solutions of Electrolytes : Colligative Properties of Electrolytic Solutions

$$\mathbf{F}$$
 KCl \rightarrow K⁺ + Cl i = 2

© CaSO4 →
$$Ca^{+2} + So^{-2} + i = 2$$

$$\P$$
 Na2SO4 \rightarrow 2Na +So4 i =3

$$A|C|3 \rightarrow A| + 3C| i = 4$$



Solutions of Electrolytes : Colligative Properties of Electrolytic Solutions

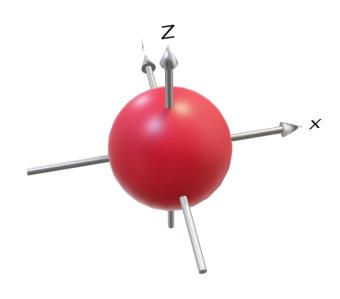
The colligative properties in dilute solutions of electrolytes are expressed on the molal scale by the equations

$$\Delta P / P^{\circ} = 0.018$$

$$\Delta T_b = i K_b m$$

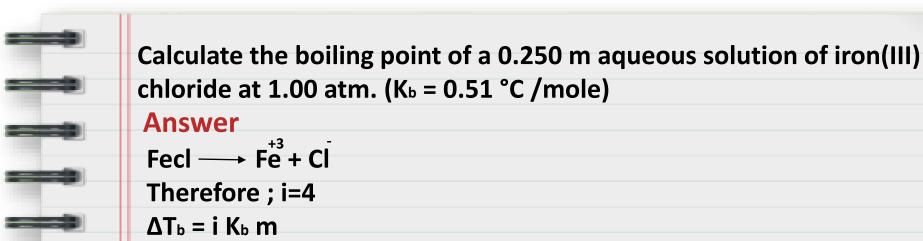
$$\Delta T_f = i K_f m$$

$$\pi = i RTc Or \pi = i RTm$$





Example:



$$\Delta T_b = T_b \text{ solution} - T_b \text{ solvent}$$

$$0.51 = T_b \text{ solution} - 100$$

$$T_b \text{ solution} = 100.51 \text{°C}$$

 $= 4x 0.51x 0.25 = 0.51 ^{\circ}C$



Example:

Calculate the vapor pressure, boiling point and freezing point of 1.25m NaOH solution and compare your results with that of glucose solution of the same concentration. Knowing that the vapor pressure of pure water is 23.8 mmHg, Kb=0.51°C /mole and Kf = 1.86°C /mole

Answer: NaOH

Na OH
$$\longrightarrow$$
 Na + OH $\triangle P = P_{solvent} - P_{solution} =$

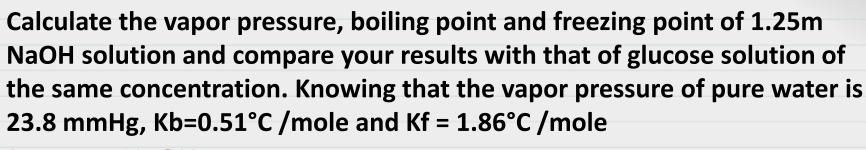
$$\Delta P / P^{\circ} = 0.018$$
 1.071= 23.8 - P solution

$$\Delta P = i \ 0.018 \ m \ P^{\circ}1$$
 $P \ solution = 22.729 \ mmHg$

$$= 2 \times 0.018 \times 1.25 \times 23.8$$



Example:



Answer: NaOH

ΔTb = i Kb m	$\Delta T_f = i K_f m$
= 2 x 0.51 x 1.25	= 2 x 1.86 x 1.25
= 1.275°C	= 4.65°C

$$\Delta T_b = T_b \text{ solution} - T_b \text{ solvent}$$

$$1.27 = T_b \text{ solution} - 100$$

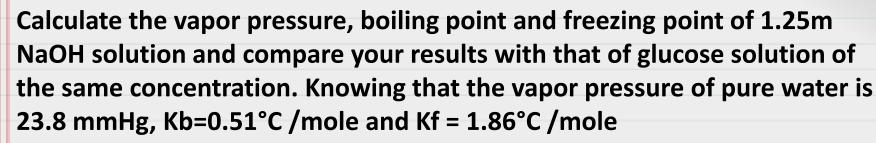
$$T_b \text{ solution} = 101.27 \text{ °C}$$

$$\Delta T_f = T_f \text{ solvent} - T_f \text{ solution}$$

$$T_f \text{ solution} = -4.65 \text{ °C}$$



Example:



Answer: Glucose

Glucose → Glucose

Nonelectrolyte

 $\Delta P / P^{\circ} = 0.018$

 $\Delta P = 0.018 \text{ m } P^{\circ}1$

 $= 0.018 \times 1.25 \times 23.8$

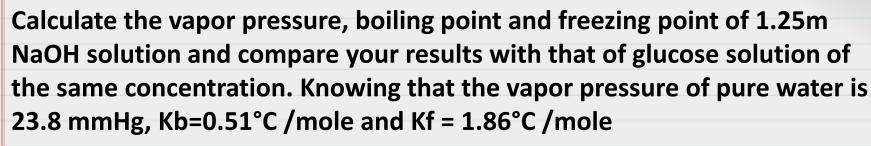
= 0.536 mmHg







Example:



Answer: Glucose

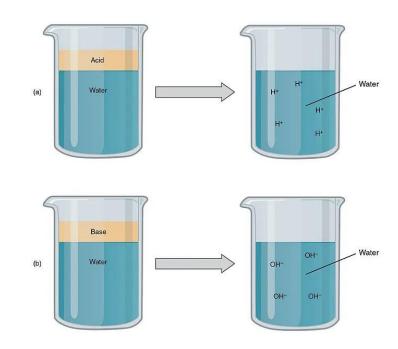
ΔTb = Kb m	$\Delta T_f = K_f m$
= 0.51 x 1.25	= 1.86 x 1.25
= 0.638°C	= 2.325°C

$\Delta T_b = T_b$ solution $-T_b$ solvent	$\Delta T_f = T_f \text{ solvent} - T_f \text{ solution}$
$0.638 = T_{b \text{ solution}} - 100$	2.325= zero - Tf solution
Tb solution = 100.638°C	Tf solution = - 2.325°C



Weak and Strong Electrolytes

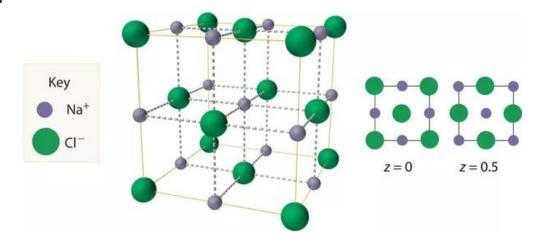
- The large number of oppositely charged ions in solutions of electrolytes influences one another through interionic attractive forces.
- Although this interference is negligible in dilute solutions, it becomes significant at moderate concentrations.
- In solutions of weak electrolytes, regardless of concentration, the number of ions is small and the interionic attraction is non-significant.





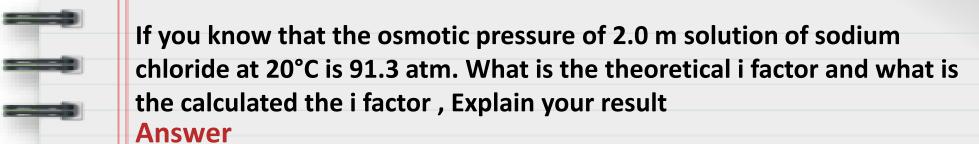
Weak and Strong Electrolytes

- For example: (NaCl)
- Ions may associate at high concentration into groups known as ion pairs (e.g., Na+Cl-)and ion triplets (Na+Cl-Na+).
- b. So ions are not completely dissociated from each other and do not exert their full effecti.e, i less than 2





Weak and Strong Electrolytes Example: 1



Na Cl
$$\longrightarrow$$
 Na⁺ + Cl⁻

Therefore, theoretical i factor is 2

$$\pi = i RTm$$

$$91.3 = i \times 0.082 \times (20 + 273) \times 2 = i = 1.9$$

Since the calculated i factor is less than 2., That is mean there is an association of ions



Weak and Strong Electrolytes

- Because of the electrostatic attraction and ion association in moderately concentrated solutions of strong electrolytes, the values of the colligative properties are less than expected for solutions of unhindered ions (dilute solutions).
- Consequently, a strong electrolyte may be completely ionized, yet incompletely dissociated into free ions



Weak and Strong Electrolytes: Q22

