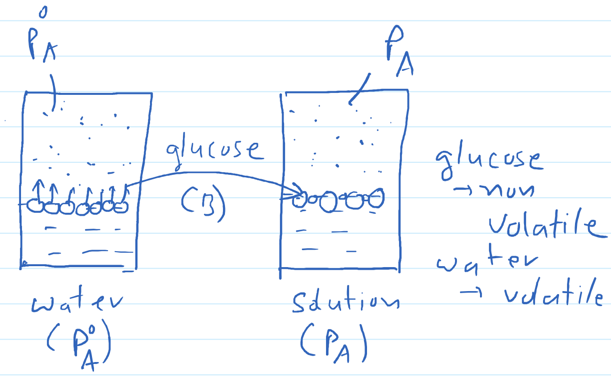
Raoult's Law



Vapour pressure of volatile component of a solution is directly proportional to mole fraction of that component in solution.

$$P_A \propto x_A$$

$$P_A = \underline{k}\, x_A$$

For $x_A = 1$, $x_B = 0$

$$P_A = P_A^o = k(1)$$

$$k = P_A^o$$

$$\boxed{P_A = P_A^o x_A}$$

$$x_A = \frac{n_A}{n_A + n_B}, \quad x_B = \frac{n_B}{n_A + n_B}$$

Question

Vapour pressure of water at 293K is 17.535 mmHg. Calculate the vapour pressure of water at 293K, when 25g of glucose is dissolved in 450g water.

Answer

Raoult's law:

A → water
B → Glucose

$$P_A = P_A^o x_A$$

$$= 17.535 \frac{n_A}{n_A + n_B}$$

$$= 17.535 \left[\frac{450/18}{450/18 + 25/180} \right]$$

$$= 17.535 \left[\frac{4500}{4500 + 25} \right]$$

$$= 17.49 \text{ mmHg}.$$

Question

The vapour pressure of water is 12.3 kPa at 300K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.

Answer :

1 molal means

A → water

B → non-volatile solute

1 mole solute in 1000 gm water

1mole solute in $\frac{1000}{18}$ mole water.

$$x_A = \frac{n_A}{n_A + n_B} = \frac{1000/18}{1000/18 + 1}$$

Raoult's law:

$$P_A = P_A^\circ x_A$$

$$= 12.3 \times \left(\frac{1000/18}{1000/18 + 1} \right)$$

$$= 12.3 \left(\frac{1000}{1000 + 18} \right)$$

$$= 12.08 \text{ kPa.}$$

Question

A solution containing 30g of non-volatile solute exactly in 90g of water has a vapour pressure of 2.8 kPa at 298 K. Further 18g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate:

i) Molar mass of the solute

ii) Vapour pressure of water at 298 K.

Answer

A → water

B → non volatile solute

$$n_B = \frac{30}{M_B}$$

Case I

$n_A = \frac{90}{18} = 5$ moles

Case II

$n = \frac{108}{18} = 6$ moles

Case I

$n_A = \frac{90}{18} = 5$ moles

$P_A = 2.8$ kPa

$P_A = P_A^o x_A$

$2.8 = P_A^o \left(\frac{5}{5 + \frac{30}{M_B}}\right)$ — I

Case II

$n_A = \frac{108}{18} = 6$ moles

$P_A = 2.9$ kPa

$P_A = P_A^o x_A$

$2.9 = P_A^o \left(\frac{6}{6 + \frac{30}{M_B}}\right)$ — II

II ÷ I

$$\frac{2.9}{2.8} = \frac{6}{\left(6 + \frac{30}{M_B}\right)} \frac{\left(5 + \frac{30}{M_B}\right)}{5}$$

$$\frac{2.9}{2.8} = \frac{6}{5} \frac{(5M_B + 30)}{(6M_B + 30)}$$

$M_B = 23$ gm

Put M_B in eq I

$P_A^o = 3.53$ kPa

$P_A = P_A^o x_A$

$P_A = P_A^o (1 - x_B)$ $[x_A + x_B = 1]$

$P_A = P_A^o - P_A^o x_B$

$P_A^o x_B = P_A^o - P_A$ = Lowering of vapour pressure

$x_B = \frac{P_A^o - P_A}{P_A^o}$ = Relative lowering of vapour pressure

Relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P_A^o - P_A}{P_A^o} = \frac{n_B}{n_A + n_B}$$ ✓

$$\frac{P_A^o}{P_A^o - P_A} = \frac{n_A + n_B}{n_B}$$

$$\frac{P_A^o}{P_A^o - P_A} - 1 = \frac{n_A + n_B}{n_B} - 1$$

$$\frac{P_A^o - (P_A^o - P_A)}{P_A^o - P_A} = \frac{n_A + n_B - n_B}{n_B}$$

$$\frac{P_A}{P_A^o - P_A} = \frac{n_A}{n_B}$$

$$\boxed{\frac{P_A^o - P_A}{P_A} = \frac{n_B}{n_A}}$$

$$\boxed{\frac{P_A^o - P_A}{P_A} = \frac{w_B \times M_A}{M_B \times w_A}}$$

Question

An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

Answer: $M_B = ?$

2% $\left(\frac{w}{w}\right)$, $\left(\frac{w}{V}\right)$, $\left(\frac{V}{V}\right)$

weight related

$$x_A, x_B = \frac{n_B}{n_A + n_B} = \frac{w_B/M_B}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}$$

$P_A = 1.004$ bar

$P_A^o = 1$ atm $= 1.013$ bar

$$\frac{P_A^o - P_A}{P_A} = \frac{n_B}{n_A}$$

$$\frac{1.013 - 1.004}{1.004} = \frac{w_B \times M_A}{M_B \times w_A}$$

2% $\frac{w}{w}$

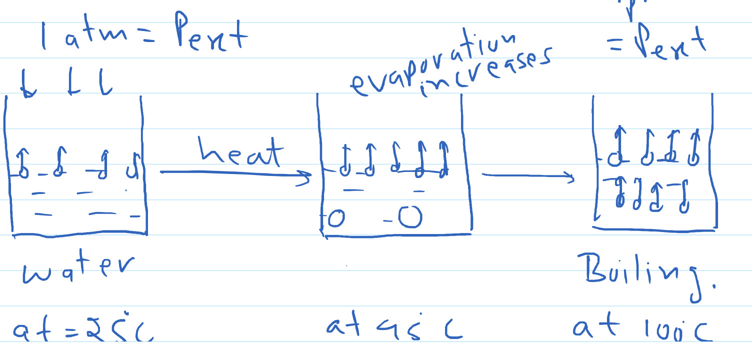
2 gm solute in 98 gm water

$$\frac{1.013 - 1.004}{1.004} = \frac{2 \times 18}{M_B \times 98}$$

$M_B = 41$ gm.

Boiling point:

When vapour pressure of a liquid becomes equal to external pressure, this



external pressure, this phenomenon is called boiling and temperature at which boiling occurs is called boiling point.

at = 25°C   at 45°C   at 100°C

Normal boiling point:

When $P_{ext} = 1\ atm = 1.013\ bar$, then boiling point is called normal boiling point.

$$P_A = P^0_A x_A$$