

COLLIGATIVE PROPERTIES

Lecture 14



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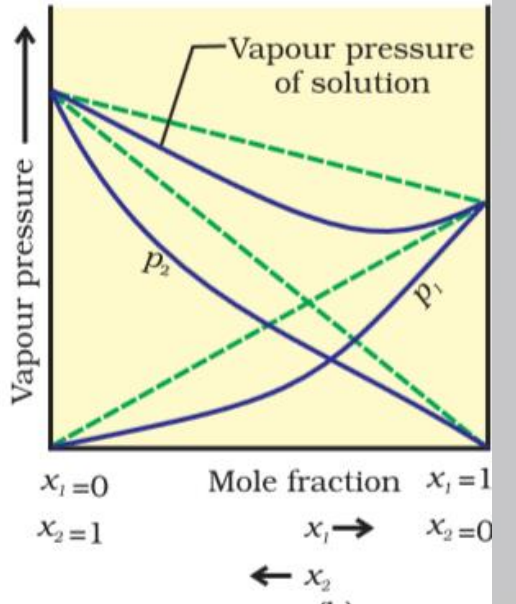
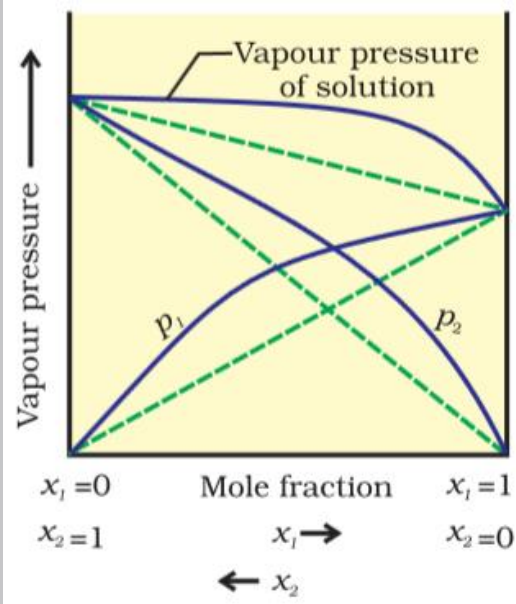
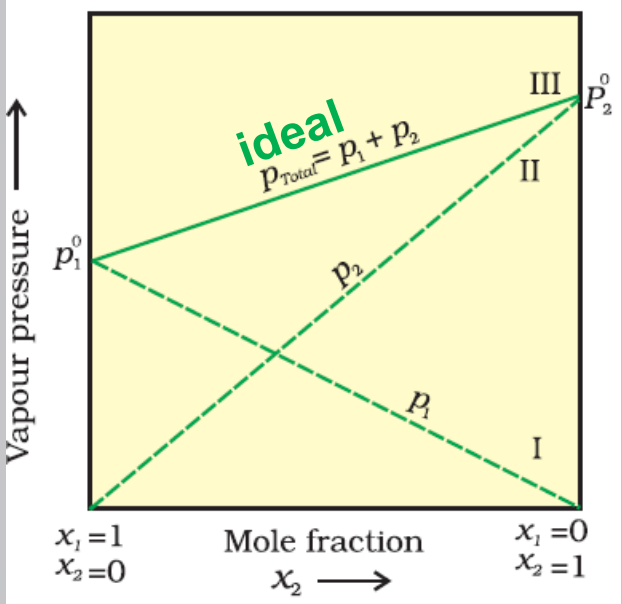
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COLLIGATIVE PROPERTIES

- properties of a liquid that change when the solute is added
- magnitude of change depends on the relative number of solute molecules and not on their chemical identity
- four colligative properties:
 1. The lowering of the vapour pressure of the solvent
 2. The raising of its boiling point (boiling point elevation)
 3. The lowering of its freezing point (freezing point depression)
 4. The tendency of a solvent to flow through a membrane into solution (osmosis)



RAOULT'S LAW FOR VOLATILE MIXTURES



- obeys Raoult's law over the entire range of concentration
- forces between solute and solvent molecules are the same as between solvent molecules

$$P_1 \text{ (vapour)} = P_1^0 \times \chi_1$$

$$P_2 \text{ (vapour)} = P_2^0 \times \chi_2$$

$$P \text{ (total)} = P_1 + P_2$$

- intermolecular attractive forces 1 and 2 are weaker
- molecules of solute in solution evaporate easier than in a pure state.
- vapour pressure will increase

$$P_1 \text{ (vapour)} > P_1^0 \times \chi_1$$

$$P_2 \text{ (vapour)} > P_2^0 \times \chi_2$$

$$P \text{ (total)} > P_1 + P_2$$

- intermolecular attractive forces 1 and 2 are stronger
- vapour pressure decreases resulting in

$$P_1 \text{ (vapour)} < P_1^0 \times \chi_1$$

$$P_2 \text{ (vapour)} < P_2^0 \times \chi_2$$

$$P \text{ (total)} < P_1 + P_2$$



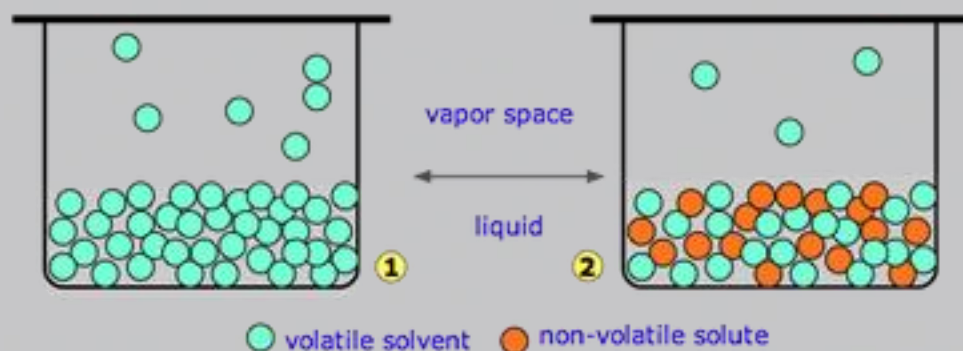
RAOULT'S LAW – NON VOLATILE SOLUTE

Raoult's law: the vapor pressure of a solvent in a presence of a nonvolatile solute is proportional to the mole fraction of the solvent.

$$P(\text{vapour}) = P^0 \times \chi_{\text{solvent}}$$

P^0 - P (vapour) of pure solvent

- for a solution of a non-volatile solute P (vapour) of the solution is from the solvent alone
- lower than the vapour pressure of the pure solvent at the same temperature



Solute particles take up space on the surface of the liquid. As more solute particles are added, more of the surface is occupied by them and therefore less solvent molecules can vaporise

- the more non-volatile particles there are, the harder for solvent it is to escape
- the decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature.



Calculate the vapor pressure at 25 degC of an aqueous solution of a glucose (C₆H₁₂O₆) in which 18 g of glucose were dissolved in 180 g water. The vapor pressure of water at 25 degC is 24 mmHg

$$V_p(\text{solution}) = V_p(\text{pure solvent}) \times X_{\text{solvent}}$$

$$n_g = 18 \text{ g} / 180 \text{ g/mol} = \boxed{0.1 \text{ mol}}$$

$$n_{\text{H}_2\text{O}} = 180 \text{ g} / 18 \text{ g/mol} = \boxed{10 \text{ mol}}$$

$$X_{\text{H}_2\text{O}} = \frac{10}{10+0.1} = \boxed{0.99}$$

$$V_p(\text{solution}) = 24 \text{ mmHg} \times 0.99$$

$$= \boxed{23.76 \text{ mmHg}} \quad \text{less ...}$$

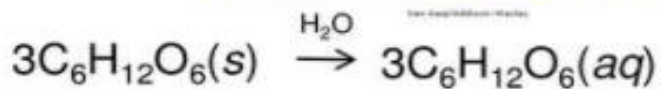


LOWERING OF THE VAPOUR PRESSURE OF THE SOLVENT

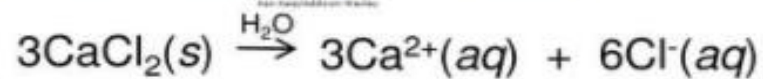
The greater the number of solute particles in a solvent the lower the resulting vapour pressure

Which solution will have the lowest vapor pressure?

Produces **6 mol of particles**
because each formula unit
of NaCl dissociates into two ions.



Produces **3 mol of particles**
because glucose
does not dissociate.



Produces **9 mol of particles**
because each formula unit
of CaCl_2 dissociates into three ions.

The greater the number of solute particles in a solvent the lower the resulting vapour pressure

Ionic compounds that dissociate have a greater effect on vapor pressure than molecular compounds because.....

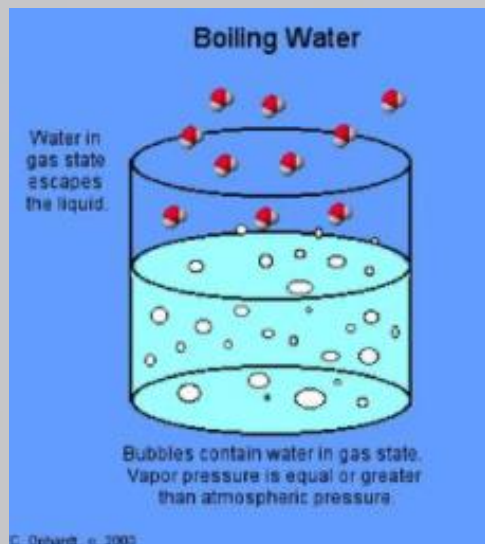
Dissociation is the process by which ionic compounds such as salts break down into simpler constituents – ions, usually in a reversible manner



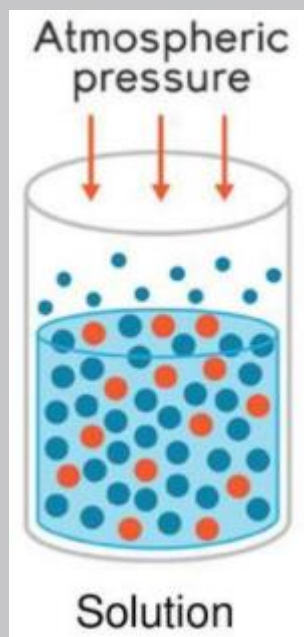
BOILING POINT ELEVATION

Volatile liquid solvent
Non-volatile solute

A liquid boils when its vapor pressure equals atmospheric pressure



In a solution containing a nonvolatile solute, its vapour pressure is **LOWER**



When this solution is heated and the temperature is raised to the boiling point of the pure solvent the resulting vapor pressure is still less than atmospheric pressure and the solution will not boil.

BP INCREASES !!!

The solution must be heated to a higher temperature to raise the vapour pressure to atmospheric pressure. The temperature difference between a solution's boiling point and a pure solvent is called **boiling point elevation**

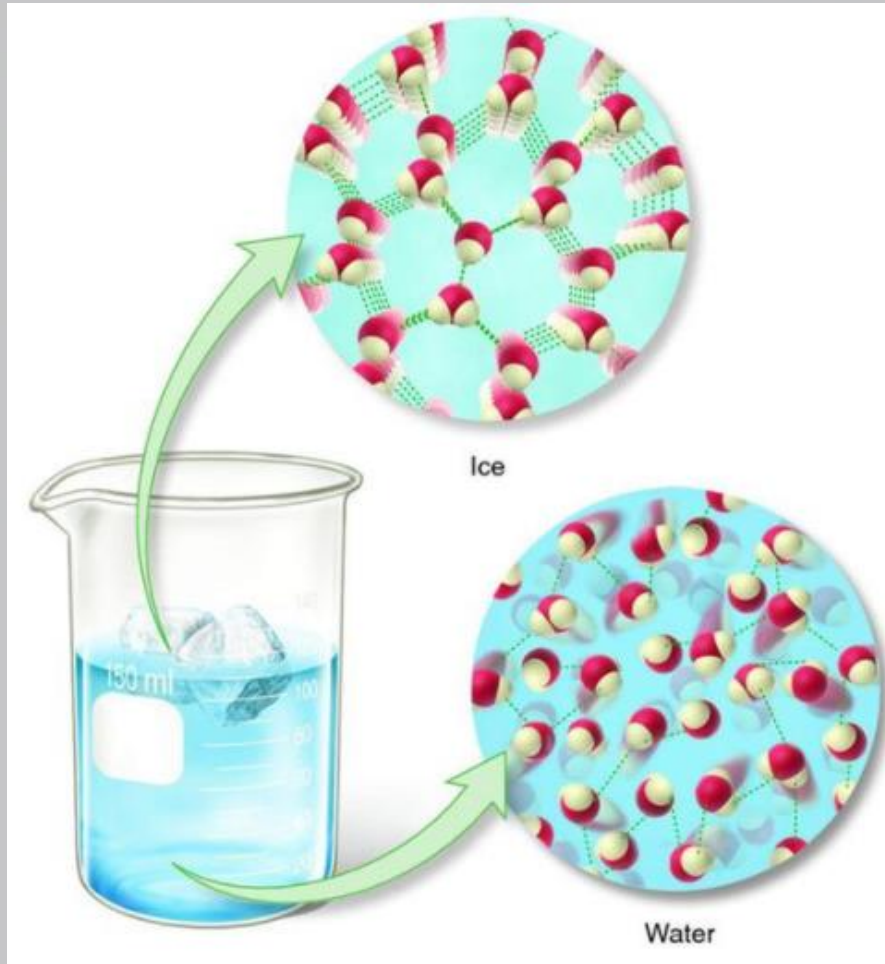


The fluid circulating through a car's cooling system is a solution of water and ethylene glycol, or antifreeze. Ethylene glycol raising the boiling point of the solution to above the boiling point of water. This helps protect the car from overheating in the summer.



FREEZING POINT DEPRESSION

The salt added to the ice lowers the freezing point of the ice so that the temperature surrounding the ice cream is even colder than freezing



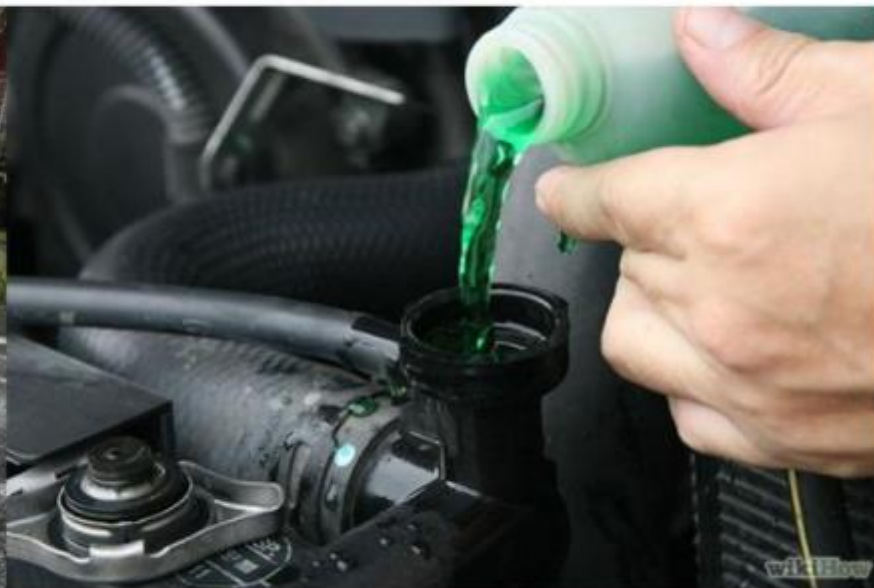
When a liquid is cooled, the kinetic energy of its particles decreases. As the particles slow down, the intermolecular forces draw the particles close together and the liquid freezes to a solid



The freezing point of a solution is lower than that of a pure solvent.



Salt lowers the freezing point of water.



Antifreeze lowers the freezing point of water.

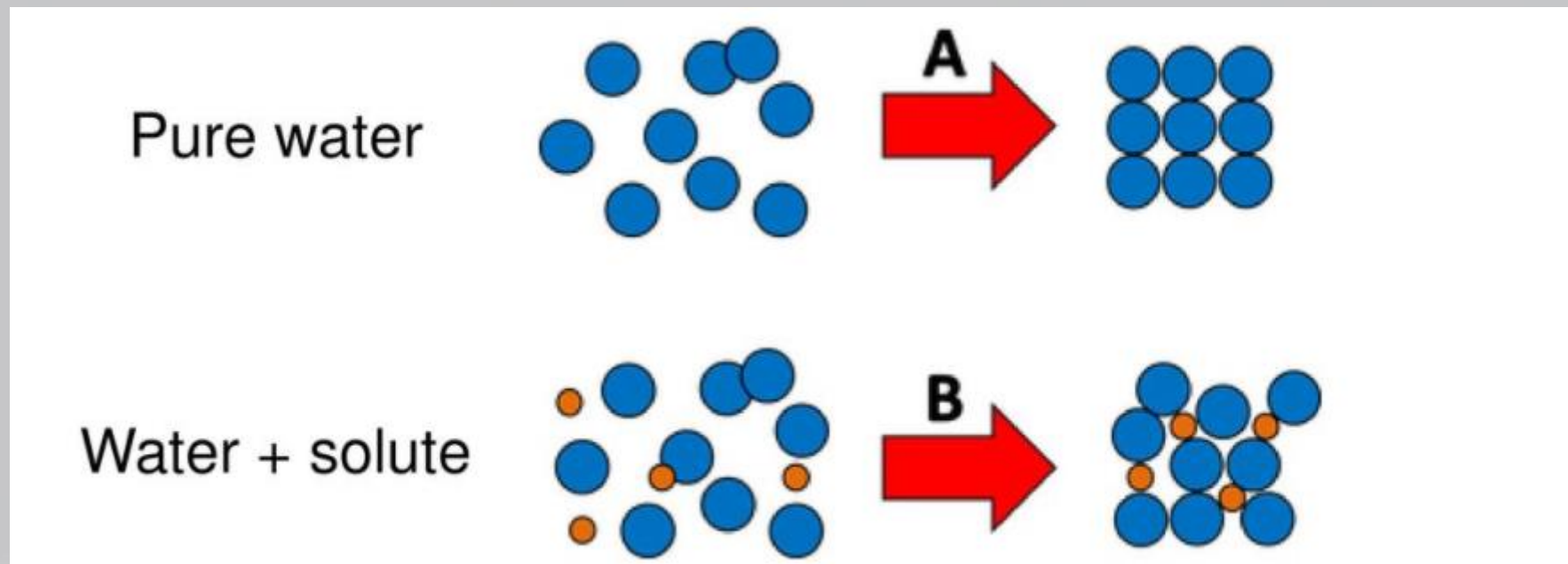


FREEZING POINT DEPRESSION

Volatile liquid solvent

Non-volatile solute

In a solution, the solute particles interfere with the attractive force among the solvent particles. This prevents the solvent from entering the solid state at its normal freezing point. The temperature must be lower further until the particles draw close together and the solution freezes.



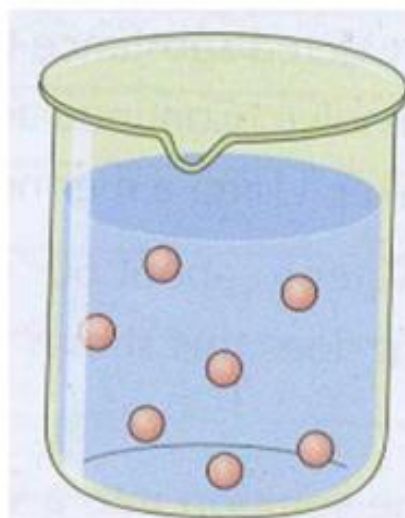
FP INCREASES !!!



FREEZING POINT DEPRESSION

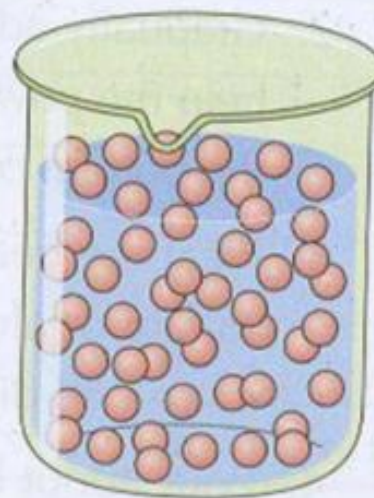
The greater the number of solute particles in a solvent, the lower the freezing point of the solution

1 mol of solute particles
(in 1000 g of water) lowers
the freezing point by **1.86°C**.



Dilute solution

2 mol of solute particles
(in 1000 g of water) lowers
the freezing point by **3.72°C**.



Concentrated solution



MOLALITY DEPENDANCE

The magnitude of the freezing-point depression (ΔT_f) and the boiling-point elevation (ΔT_b) of a solution are directly proportional to the molal concentration (m), assuming the solute is molecular, not ionic.

$$\text{Molality } (m) = \frac{\text{moles of solute (mol)}}{\text{kilogram of solvent(kg)}}$$

$$\Delta T_f = K_f \times m$$

$$\Delta T_b = K_b \times m$$

K_f and K_b Values for
Some Common Solvents

Solvent	K_f ($^{\circ}\text{C}/m$)	K_b ($^{\circ}\text{C}/m$)
Acetic acid	3.90	3.07
Benzene	5.12	2.53
Camphor	37.7	5.95
Cyclohexane	20.2	2.79
Ethanol	1.99	1.19
Nitrobenzene	7.00	5.24
Phenol	7.40	3.56
Water	1.86	0.512



Example: Calculate the boiling and freezing points of an aqueous solution of glucose ($C_6H_{12}O_6$) in which 18 g of glucose were dissolved in 180 g water. K_b for water is 0.512 degC/m and K_f is 1.86 degC/m . Assume normal conditions.

$$\begin{aligned}\text{molarity} &= \frac{\text{moles solute}}{\text{kg solvent}} \\ &= \frac{0.1 \text{ mol}}{0.180 \text{ kg}} \\ &= 0.556 \text{ m}\end{aligned}$$

$$\begin{aligned}\Delta T_b &= K_b \times m = \\ &= 0.512 \text{ }^\circ\text{C/m} \times 0.556 \text{ m} = \\ &= 0.284 \text{ }^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{BP} &= 100 + 0.284 = \\ &= \boxed{100.3 \text{ }^\circ\text{C}}\end{aligned}$$

$$\begin{aligned}\Delta T_f &= K_f \times m = \\ &= 1.86 \text{ }^\circ\text{C/m} \times 0.556 \text{ m} = \\ &= 1.03 \text{ }^\circ\text{C}\end{aligned}$$

$$\begin{aligned}\text{FP} &= 0 - 1.03 \text{ }^\circ\text{C} \\ &= \boxed{-1.03 \text{ }^\circ\text{C}}\end{aligned}$$



Question 1 Calculate the vapor pressure (in torr) at 298 K in a solution prepared by dissolving 46 g of the non-volatile non-electrolyte urea $\{\text{CO}(\text{NH}_2)_2\}$ in 132 g of ethanol. The vapor pressure of ethanol at 298 K is 58.9 torr.

Question 2 Two solutions are formed, one from adding 10 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) to 1 L of water and the other by adding 10 g of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) to 1 L of water. Which solution has the:

- (I) lower vapor pressurea)
- (II) higher freezing pointb)
- (III) lower boiling pointc)

- a) glucose, glucose, sucrose
- b) sucrose, sucrose, sucrose
- c) glucose, sucrose, glucose
- d) sucrose, sucrose, glucose
- e) glucose, sucrose, sucrose

Question 3 1.18 grams of an unknown non-electrolytic solute were dissolved in 60.0 g of water ($K_{\text{fp}} = 1.86 \text{ K/m}$). If the freezing point of the solution was -0.110°C , determine the molar mass of the unknown solute.

- a) .33 g/mol b) 346 g/mol c) 1.16 g/mol d) 333 g/mol e) 860 g/mol

Question 4 Yttrium(III) chloride dissolves in water according to: $\text{YCl}_3(\text{s}) \rightarrow \text{Y}^{3+}(\text{aq}) + 3 \text{Cl}^{-}(\text{aq})$. What is the boiling point of the solution when 0.1953 g of LaCl_3 (molar mass 195.3 g/mol) is dissolved in 10.0 g of H_2O ? (K_b of water is 0.512°C/m .)

- a) 100.0512 $^\circ\text{C}$ b) 0.0512 $^\circ\text{C}$ c) 99.9482 $^\circ\text{C}$ d) 99.795 $^\circ\text{C}$ e) 100.205 $^\circ\text{C}$

