

THE FREEZING POINT OF A NON-VOLITILE SOLUTE SOLUTION

NHIỆT ĐỘ ĐÔNG ĐẶC CỦA DUNG DỊCH CHỨA CHẤT TAN KHÔNG BAY HƠI

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Tóm tắt:

Bài viết trình bày về độ giảm nhiệt độ đông đặc của dung dịch chứa chất tan không bay hơi. Ảnh hưởng của nồng độ chất tan đến độ giảm nhiệt độ đông đặc của dung dịch, tầm quan trọng của tính chất này đối với các hiện tượng tự nhiên cũng như những ứng dụng công nghệ sẽ được đề cập trong bài viết. Hòa tan một chất tan không bay hơi vào dung môi sẽ làm nhiệt độ đông đặc của dung dịch giảm. Độ hạ nhiệt độ đông đặc có nhiều ứng dụng thực tế như sử dụng muối để khử băng trên đường, dùng ethylene glycol (EG) để khử băng cho máy bay và làm chất làm mát/chống đông trong bộ tản nhiệt ô tô. Hy vọng sẽ mang đến bạn đọc những thông tin hữu ích về tính chất của dung dịch.

Từ khóa: nhiệt độ (điểm) đông đặc, dung dịch chất tan không bay hơi, tính chất tập hợp, áp suất hơi.

Abstract:

The paper attempts to present the freezing point depression of a solution with a non-volatile solute. The information such as the effect of solute concentration on freezing point depression and the importance to many natural phenomena and technological applications will be covered in this paper. When a non-volatile solute is dissolved in a solvent, the freezing point of the solution is lowered. The freezing-point depression has many practical applications such as using salts to remove ice from roadways, using ethylene glycol to de-ice an aircraft or to keep the coolant from freezing in automobile radiators, the survival of fish and other cold-blooded sea animals at temperatures below 0°C... It is hoped that useful information will help you to know more about the properties of a solution.

Keywords: freezing point, non-volatile solution, colligative propertie, vapor pressure.

1. The properties of solutions with a non-volatile solute

In chemistry, a solvent is something that a solute is dissolved into. A non-volatile solute is a substance that does not readily evaporate into a gas under existing conditions. Sucrose, ethylene glycol, sodium chloride, and calcium chloride are examples of non-volatile solutes.

The presence of solute gives a solution different physical properties than the pure solvent. Most of solution properties are dependent upon the chemical identity of the solute. However, a few solution properties depend only upon the total concentration of solute, are called colligative properties. They include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. The colligative properties have many technological applications and the importance to many natural phenomena.

2. The freezing point of solutions with a non-volatile solute

2.1. The freezing point of the non-volatile nonelectrolyte solutions

Solutions of non-volatile non-electrolytes provide the clearest examples of the colligative properties.

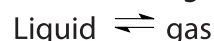
The colligative effects on vapor pressure, boiling point, and freezing point are summarized by comparing the phase diagrams for a pure solvent and a solution derived from that solvent.

- *Vapor pressure lowering*

A non-volatile solute is one whose

vapor pressure is negligible ($P^\circ \approx 0$), and so the vapor pressure above a solution containing only non-volatile solutes is due only to the solvent.

The equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:



Dissolving a non-volatile solute (sucrose) in a volatile solvent (water) results in a lowering of the solvent's vapor pressure. To vaporize, solvent molecules must be present at the surface of the solution. A non-volatile solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. The condensation is unaffected by the presence of a solute, so the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase Figure 1.

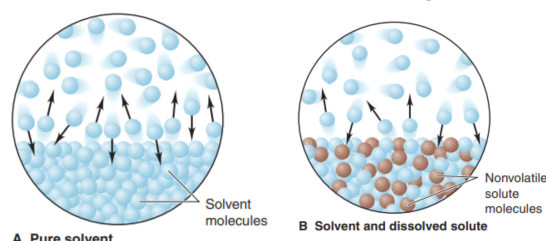


Figure 1. The presence of non-volatile solutes lowers the vapor pressure of a solution [2].

The relationship between the vapor pressures of solution components and the concentrations of those components is described by *Raoult's law* (the French chemist François-Marie Raoult): *The partial pressure exerted by any component of an*

ideal solution (P_{solvent}) is equal to the vapor pressure of the pure component (P_{solvent}^o) multiplied by its mole fraction (X_{solvent}) in the solution.

$$P_{\text{solvent}} = X_{\text{solvent}} P_{\text{solvent}}^o \quad (1)$$

Since X_{solvent} is less than 1 in a solution, P_{solvent} is less than P_{solvent}^o . An ideal solution is one that follows Raoult's law at any concentration.

Phase diagrams for water and an aqueous solution are shown in Figure 2.

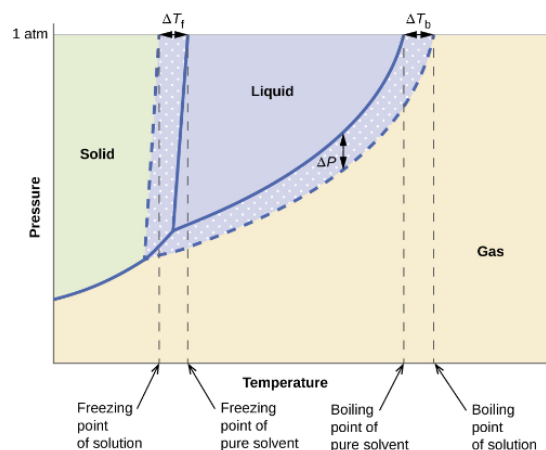


Figure 2. These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves) [5].

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure lowering, ΔP , that results from the dissolution of non-volatile solute. Consequently, at any given pressure, the solution's boiling point is observed

at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b , associated with the presence of non-volatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f , that accompanies solution formation.

2.2. Freezing point depression

A solution freezes at a lower temperature than the pure solvent, and this colligative property also results from vapor pressure lowering.

Notice that the freezing point of a substance or a mixture is the temperature at which the solid and liquid phases are in equilibrium at 1 atm of pressure. The addition of a solute to a solvent will decrease the freezing point (temperature) of the solvent. The decrease in freezing point, ΔT_f , when a non-volatile, non-ionizing solute is dissolved in a solvent is proportional to the molal concentration, m , of the solute present in the solution.

$$\Delta T_f = K_f m \quad (2)$$

where m is the solution molality and K_f is the molal freezing point depression constant, which also has unit of $^{\circ}\text{C}/m$.

The freezing point depression constants are characteristic properties whose values depend on the chemical

identity of the solvent. Values of K_f for several solvents are listed in Table 1.

Table 1. Freezing point depression constants for several solvents [5]

Solvent	Freezing point (°C at 1 atm)	K_f (Cm ⁻¹)
Water	0.0	1.86
Hydrogen acetate	16.6	3.9
Benzene	5.5	5.12
Chloroform	-63.5	4.68
Nitrobenzene	5.67	8.1

Molality is used because it relates to mole fraction and it is not affected by temperature.

Since $\Delta T_f > 0$, we subtract the lower solution T_f from the higher solvent T_f :

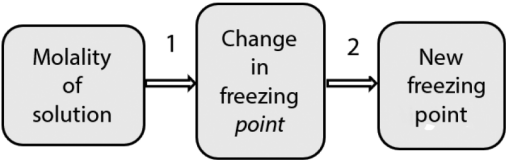
$$\Delta T_f = T_{f(solvent)} - T_{f(solution)} \tag{3}$$

2.3. Problems of freezing point depression

2.3.1. Calculate the freezing point of a solution

Example 1 What is the freezing point of the 0.50 m solution of a non-volatile nonelectrolyte solute in benzene?

Solution Use the equation relating freezing point depression to solute molality (2) to solve in two steps.



• Calculate the change in freezing point.

$$\Delta T_f = K_f m = 5.12 \times 0.5 = 2.56^\circ\text{C}$$

• Subtract the freezing point change observed from the pure solvent's freezing point.

The freezing point = 5.5 – 2.56 = 2.94°C

Example 2 What is the freezing point of a 2 m solution of sucrose in water?

Solution Use the equation relating freezing point depression to solute molality (2) to solve in two steps.

• Calculate the change in freezing point.

$$\Delta T_f = K_f m = 1.86 \times 2 = 3.72^\circ\text{C}$$

• Subtract the freezing point change observed from the pure solvent's freezing point.

The freezing point = 0 – 3.72 = -3.72°C

2.3.2. Calculate a molar mass from a freezing point depression

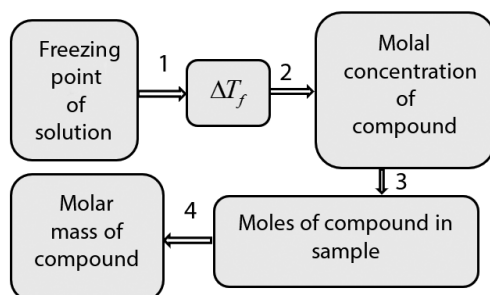
Colligative properties are proportional to solute concentration. Thus, by measuring the lower freezing point, determine the mol of solute particles, the mass of solute, and the molar mass.

The next example illustrates how to use the experimentally measured decrease of freezing point, ΔT_f , to calculate the molar mass of an unknown non-volatile non-electrolyte solute.

Example 3 A solution of 5.30 g of a non-electrolyte dissolved in 90.0 g of benzene is found to freeze at 2.94 °C. What is the molar mass of this compound?

Solution Solve this problem using the

following steps.



- Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene (Table 1).

$$\Delta T_f = 5.5 - 2.94 = 2.56^\circ\text{C}$$

- Determine the molal concentration from K_f , the freezing point depression constant for benzene (Table 1), and ΔT_f .

$$\text{Molal concentration} = \frac{\Delta T_f}{K_f} = 0.5 \text{ m}$$

- Determine the number of moles of compound in the solution.

$$\text{Moles of solute} = \frac{0.5}{1} * 0.09 = 0.045 \text{ mol}$$

- Determine the molar mass from the mass of the solute and the number of moles in that mass.

$$\text{Molar mass} = \frac{5.3}{0.045} = 118 \text{ g mol}^{-1}$$

Example 4 The freezing point of cyclohexane is 6.50°C . Dissolving 0.6570g of an unknown solute in 33.50 g cyclohexane, the freezing point of the solution is 4.32°C . Calculate the molar mass of the unknown solute. K_f for cyclohexane is $20.0^\circ\text{C.kg/mole}$.

- Determine the change in freezing point

$$\Delta T_f = 6.5 - 4.32 = 2.18^\circ\text{C}$$

- Determine the molal concentration from K_f and ΔT_f

$$\text{Molal concentration} = \frac{2.18}{20} = 0.109 \text{ m}$$

- Determine the number of moles of compound in the solution

$$\text{Moles of solute} = 0.00365 \text{ mol}$$

- Determine the molar mass from the mass of the solute and the number of moles in that mass.

$$\text{Molar mass} = \frac{0.657}{0.00365} = 180 \text{ g mol}^{-1}$$

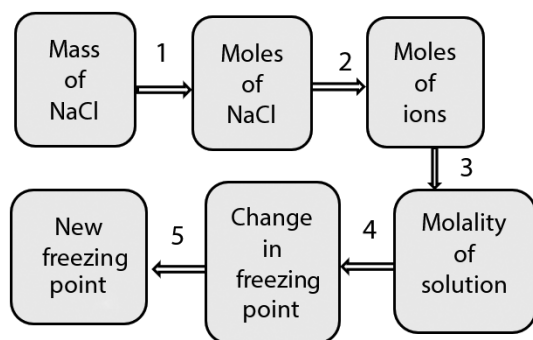
2.4. The freezing point depression of solution of electrolytes

The colligative properties of a solution depend only on the number of solute species dissolved. 1 mole of any non-electrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms 2 moles of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

Example 5 The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of

water as a nonelectrolyte molecule, and determine the freezing temperature the solution.

Solution Solve this problem using the following series of steps.



- Using the molar mass of NaCl, convert from grams to moles of NaCl.

Moles of NaCl: 0.07 mol NaCl

- Determine the number of moles of ions present in the solution: 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl).

Moles of ions = 0.14 mol ions

- Determine the molality of the ions in the solution.

$$\text{Molality of the ions} = \frac{0.14}{0.125} = 1.12 \text{ m}$$

- Determine the freezing point changes.

$$\Delta T_f = K_f m = 1.86 * 1.12 = 2.1$$

- Determine the new freezing point from the freezing point of the pure solvent and the change.

$$T_f = 0 - 2.1 = -2.1 \text{ } ^\circ\text{C}$$

The chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in

an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles.

In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table 2 are for 0.05 m solutions, at which concentration the value of i for NaCl is 1.9, as opposed to an ideal value of 2.

Thus, the freezing point depression of a 0.10 m solution of sodium chloride, with 2 mol of ions per mole of NaCl in solution, to be exactly twice that of a 0.10 m solution of glucose, with only 1 mol of molecules per mole of glucose in solution. In reality, this is not always the case. Instead, the observed change in freezing points for 0.10 m aqueous solutions of NaCl and KCl are significantly less than expected ($-0.348 \text{ } ^\circ\text{C}$ and $-0.344 \text{ } ^\circ\text{C}$, respectively, rather than $-0.372 \text{ } ^\circ\text{C}$), which suggests that fewer particles than we expected are present in solution.

The relationship between the actual number of moles of solute added to form a solution and the apparent number as determined by colligative properties is called **the van't Hoff factor** (*i*) and is defined as follows:

$$i = \frac{\text{apparent number of particles in solution}}{\text{number of moles of solute dissolved}} \quad (4)$$

As the solute concentration increases the van't Hoff factor decreases.

The van't Hoff factor is therefore a measure of a deviation from ideal behavior. The lower the van't Hoff factor, the greater the deviation. As the data in Table 2 show, the van't Hoff factors for ionic compounds are somewhat lower than expected. As the concentration of the solute increases, the van't Hoff factor decreases because ionic compounds generally do not totally dissociate in aqueous solution.

Instead, some of the ions exist as ion pairs, a cation and an anion that for a brief time are associated with each other without an intervening shell of water molecules (Figure 3). Each of these temporary units behaves like a single dissolved particle until it dissociates. Highly charged ions such as Mg^{2+} , Al^{3+} , SO_4^{2-} , PO_4^{3-} , have a greater tendency to form ion pairs because of their strong electrostatic interactions. The actual number of solvated ions present in a solution can be determined by measuring a colligative property at several solute concentrations.

Table 2. *van't Hoff factors for 0.050m aqueous solutions of selected compounds at 25 °C [3].*

Compound	i (measured)	i (ideal/predicted)
Glucose	1.0	1.0
Sucrose	1.0	1.0
NaCl	1.9	2.0
HCl	1.9	2.0
MgCl ₂	2.7	3.0
FeCl ₃	3.4	4.0
Ca(NO ₃) ₂	2.5	3.0
AlCl ₃	3.2	4.0
MgSO ₄	1.4	2.0

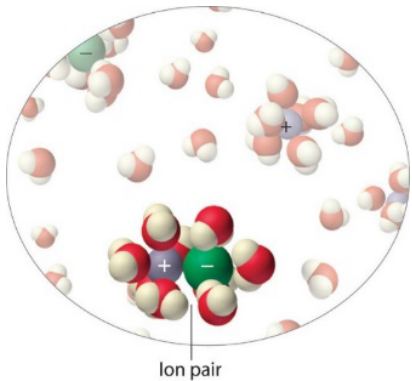


Figure 3. *Ion pairs. In concentrated solutions of electrolytes like NaCl, some of the ions form neutral ion pairs that are not separated by solvent and diffuse as single particles [3].*

2.5. Some applications of freezing point depression

The freezing point depression of solution is exploited in de-icing schemes that use salt, calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an antifreeze in automobile radiators.

- A common example is found when salt is used on icy roadways in winter to melt the ice and make driving safer. CaCl_2 is substantially more effective at lowering the freezing point of water because its solutions contain three ions per formula unit. In fact, CaCl_2 is the salt usually sold for home use, and it is also often used on highways.



Figure 4. Freezing point depression is exploited to remove ice from roadways [5].

The de-icing of planes is another common example of freezing point depression in action. A number of solutions are used, but commonly a solution such as ethylene glycol $\text{C}_2\text{H}_4(\text{OH})_2$, or a less toxic monopropylene glycol $\text{C}_3\text{H}_6(\text{OH})_2$, is used to de-ice an aircraft. The aircrafts are sprayed with the solution when the temperature is predicted to drop below the freezing point.



Figure 5. Freezing point depression is exploited to remove ice from the control surfaces of aircraft [5].

Antifreeze is used in automobile radiators to keep the coolant from freezing. In geographical areas, winter temperatures go below the freezing point of water, using pure water as the coolant could allow the water to freeze. Since water expands when it freezes, freezing coolant could crack engine blocks, radiators, and coolant lines. The main component in antifreeze is ethylene glycol (EG), $\text{C}_2\text{H}_4(\text{OH})_2$. The freezing point of the 30.2% solution of ethylene glycol in water dropped by 13°C .

- Salts, such as NaCl , can be used to prepare a slush bath, a mixture used to cool or freeze something. One example is the mixture of ice and NaCl used to freeze ice cream in a home ice-cream maker.

The freezing point depression is also important to many natural phenomena.

- Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0°C . The body fluids of fish and other cold-blooded sea animals that live in these oceans remain unfrozen at temperatures below 0°C .

- The juice in the fruit has enough dissolved solutes to lower the freezing point by a degree or two. The growers must protect lemons sooner than oranges because lemons have a lower concentration of dissolved solutes (sugars) than do oranges. Water sprayed on citrus fruit releases its heat of fusion as it freezes into a layer of ice that acts as a thermal insulator. For a time, the

temperature remains at 0°C. The juice of the fruit, having a freezing point below is protected from freezing.



Figure 6. Water sprayed on citrus fruit [3].

3. Summary

Thus, through the above content, we can see that freezing points of solutions with a non-volatile solute are lower than the freezing points of the pure solvents. Additionally, ionic compounds split into ions when they dissolve, forming more particles, covalent compounds stay as complete molecules when they dissolve. Finally, basing on colligative properties, ionic compounds of the same concentration solutions will give a lower freezing temperature than covalent compounds.

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