

# Colligative properties

CH102 General Chemistry, Spring 2014, Boston University

There are four colligative properties.

- vapor-pressure lowering
- boiling-point elevation
- freezing-point depression
- osmotic pressure

Each of these properties is due to the effect of solute on entropy changes and so spontaneity. We will see that the cause of each of the properties is changes necessary to keep free energy in balance.

## ■ Vapor-pressure lowering

Provided the amount of solute is small, that is, the mole fraction of the solvent is close to 1, the vapor pressure decreases linearly with the solvent mole fraction  $X_1$ ,

$$P_1 = X_1 P_1^\circ$$

This is known as Raoult's law. If there is no solute at all, so that  $X_1 = 1$  (pure solvent), then the vapor pressure  $P_1$  is  $P_1^\circ$ , the vapor pressure of the pure solvent. We can rewrite this expression in terms of the solute mole fraction,  $X_2 = 1 - X_1$ , as

$$P_1^\circ - P_1 = X_2 P_1^\circ$$

This relations shows that the solute mole fraction is the fractional change in pressure of the solvent.

$$X_2 = (P_1^\circ - P_1)/P_1^\circ.$$

That is, the reduction in solvent vapor pressure is proportional to the mole fraction.

$$-\Delta P_1 = X_2 P_1^\circ$$

## Entropy change

Vapor pressure is due to equilibrium between a solvent and its vapor. This equilibrium means that the free energy of the solvent and vapor are equal,

$$G_{\text{vapor}}^0 = H_{\text{vapor}} - T S_{\text{vapor}}^0 = G_{\text{solvent}} = H_{\text{solvent}} - T S_{\text{solvent}}$$

We can rearrange this equality to see that the entropy of the vapor above the pure solvent,  $S_{\text{vapor}}^0$ , exceeds the entropy of the solvent by is  $+\Delta H_{\text{vap}}/T$ ,

$$S_{\text{vapor}}^0 = S_{\text{solvent}} + \frac{H_{\text{vapor}} - H_{\text{solvent}}}{T} = S_{\text{solvent}} + \frac{\Delta H_{\text{vap}}}{T}$$

A way to understand this additional entropy is that it is due to the corresponding *lowering* of the entropy of the surroundings by  $-\Delta H_{\text{vap}}/T$ , because of the heat  $\Delta H_{\text{vap}}$  *removed* from the surroundings, necessary to provide the energy for the vaporization.

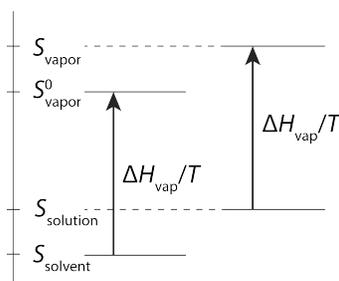
Adding solute to the pure solvent results in a solution with more arrangements than the pure solvent. This means that adding solute to the pure solvent raises the entropy of the solution relative to that of the pure solvent. If we assume that the concentration of the solute is very small so that its overall interaction with the solvent molecules is negligible, then the enthalpy of the solvent is unaffected by the presence of the solute,

$$H_{\text{solution}} = H_{\text{solvent}}$$

This means that the entropy of the vapor over the solution must increase by the *same amount* as does the entropy of the vapor over the solvent,

$$S_{\text{vapor}} = S_{\text{solution}} + \frac{H_{\text{vapor}} - H_{\text{solution}}}{T} = S_{\text{solution}} + \frac{H_{\text{vapor}} - H_{\text{solvent}}}{T} = S_{\text{solution}} + \frac{\Delta H_{\text{vap}}}{T}$$

Adding  $\Delta H_{\text{vap}}/T$  to this higher initial entropy value means the entropy of the vapor is raised. This is illustrated in the following diagram.



Adding non-volatile solute raises the entropy of the solvent vapor.

Increased vapor entropy corresponds to lower vapor pressure, that is, fewer particles in a given volume and so a greater number of arrangements  $W$ .

### Examples: Oxtoby and Nachtrieb, 3e, problem 4-44

The vapor pressure of diethyl ether (molar mass, 74.12 g/mol) at 30 °C is 0.8517 atm. Suppose 1.800 g of maleic acid,  $C_4H_4O_4$ , is dissolved in 100.0 g of diethyl ether at 30 °C. Calculate the vapor pressure of diethyl ether above the resulting solution.

- | Calculate that there are 1.349 mol ether and 0.01551 mol acid, and so that the ether mole fraction is 0.9886.
- | Calculate the ether vapor pressure. Answer: 0.8420 atm.

### ■ Boiling-point elevation

If we are at the boiling point, then  $P^{\circ}_1 = 1$  atm. This means that if we add any solute at all, boiling will stop, since  $P$  will then be less than 1 atm. For boiling to resume, we must increase the temperature enough to offset the reduction in vapor pressure from 1 atm. The text shows that the change in temperature needed to restore boiling is proportional to the solute molality,

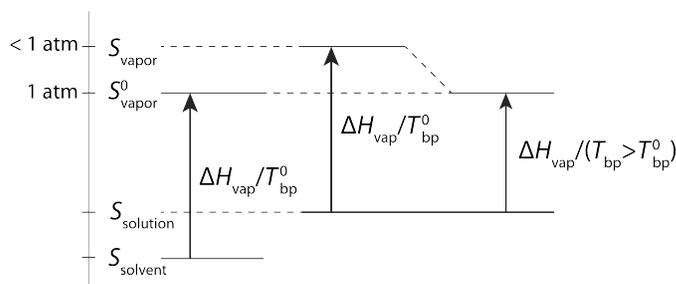
$$T_b' - T_b = K_b m.$$

Here  $T_b'$  is the new boiling point and  $T_b$  is the boiling point of the pure solvent;  $K_b$  is known as the boiling-point elevation constant, and it must be determined experimentally for each solvent.

## Entropy change

The normal boiling point,  $T_{\text{bp}}$  is the temperature at which vapor pressure is 1 atm. At the boiling point, the entropy change of the system for vaporization is  $+\Delta H_{\text{vap}}/T_{\text{bp}}$ . Adding solute lowers the vapor pressure below 1 atm, and boiling stops. The only way to resume boiling is to raise the vapor pressure back to 1 atm. This in turn means that the entropy of the vapor needs to be *reduced* to that value corresponding to 1 atm. This is done by *increasing* the temperature, so that there is less entropy change,  $(\Delta H_{\text{vap}}/T) < (\Delta H_{\text{vap}}/T_{\text{bp}})$ , going from solvent to vapor.

This effect of a non-volatile solute on the boiling point is illustrated in the following diagram.



Adding solute at the boiling point raises the entropy and so lowers the pressure of the vapor below 1 atm. The result is that boiling stops. The temperature must be raised to increase the pressure of the vapor to 1 atm and so resume boiling.

### Example: Oxtoby and Nachtrieb, 3e, problem 4-46

When 2.62 g of the non-volatile solid anthracene,  $\text{C}_{14}\text{H}_{10}$ , is dissolved in 100.0 g of cyclohexane,  $\text{C}_6\text{H}_{12}$ , the boiling point of the cyclohexane is raised by  $0.41^\circ\text{C}$ . Calculate  $K_b$  for cyclohexane.

- | Calculate the moles and molality of anthracene. Answer: 0.0147 mol, 0.147 mol/kg.
- | Evaluate  $K_b$  for cyclohexane. Answer: 2.8 K kg/mol.

## Freezing-point depression

A non-volatile solute in a liquid solvent lowers the freezing point of the solvent. The difference between the new freezing point  $T_{\text{fp}}'$  and the freezing point  $T_{\text{fp}}$  of the pure solvent is also proportional to the molality,

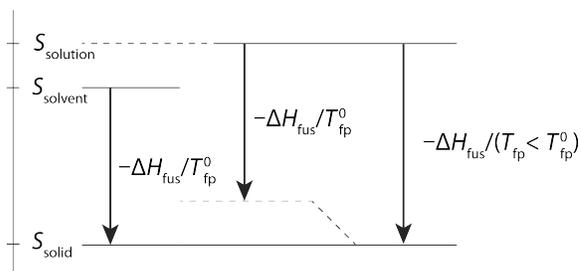
$$T_{\text{fp}} - T_{\text{fp}}' = K_f m,$$

where  $K_f$  is the freezing-point depression constant, which must be determined for each solvent.

## Entropy change

The normal freezing (melting) point,  $T_{\text{fp}}$  is the temperature at which the pure solvent and solid are in equilibrium. At the freezing point, the entropy change of the system for the process solvent  $\rightarrow$  solid is  $-\Delta H_{\text{fus}}/T_{\text{fp}}$ , since heat is released on freezing. Adding solute to the solvent results in a solution with more arrangements than the pure solvent. Subtracting  $\Delta H_{\text{fus}}/T_{\text{fp}}$  from this higher initial entropy value means the entropy of the solid is now too high, and so freezing will no longer occur at  $T_{\text{fp}}$ . For freezing to resume, the entropy change needs to be increased, to offset the raised entropy of the solution. This is done by *decreasing* the temperature, so that there is more entropy change,  $(\Delta H_{\text{vap}}/T) > (\Delta H_{\text{fus}}/T_{\text{fp}})$ , going from solution to solid.

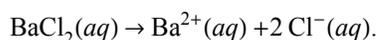
This effect of a non-volatile solute on the freezing point is illustrated in the following diagram.



Adding solute at the freezing point makes the entropy of the solid too high to form. The result is that freezing stops. The temperature must be lowered to decrease the entropy to that of the pure solid and so resume freezing.

### Solute ionization

One striking aspect of freezing point depression is the effect of solute ionization. For example,  $\text{BaCl}_2$  ionizes in water to form hydrated  $\text{Ba}^{2+}$  ions and hydrated  $\text{Cl}^-$  ions,



This means that every mole of  $\text{BaCl}_2$  produces three moles of solute particles, and as a result, the freezing point depression will be three times larger than we would predict just based on the molality of the  $\text{BaCl}_2$ . Indeed, freezing point depression is one way to determine the ionic character of compounds.

### Demonstration

Here is an extraordinary demonstration of freezing point depression. Fill a beaker with crushed ice, and measure its temperature to be  $0^\circ\text{C}$ . Then add table salt (essentially  $\text{NaCl}$ ). The ice immediately melts and the temperature of the ice-liquid mixture goes down to about  $-18^\circ\text{C}$ !

Here is what happened. At  $0^\circ\text{C}$ , ice and water are in equilibrium, that is, the rate at which water molecules leave the ice phase is exactly balanced by the rate at which the water molecules leave the liquid phase. This means the mass of ice is constant — neither melting nor freezing occurs. Now, when the salt is added, the  $\text{Na}^+$  and  $\text{Cl}^-$  raise the entropy of the solution, preventing freezing at  $0^\circ\text{C}$  and so effectively lowering the rate at which water molecules leave the liquid phase. As a result, there is a net flow of water molecules from the ice phase, that is, the ice melts.

But what about the lowering of the temperature? As we have seen, the molecules in ice are arranged in a regular structure, held in place by inter-molecular, hydrogen bonds. It requires energy to break these bonds. This energy comes from the thermal motion of the surrounding liquid, and as a consequence the liquid cools.

The last thing to understand is why the cooling levels off. As the temperature goes down, the thermal energy available goes down. This means that the rate of water molecules leaving the solid phase goes down. When the rate gets down to the rate of the water molecules leaving the liquid phase, equilibrium is established once again and the temperature stops changing.

### Example

What mass of  $\text{NaCl}$  ( $K_f = 1.86 \text{ K kg/mol}$ ) must be added to  $1.00 \text{ L} = 1.00 \text{ kg}$  of water to lower its freezing point by  $5^\circ\text{C} = 5.0 \text{ K}$ ?

▮ Determine the needed molality. Answer: 2.69 m.

▮ Determine the corresponding moles and then mass of  $\text{NaCl}$ . Answer: 1.34 mol, 78.6 g.

## ■ Osmotic pressure

Osmotic pressure arises when a membrane separates a solution from pure solvent, and only the solvent particles can pass through the membrane; such a membrane is said to be semi-permeable. The result is that there is a net flow of solvent particles from the pure solvent into the solution. This flow continues until the ensuing level difference creates a back pressure sufficient to restore the balance of solvent flow. We can compute this pressure  $\Pi$  as

$$\Pi = \rho g h,$$

where

- $\rho$  is the density of the solution,
- $g = 9.80665 \text{ m/s}^2$  is the acceleration due to gravity, and
- $h$  is the difference in height of the pure solvent and the solution with added solute.

Van't Hoff discovered that the osmotic pressure is related to the molarity  $M$  of the solution as

$$\Pi = M R T.$$

Writing  $M$  as the number of solute particles per solution volume,  $n/V$ , we can write this equation as

$$\Pi V = n R T,$$

that is, in a form analogous to the ideal gas law. We need to keep in mind, however, the different interpretation of variables in this equation compared to the ideal gas law. Here

- $\Pi$  is the osmotic pressure, rather than the pressure of the gas,
- $V$  is the volume of the solution, rather than the volume of the gas, and
- $n$  is the number of mole of solute, rather than the moles of the gas.

### Microscopic, statistical origin of osmotic pressure

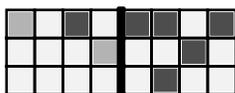
Osmotic pressure is due to maximizing the entropy change due to passage of solvent particles through the semipermeable membrane. Here is a model that illustrates this. The model consists of 2 particles of one kind (light squares) and 6 particles of another kind (dark squares). The membrane is impermeable to the light colored particles but permeable to the dark colored particles.

Here is an initial arrangement.



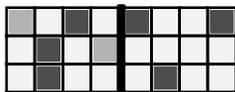
$$W = W_{\text{left}} W_{\text{right}} = \frac{(2 + 2 + 8)!}{2! 2! 8!} \frac{(4 + 8)!}{4! 8!} = 2970 \times 495 = 1\,470\,150.$$

If one solvent particle moves to the right, there is a decrease in the number of arrangements.



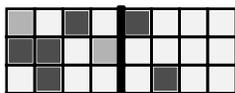
$$W = W_{\text{left}} W_{\text{right}} = \frac{(2 + 1 + 9)!}{2! 1! 9!} \frac{(5 + 7)!}{5! 7!} = 660 \times 792 = 522\,720.$$

If instead one solvent particle moves to the left, there is an increase in the number of arrangements.



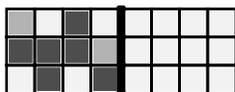
$$W = W_{\text{left}} W_{\text{right}} = \frac{(2 + 3 + 7)!}{2! 3! 7!} \frac{(3 + 9)!}{3! 9!} = 7920 \times 220 = 1\,742\,400.$$

If a second solvent particle moves to the left, there is a decrease in the number of arrangements.



$$W = W_{\text{left}} W_{\text{right}} = \frac{(2 + 4 + 6)!}{2! 4! 6!} \frac{(2 + 10)!}{2! 10!} = 13\,860 \times 66 = 914\,760.$$

If all of the solvent particles move to the left, there is a large decrease in the number of arrangements.



$$W = W_{\text{left}} W_{\text{right}} = \frac{(2 + 6 + 4)!}{2! 6! 4!} \frac{(0 + 12)!}{0! 12!} = 13\,860 \times 1 = 13\,860.$$

The maximum number of arrangements corresponds to equal numbers of the dark particles on either side of the membrane,  $n_{\text{dark, left}} = n_{\text{dark, right}}$ . Since the light particles cannot pass through the membrane, there is a pressure difference when the number of arrangements is a maximum,

$$\Pi = p_{\text{left}} - p_{\text{right}} = \frac{n_{\text{light}} + n_{\text{dark, left}}}{V} R T - \frac{n_{\text{dark, right}}}{V} R T = \frac{n_{\text{light}}}{V} R T.$$

This pressure difference—the osmotic pressure  $\Pi$ —depends only on the concentration of the particles that cannot pass through the membrane.

### Example: Determination of molar mass

An important application of osmotic pressure is in the determination of molar masses of large molecules, such as proteins. The reason is that usually proteins are able to be isolated only in small quantities, and yet even a very small number of moles (e.g.,  $\sim 10^{-6}$ ) can result in large (tens of centimeters) height differences and so in a readily determined osmotic pressure. The effect of the same number of moles in a freezing-point depression measurement, for example, would be only about 0.001 K!

To use osmotic pressure to determine molar mass, the first step is to prepare the solution by adding a known mass of solute, measuring the resulting height difference and then computing the osmotic pressure. Then the van't Hoff equation is used to determine the number of moles of solute. Finally, the molar mass can be computed by dividing the number of moles into the mass of the solute.

Here is an example, Oxtoby and Nachtrieb, 3e, problem 4-56: Suppose 2.37 g of a protein is dissolved in water and diluted to a total volume of 100.0 mL. The osmotic pressure of the resulting solution is 0.0319 atm at 20.°C. What is the molar mass of the protein?

First, we can use the measured osmotic pressure to determine the molarity, that is, how many moles of particles there are per liter of solution. Answer: 0.00133 mol/L.

Once we know the molarity, we can figure out how many moles of protein we have. Answer: 0.000133 mol.

Finally, since we know the mass of this number of moles, we can compute the molar mass. Answer: 17900 g/mol.

### Example: Predicting osmotic pressure

Here is an example which illustrates the sensitivity of osmotic pressure to molar mass. Assume we have 0.00114 g of a protein with molar mass  $1.00 \times 10^5$ —a quite large molecule. What osmotic pressure would it generate when dissolved in 0.1000 mL water at 15.0 °C? How high would a column of water need to be to balance this osmotic pressure?

First, we need to compute the molarity of the protein. Answer: 0.000114 mol/L.

That is, the concentration is very small.

Next, we can use the molarity to compute the osmotic pressure. Answer: 0.00270 atm.

Finally, we can compute the height of a water column needed to balance this osmotic pressure. To do this, we can assume the solute does not affect the density of water. Answer: 0.000275 atm mL s<sup>2</sup> g<sup>-1</sup> m<sup>-1</sup>.

To express the height explicitly as a length, we need to apply a series of conversions  $1 \text{ atm} = 101325 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ,  $L = (10^{-1} \text{ m})^3$ , and  $m = 100 \text{ cm}$ .

Apply these conversions to show that 0.000275 atm mL s<sup>2</sup> g<sup>-1</sup> m<sup>-1</sup> corresponds to 2.79 cm.

This is an easily measured height. It is remarkable that in this way the molar mass of such a large protein can be determined.