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Vapor Pressure, Boiling and Freezing Temperatures of a Solution

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Addition of solute molecules to a liquid elevates its boiling temperature and reduces its vapor pressure and freezing temperature. These phenomena, as well as osmosis, depend only on the solute concentration and not on its type, and are called colligative properties of solutions.

The process of elastic collisions of particles with a moving wall is a general mechanism of transforming their microscopic kinetic energy into macroscopic mechanical work, and vice versa [1]. This mechanism accounts for the colligative properties [2].

Whenever molecules evaporate from a liquid the boundary layer between the liquid and the vapor will move. When the liquid contains a non volatile solute, the moving boundary will transfer energy to the solute molecules. This energy is included in the evaporation process, therefore, it will affect the vapor pressure and boiling temperature of a solution. Similarly, during freezing, or melting, the boundary movement between the solution and pure solid will affect the freezing temperature. In both cases the moving boundary works against the osmotic pressure generated by the solute.

Vapor pressure of a solution:

Consider a vessel of constant volume that contains a liquid and its vapors. A molecule at the liquid surface will leave it to the vapor phase if its kinetic energy is higher than the binding energy to the liquid. On the other hand, all molecules at the vapor phase that hit the liquid surface will stay with it. During equilibrium the rate of evaporation from the liquid will be equal to the rate of condensation to it.

According to the Maxwell- Boltzmann distribution function the evaporation rate is proportional to $e^{-Li/RT}$, while the condensation rate is proportional to the vapor concentration (N/V). L_i is the molar heat of evaporation. It is the amount of heat supplied to a liquid in order to evaporate one mole. R is the gas constant and T the absolute temperature.

The condensation rate is proportional to the vapor concentration, and therefore, also to the pressure $p = (N/V)RT$. Therefore, at equilibrium:

$$p = \alpha RT\, e^{-Li/RT} \quad (1)$$

where α is a proportion factor.

When liquid evaporates from a solution surface, the boundary will do work against the osmotic pressure of the solute. This work is included in the evaporation process and there will be a need of more energy for it. Therefore, the evaporation rate from a solution is somewhat slower than evaporation from a pure liquid, and consequently, the solution's vapor pressure is lower than that of a pure liquid.

When one mole of a liquid evaporates from a solution surface, the surface will do the work πv against the osmotic pressure π. v is the volume of one mole of solution. By van't Hoff formula the osmotic pressure is $\pi = cRT$, where c is the solute concentration.

The solution heat of evaporation is:

$$L_s = L_i + \pi v = L_i + cRTv \text{ (2)}$$

therefore, the solution vapor pressure will be:

$$p_s = \alpha RT\, e^{-Ls/RT} = \alpha RT\, e^{-(Li/RT + x)} \text{ (3)}$$

where $x = cv$ is the molar fraction of the solute.

Division of equations (1)-(3), and exponent expansion to first order, yields for dilute solutions:

$$p_s/p = e^{-x} = 1\text{-}x \text{ (4)}$$

This is Raoult's law. It relates the vapor pressure reduction of a solution, compared to the pure liquid, to the solute's molar fraction.

Boiling temperature elevation:

Boiling occurs in a liquid in an open vessel when its vapor pressure is equal to the external pressure $p_{external}$. The liquid heats up and its vapor pressure increases until it reaches the external pressure. Then boiling starts. Since the vapor pressure of a solution is lower than that of the pure liquid it will reach the external pressure at higher temperature. Consequently, the boiling temperature of the solution will be higher than that of the pure liquid.

The boiling condition for a pure liquid is determined by equation (1):

$$p_{external} = \alpha RT_i\, e^{-Li/RTi} \text{ (5)}$$

where T_i is the boiling temperature of the pure liquid. Similarly, the boiling condition for the solution is given by equation (3):

$$p_{external} = \alpha RT_s\, e^{-(Li/RTs + x)} \text{ (6)}$$

where T_s is the boiling temperature of the solution. $p_{external}$ is eliminated from these two equations:

$$T_i e^{-(Li/R)(1/Ti - 1/Ts)} = T_s e^{-x} \quad (7)$$

Both exponent terms in equation (7) are small, therefore, they can be expanded to first order ($e^{-x} = 1 - x$), and after some algebra:

$$T_s - T_i = T_s x - (T_s - T_i)(L_i/RT_s) \quad (8)$$

Denoting $\Delta T = T_s - T_i$, and after more algebra:

$$\Delta T = (R(T_s)^2/(L_i + RT_s))x \quad (9)$$

This approximate formula relates the change of the boiling temperature ΔT to the molar fraction of the solute x.

Freezing temperature reduction:

The reduction of the freezing temperature is similar to the elevation of the boiling temperature. When the solid melts the boundary between it and the liquid will move. If the liquid contains solute molecules, then the work done by the osmotic pressure will supply some of the heat of melting and less heat will be required externally. This effect results the reduction of the melting or freezing temperature. Similar calculation yields temperature reduction:

$$\Delta T = -(RTT_s/L)x \quad (10)$$

where L is the molar heat of melting.

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See:
Osmosis Reverse Osmosis and Osmotic Pressure what they are
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van't Hoff's Evidence

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Links:

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2. Thermodynamik - Warmelehre, http://www.schulphysik.de/thermodyn.html
3. The Blind Men and the Elephant
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7. "Faster, Faster!"
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