Colligative properties

There are a number of properties of a dilute solution that depend only on the number of particles and not on their kind. Colligative properties include the lowering of the vapor pressure of a solvent and elevation of the boiling temperature by the addition of a nonvolatile solute, the depression of the freezing point of a solution by a solute, and osmotic pressure.

They all have a common treatment using the chemical potential of the pure substance compared to the chemical potential of the mixture. In this case the mixture consists of a non-volatile (solid) solute.

Freezing point depression

At the freezing point of a solution, solid solvent is in equilibrium with the solvent in solution. As we have seen, this equilibrium implies that the chemical potential of each phase is equal to the other:

\[ \mu^{\text{solid}}(T_{\text{fus}}) = \mu^{\text{solid}}(T_{\text{fus}}) \]

where subscript 1 denotes solvent and \( T_{\text{fus}} \) is the freezing point of the solution.

\[ \mu^{\text{solid}}(T_{\text{fus}}) = \mu^{\text{liq}}_1 + RT \ln x_1 = \mu^{\text{liq}}_1 + RT \ln x_1 \]

So that we can equate \( \mu \) for the liquid and solid

\[ \mu^{\text{solid}} = \mu^{\text{liq}}_1 + RT \ln x_1 \]

Justification: \( \ln(1-x) \approx -x \)

The derivative is:

\[ f(x) = \sum_{n=1}^\infty \left( \frac{d^n f(x)}{dx^n} \right) \frac{x^n}{n!} \]

The derivative is:

\[ \frac{d \ln(1-x)}{dx} = -1 \frac{1}{1-x} \]

and we are expanding about 0 so that we will need to substitute 0 in for \( x \) in the derivative. The first term in the Taylor expansion is:

\[ -1/(1-0)x = -x \]
Boiling point elevation

We can determine the value of $K_b$ for water. The phenomenon of boiling point elevation can be derived in a completely analogous fashion. In both cases the physics behind the effect is a lowering of the chemical potential of the solution relative to the pure substance. This can be seen in the diagram below where we plot the chemical potential as a function of the temperature.

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Question

Which mathematical term explains why the chemical potential of a solution lowered relative to pure liquid?
A. $\Delta_{vapH}/RT^2 \Delta T$
B. $-\Delta_{vapH}/RT^2 \Delta T$
C. $RT \ln x_1$
D. $-RT \ln x_1$

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Question

Which is an accurate expression of the boiling point elevation in terms of the activity of the solvent?
A. $\ln x_1 = \Delta_{vapH}/R(1/T - 1/T^*)$
B. $x_2 = \Delta_{vapH}/R(1/T - 1/T^*)$  
Activity of the solute
C. $RT^2/\Delta_{vapH} (M_1/1000 g kg^{-1})$  
Molality of the solute
D. $\mu_{1}\text{soln} = \mu_{1}\text{liq} + RT \ln x_1$  
Chemical potential (not boiling point elevation)

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Boiling point elevation

In this plot notice that the slope increases as the phase changes from solid to liquid and then to vapor. The slope is proportional to $-S$ (since $\partial \mu/\partial T = -S$) and the entropy increases in the same order. Notice that the violet line representing the chemical potential as a function of temperature is shifted down by the addition of solute. Mathematically this is due to $\mu_{1}\text{soln} = \mu_{1}\text{liq} + RT \ln x_1$

Because the chemical potential of the solid and vapor are not shifted by the addition of solute the intersection point (i.e. temperature of phase transition) goes down for fusion, but goes up for vaporization.
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What is the slope of the chemical potential with temperature?

A. free energy
B. enthalpy
C. entropy
D. none of the above

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What is $K_f$ for water?

$K_f = \frac{RT^2}{\Delta_f H_{\text{M1/1000 g kg}^{-1}}}$

A. 3.46 K$^{-1}$ mol$^{-1}$ kg
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What concentration of salt must be achieved to cause a 1 °C decrease in the melting temperature of the ice on a road?

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Osmotic pressure

Osmotic pressure arises from requirement that the chemical potential of a pure liquid and its solution must be the same if they are in contact through a semi-permeable membrane. Osmotic pressure is particularly applied to aqueous solutions where a semi-permeable membrane allows water to pass back and forth from pure water to the solution, but the solute cannot diffuse into the pure water. The point here is that the solute lowers the chemical potential on the solution side of the membrane and therefore there will be a tendency for water to move across the membrane to the solution side. Ultimately, there will be a balance of forces if a pressure builds up on the solution side of the membrane. This pressure can arise due to an increase in the hydrostatic pressure due to a rise in a column of solution or due to pressure inside a closed membrane. The easiest to visualize is a column of water.

The flow of solvent leads to an increase in hydrostatic pressure

Recall that the pressure at the bottom of a column of a fluid is given by $P = \rho g h$. If water flows into the solution the height of the column of solution increases and the hydrostatic pressure also increases. At some point the chemical potential due to the concentration difference is exactly opposed to the chemical potential due to the pressure difference. We express this as

$$\mu^*_{\text{soln}}(T,P+\Pi) = \mu^*_{\text{soln}}(T,P) + RT \ln x_1$$

The chemical potential of the solution is

$$\mu^*_{\text{soln}}(T,P) = \mu^*_{\text{soln}}(T,P+\Pi, x_1) = \mu^*_{\text{soln}}(T, P+\Pi) + RT \ln x_1$$

Recall that $\mu^*_{\text{soln}}(T,P) = \int V_{\text{m}} dP$ (subscript for molar volume) so

$$\mu^*_{\text{soln}}(T, P+\Pi, x_1) - \mu^*_{\text{soln}}(T, P) = \int_{V_{\text{m}}}^{V_{\text{m}} + \Delta V} V_{\text{m}} dP$$
Osmotic pressure

Thus, assuming $V_m$ does not vary with applied pressure, we can write

$$\int V_m \, dP + RT \ln x_1 = 0$$

For a dilute solution and $\ln x_1 \approx \ln(1-x_2) = -x_2$

we have that

$$\int V_m \, dP + RT \, x_2 = 0$$

which be expressed as

$$\Pi = n_2RT.$$

The above expression bears a surprising similarity to the ideal gas law. Keep in mind, however, that $\Pi$ is the osmotic pressure and $n_2$ is the number of moles of solute.

Question

What is the height of a column of water that will result from addition of enough NaCl to make a 0.1 M solution.

A. 25 m  
B. 2.5 m  
C. 0.25 m  
D. 0.025 m

Use of osmotic pressure to determine molar mass

The van't Hoff equation can be modified to form used for the determination of molar mass by osmometry.

$$\Pi = cRT$$

$$\Pi = \frac{W}{M}RT$$

Here we related to the concentration $c$ in moles/liter to the concentration $w$ in grams/liter and the molar mass $M$ in grams/mole.

The experimental configuration uses the measurement of height as an estimate of the osmotic pressure. The equation $\Pi = \rho gh$ is used ($h = \Pi / \rho g$).

Use of osmotic pressure to determine molar mass

Pure H₂O  

Pure H₂O
Use of osmotic pressure to determine molar mass

A sample of 1.5 mg. of a protein of unknown molar mass is added to an osmometer. The solution volume is 1 mL. The solution height increases by 1 cm. The measurement temperature is 298 K. What is the molar mass of the protein?

A. 37,900  
B. 39,700  
C. 79,300  
D. 97,300

\[ M = \frac{wRT}{\Pi gh} = \frac{(1.5 \text{ kg/m}^3) (8.31 \text{ J/mol} \cdot \text{K}) (298 \text{ K})}{(1000 \text{ kg/m}^3) (9.8 \text{ m/s}^2) (0.01 \text{ m})} = 37.9 \text{ kg/mol} = 37,900 \text{ g/mol} \]