

7.5: Colligative Properties

Many properties of water are altered when salt is added to it. Specifically, the vapor pressure drops, the freezing point lowers, the boiling temperature rises, and the osmotic pressure increases. One way to remember most of these is to imagine a phase diagram where the triple point is lowered down the solid-gas line while dragging the liquid-gas and solid-liquid borders with it as shown in Fig. 7.5. At a specific temperature, the vapor pressure drop is shown by line A where you can see that the liquid-gas boundary crossing point occurs at a lower pressure. Lines B & C show that, for a given pressure, the solid-liquid and liquid-gas lines cross at different temperatures. This represents the freezing point depression and boiling point elevation.

Here we will use our knowledge of the thermodynamics of mixtures to quantitatively predict these behaviors that are called “colligative properties”. For the most part, the accuracy of these relationships is modest, but they reveal what causes the solvent to react to the addition of a solute. *We will assume that the solutions are ideal, and that all species are at equilibrium from here on.*

7.5.1 Chemical Potentials and Equilibrium. As discussed in the previous section, the change in Gibbs Energy per mole (i.e. the chemical potential) of a liquid is the same as the vapors with which it is in equilibrium. We will use this fact to predict colligative properties. For example, we have already shown how Raoult’s Law is predicated on the lowering of a solvent’s vapor pressure by addition of a solute, specifically in proportion of the liquid state’s mole fraction:

$$P = P^* \cdot \chi_{liq} = P^* \cdot (1 - \chi_{salt})$$

where χ_{liq} is the mole fraction of liquid water and χ_{salt} is for the added salt. When working on numerical problems related to Raoult’s Law, you must recall that salts disproportionate into two or more species upon dissolution when calculating χ_{salt} . While this one was easy, the changes in phase behavior are more challenging as discussed below.

7.5.1.1 Melting Point Depression. Concerning the lowering of melting point of a solution, we begin by stipulating that both the liquid and solid phases that co-exist in equilibrium must have the same chemical potential:

$$\mu_{solid}^{\circ} = \mu_{liq}^{\circ}$$

where the $^{\circ}$ symbol refers to chemicals in the standard state (25 °C and 1 bar pressure). From here on we will use an example of adding salt to an equilibrium solution of water with an ice cube (solid water) floating in it. First, the chemical potential of liquid water is lowered by the dissolution of salt as stipulated by Raoult’s Law. Next, the system adjusts to maintain equilibrium, which mathematically means:

$$\mu_{solid}^{\circ} = \mu_{liq}^{\circ} + RT \cdot \ln(\chi_{liq})$$

See how the liquid’s chemical potential is lowered on the right yet the ice on the left isn’t affected? This makes sense if the ions do not permeate into the ice, which leaves its chemical potential unaltered.

Recall that the Gibb’s energy of formation per mole is the chemical potential: $\Delta_f G_m^{\circ} = \mu^{\circ}$, and some simple manipulation yields:

$\mu_{solid}^{\circ} = \mu_{liq}^{\circ} + RT \cdot \ln(\chi_{liq})$

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$\Delta_f G_m^\circ$ is the change in Gibbs energy per mole for fusion (note that “fusion” is the IUPAC word for melting). The above relationship can be simplified as:

$$\frac{-\Delta_f G_m^\circ}{RT} = \ln(\chi_{liq}) \quad (7.5.1)$$

Equation 7.5.1 uses the standard state fusion Gibbs energy per mole, which can be found in most thermodynamic data tables. However, Equation 7.15 uses standard state data, so the temperature must be $T = 25^\circ\text{C}$ and this is a problem because ice and salty water are not at equilibrium at room temperature! Rather, the temperature should be 0°C or less! Thus, we must use the correct fusion temperature T_{fus} in Equation 7.15, and furthermore the correct thermochemistry data for the change in Gibbs energy $\Delta_f G_m$ that occurs at the T_{fus} temperature. This is expressed as:

$$\frac{-\Delta_f G_m}{RT_{fus}} = \ln(\chi_{liq}) \quad (7.5.2)$$

This equation works just fine, and to demonstrate, pure H_2O water and ice are in equilibrium at 1 bar pressure and 0°C , which means that their chemical potentials are equal:

$$\mu_{solid} - \mu_{liquid} = \Delta_f G_{solid,m} - \Delta_f G_{liq,m} = -\Delta_f G_m = 0 \text{ J/mol}$$

As a result:

$$\frac{-\Delta_f G_m}{RT_{fus}} = 0 = \ln(\chi_{liq})$$

This is only true if $\chi_{liq} = 1$, meaning that the liquid is perfectly pure! Of course it is, since only pure water and ice are at equilibrium at 0°C ! If you are confused by the fact that the mole fraction of the liquid is $\chi_{liq} = 1$ when there is ice present, this is because the solid ice and liquid water don't interact very much, and you can say that each has its own mole fraction that is independent of the other. However, when we add salt to the water, then χ_{liq} will go down.

The relationship above allows us to provide a simple thermodynamic explanation for freezing point depression. Adding salt lowers the water's chemical potential. Ice doesn't “see” the salt and thus its chemical potential is unaffected, making it appear that there is a problem with maintaining equilibrium via equal chemical potentials. However, chemical potentials are temperature-dependent; thus, the temperature decreases to re-align the chemical potentials of the ice and the salted liquid so that they become equal again. As a result, the freezing point drops.

This leaves us with one final task, which is to derive a quantitative formula for the drop in freezing temperature ΔT as a function of salt content χ_{salt} . As a mathematical description of this process involves changes in salt mole fractions, chemical potentials and temperature, we must use the calculus of derivatives to derive a proper relationship. And although it's probably confusing just where to start, we do know that adding salt lowers the mole fraction of water (χ_{liq}) and changes the freezing temperature T_{fus} . Consequently, let's work on $\frac{\partial T_{fus}}{\partial \chi_{liq}}$ and see if we can accomplish our goal with it. However, it turns out that it is much easier solve the inverse relationship $\frac{\partial \chi_{liq}}{\partial T_{fus}}$. To calculate this derivative we can use Equation 7.16: $\ln(\chi_{liq}) = \frac{-\Delta_f G_m}{RT_{fus}}$, which means that we are going to solve: $\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}}$ rather than: $\frac{\partial \chi_{liq}}{\partial T_{fus}}$ because these derivative will basically behave the same and it is easy to solve $\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}}$ via the Gibbs-Helmholtz equation:

$$\left(\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}} \right) = \frac{\partial}{\partial T_{fus}} \left(\frac{-\Delta_f G_m}{RT_{fus}} \right)$$

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$\backslash\mathrm{nonumber}\backslash$

Here is where this gets interesting; we now integrate this derivative to account for the absolute differences in T_{fus} and χ_{liq} as salt is added by splitting up the partials of $\frac{\partial \ln(\chi_{liq})}{\partial T_{fus}}$ as so:

$\backslash\mathrm{partial}\backslash\mathrm{ln}\backslash\mathrm{left}(\{\chi\}_{liq}\backslash\mathrm{right})=\mathrm{frac}$

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$\backslash\mathrm{partial}\ T_{fus}\backslash\mathrm{nonumber}\backslash$

The limits of integration allow us to specify an initial temperature and salt concentration, which we will use $\ln(\chi_{liq}) = 0$ for the initial mole fraction (because $\chi_{liq} = 1$ for pure liquids) and $T_{fus} = 273.15\ K$ for the initial temperature (because the melting temperature of pure water is $0\ ^\circ\mathrm{C}$, which is $273.15\ K$). The upper limits of integration are the natural log of the final molar concentration $\backslash\mathrm{ln}\backslash\mathrm{left}(\{\chi\}_{liq}\backslash\mathrm{right})$ and the new melting temperature T_{fus} . Starting with the left side:

$$\int_0^{\ln(\chi_{liq})} \frac{\partial \ln(\chi_{liq})}{\partial T_{fus}} dT_{fus} = \ln(\chi_{liq})$$

We can simplify this result as: $\ln(\chi_{liq}) = \ln(1 - \chi_{salt}) \approx -\chi_{salt}$. And now we integrate the right side: $\int_{T_{fus}}^{T_{fus}} \frac{\partial T_{fus}}{\partial T_{fus}} dT_{fus} = T_{fus} - T_{fus}$

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$\backslash\mathrm{partial}\ T_{fus}=\mathrm{frac}$

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$\int_{T_{fus}}^{T_{fus}} \frac{\partial T_{fus}}{\partial T_{fus}} dT_{fus} = T_{fus} - T_{fus}$

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$\int_{T_{fus}}^{T_{fus}} \frac{\partial T_{fus}}{\partial T_{fus}} dT_{fus} = \frac{\Delta T_{fus}}{T_{fus}^2} H_m R \ln(\chi_{liq})$

where $T_{fus} - T_{fus} = \Delta T_{fus}$. We can make a few simplifications; given the fact that the new melting temperature T_{fus} is only slightly less than T_{fus} , then: $T_{fus} T_{fus} \approx T_{fus}^2$. This results in: $\frac{\Delta T_{fus}}{T_{fus}^2} H_m R \ln(\chi_{liq}) = -\chi_{salt}$ which rearranges and simplifies to:

$$\Delta T_{fus} = \frac{R \cdot T_{fus}^2 \cdot \chi_{salt}}{\Delta_{fus} H_m} \quad (7.5.3)$$

As you work some practice problems using Equation 7.17, you will find that it is decently accurate but not perfect. This clearly has to do with the approximations made in the derivation, such as the use of Raoult's Law and especially the fact that we did not account for the temperature dependence of $\Delta_{fus} H_m$ when analyzing the $\int_{T_{fus}}^{T_{fus}} \frac{\partial T_{fus}}{\partial T_{fus}} dT_{fus}$

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$\backslash\mathrm{partial}\ T_{fus}\backslash\mathrm{right})$ integral. Regardless, the relationship reveals some interesting phenomena, such as the fact that the freezing point depression is inversely proportional to the enthalpy of fusion. If the enthalpy is high for a liquid, then the effect of salt is

minimized. Also, the freezing point depression of water is enhanced by adding salts such as CaCl_2 due to the large number of dissociated ions that increases χ_{salt} ; this information helps with managing roadways during winter weather.

7.5.1.2 Boiling point elevation. Essentially the same derivation is used to calculate the increase in boiling point of a salty solution, and as a result we won't repeat the effort here. The relationship is: $\Delta T = \frac{RT_{\text{vap}}^2 \chi_{\text{salt}}}{\Delta_{\text{vap}} H_m}$

where the relevant change is vaporization and $\Delta T = T_{\text{vap}} - T$, the opposite order that appeared in the freezing point depression problem.

7.5.1.3 Osmotic Pressure. Living cells have osmotic pressure, which is to say that they experience a higher internal pressure than atmospheric resulting from the fact that the cells' cytoplasm contains dissolved salts and other biologicals such as proteins. Osmotic pressure can be measured using a system such as that shown in Figure 7.6, whereby a saltwater solution (left) is vertically displaced upwards in a column by pressure. This "push" experienced by the left side is generated by osmosis from pure water on the right side that is separated by a semi-permeable membrane. The osmotic pressure Π is equal to the applied pressure necessary to even out the liquid column levels.

Here we seek to explain exactly why this osmotic pressure differential exists and how to calculate Π . There are two simple explanations; one is that the pure water on the right side of Figure 7.6 is attempting to dilute the salty water on the left, which is an action to resist change (basically a Le Chatelier-type process). A better thermodynamic argument stipulates that the chemical potential of the salty water is less than the pure water, and as such the pure water moves towards it. This "push" of the pure water into the diluted water occurs until equilibrium is reached, at which point the chemical potentials of the salt water and pure water are equal. However, there is a problem with the application of Raoult's Law due to the fact that the chemical potential of the saltwater solution on the left: $\mu^\circ + RT \cdot \ln(\chi)$ is supposed to be equal to the chemical potential of pure water on the right μ° :

$$\mu^\circ + RT \cdot \ln(\chi_{\text{liq}}) = \mu^\circ$$

This equation is true only if $\chi_{\text{liq}} = 1$, but when we add salt to the water then $\chi_{\text{liq}} < 1$. Clearly we are missing some extra source of chemical potential, which in fact comes from osmotic pressure. Recall that the chemical potential is the Gibbs energy per mol which changes as:

$$\partial \mu = \partial G_m = -S_m \partial T + V_m \partial P$$

At constant temperature the chemical potential changes with pressure as: $\partial \mu = V_m \partial P$. If we integrate this simple relationship: $\Delta \mu = \frac{V}{n_{\text{water}}} \Delta P$, where the change in pressure ΔP the osmotic pressure Π . We apply this osmotic pressure correction to the saltwater solution to the left side the result is $\mu^\circ + RT \cdot \ln(\chi_{\text{liq}}) + \Pi \frac{V}{n_{\text{water}}}$, which we equate to the chemical potential of the pure water on the right side as:

$$\mu^\circ + RT \cdot \ln(\chi_{\text{liq}}) + \Pi \frac{V}{n_{\text{water}}} = \mu^\circ$$

Some cancellation and algebraic simplification yields:

$$\Pi \frac{V}{n_{\text{water}}} = -RT \cdot \ln(\chi_{\text{liq}})$$

As χ_{liq} is the mole fraction of the water solvent and $\chi_{\text{liq}} = 1 - \chi_{\text{salt}}$, we can apply the approximation: $\ln(\chi_{\text{liq}}) = \ln(1 - \chi_{\text{salt}}) \approx -\chi_{\text{salt}}$. Inserting this into the relationship above: $\Pi V = n_{\text{water}} RT \cdot \chi_{\text{salt}}$

Now we make one last approximation, which is that: $\chi_{\text{salt}} = \frac{n_{\text{salt}}}{n_{\text{water}} + n_{\text{salt}}} \approx \frac{n_{\text{salt}}}{n_{\text{water}}}$. This is reasonable so long as $n_{\text{salt}} \ll n_{\text{water}}$. This approximation can be inserted this into the expression for osmotic pressure: $\Pi V = n_{\text{water}} RT \cdot \chi_{\text{salt}} = n_{\text{water}} RT \cdot \frac{n_{\text{salt}}}{n_{\text{water}}} = n_{\text{salt}} RT$

Finally, we have a familiar-looking relationship:

$$\Pi V = n_{\text{salt}} RT \quad (7.5.4)$$

Note that the appearance to the perfect gas law is purely coincidental, but it does help making the osmotic pressure formula easier to remember.

Conclusion. In this chapter we introduced the concepts of thermodynamics in condensed phases, which is to say that we hijacked gas phase equations from earlier chapters and used the chemical potential as a conduit to the thermodynamics of the condensed

phase. Raoult's Law was used to predict how the vapor phase is connected to the contents of the liquid mixture from which it originates, and we were able to use it to demonstrate colligative properties. In reality Raoult's Law works well for solvents; however, most systems do not follow it. Henry's Law is a "fix it" for solutes, and when it doesn't work then we turn to activity. Activity is roughly proportional to concentration, although it has no units and is designed to make our thermodynamic equations work. In the next chapter we will make use of these concepts for further examinations of different phases, which will allow us to calculate phase diagrams including systems with more than one component.

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