

## 16.13: Colligative Properties - Solubility of a Solute in an Ideal Solution

Although the result has few practical applications, we can also use these ideas to calculate the solubility of a solid solute in an ideal solution. The arguments are similar to those we used to estimate the [freezing-point depression](#) of a solution. The freezing point of a solution is the temperature at which the solution is in equilibrium with its pure-solid solvent. The solubility of a solute is the mole fraction of the solute in a solution that is at equilibrium with pure-solid solute. In this analysis, we assume that the solid phase is pure solute. Our analysis does not apply to a solid solution in equilibrium with a liquid solution. The properties of the solvent have no role in our description of the solid-ideal-solution equilibrium state. Consequently, our analysis produces a model in which the solubility of an ideal solute depends only on the properties of the solute; for a given solute, the ideal-solution solubility is the same in every solvent.

We specify the composition of the solution by the mole fractions of  $A$  and  $B$ , again letting the solute be compound  $A$ . When we consider freezing-point depression, an  $A$ - $B$  solution of specified composition is in equilibrium with pure solid  $B$ , and we want to find the equilibrium temperature. When we consider solute solubility, the  $A$ - $B$  solution is in equilibrium with pure solid  $A$  at a specified pressure,  $P^\#$ , and temperature,  $T$ ; we want to find the equilibrium composition. Since pure solid  $A$  is present, the temperature must be less than the melting point of pure  $A$ . We let the melting point of the pure solute be  $T_{FA}$ , at the specified system pressure.

The activity of pure solid  $A$  and the system pressure are both constant; we have  $d\ln \tilde{a}_{A,\text{solid}} = 0$ ,  $dP = 0$ , and

$$d\mu_{A,\text{solid}} = -\bar{S}_{A,\text{solid}}^* dT$$

In the saturated ideal solution in equilibrium with this solid, we have  $\tilde{a}_{A,\text{solution}} = y_A$ ,  $dP = 0$ , and

$$d\mu_{A,\text{solution}} = -\bar{S}_{A,\text{solution}} dT + RT (d\ln y_A)$$

The relationship  $d\mu_{A,\text{solution}} = d\mu_{A,\text{solid}}$  becomes

$$-\bar{S}_{A,\text{solution}} dT + RT (d\ln y_A) = -\bar{S}_{A,\text{solid}}^* dT$$

and

$$d\ln y_A = \left( \frac{\bar{S}_{A,\text{solution}} - \bar{S}_{A,\text{solid}}^*}{RT} \right) dT$$

Now,  $\bar{S}_{A,\text{solution}} - \bar{S}_{A,\text{solid}}^*$  is the entropy change for the reversible (equilibrium) process in which one mole of pure solid  $A$  dissolves in a very large volume of a saturated solution; the mole fraction of  $A$  in this solution is constant at  $y_A$ . During this process, the pressure and temperature are constant at  $P^\#$  and  $T$ . Letting the heat absorbed by the system during this process be  $q_{P^\#}^{\text{rev}}$ , we have

$$\left( \bar{S}_{A,\text{solution}} - \bar{S}_{A,\text{solid}}^* \right)_{P^\#,T} = q_{P^\#}^{\text{rev}} / T$$

The heat absorbed is also expressible as the difference between the partial molar enthalpy of  $A$  in the solution and that of the pure solid; that is,

$$q_{P^\#}^{\text{rev}} = \left( \bar{H}_{A,\text{solution}} - \bar{H}_{A,\text{solid}}^* \right)_{P^\#,T}$$

One of the properties of an ideal solution is that the enthalpy of mixing is zero. Thus, the partial molar enthalpy of  $A$  in an ideal solution is independent of  $y_A$ , so that the partial molar enthalpy of  $A$  in an ideal solution is the same as the partial molar enthalpy of pure liquid  $A$ ; that is,  $\bar{H}_{A,\text{solution}} = \bar{H}_{A,\text{liquid}}^*$ , and

$$q_{P^\#}^{\text{rev}} = \left( \bar{H}_{A,\text{solution}} - \bar{H}_{A,\text{solid}}^* \right)_{P^\#,T} = \left( \bar{H}_{A,\text{liquid}}^* - \bar{H}_{A,\text{solid}}^* \right)_{P^\#,T} = (\Delta_{\text{fus}} H_A)_{P^\#,T} \approx (\Delta_{\text{fus}} H_A)_{P^\#,T_{FA}}$$

Then,

$$\left( \bar{S}_{A,\text{solution}} - \bar{S}_{A,\text{solid}}^* \right)_{P^\#, T} \approx \frac{(\Delta_{\text{fus}} H_A)_{P^\#, T_{FA}}}{T}$$

Dropping the subscript information and replacing the approximate equality, we have

$$d \ln y_A = \left( \frac{\Delta_{\text{fus}} H_A}{RT^2} \right) dT$$

At  $P^\#$  and  $T_{FA}$ ,  $\Delta_{\text{fus}} H_A$  is a property of pure  $A$  and is independent of the solution composition. When the pure solid solute melts at  $T_{FA}$ , the solute mole fraction is unity in the liquid phase with which it is in equilibrium: At  $T_{FA}$ ,  $y_A = 1$ . At temperature  $T$ ,  $y_A$  is the solute mole fraction in the liquid-phase solution that is at equilibrium with the pure-solid solute. Integrating between the limits  $(1, T_{FA})$  and  $(y_A, T)$ , we have

$$\int_1^{y_A} d \ln y_A = \frac{\Delta_{\text{fus}} H_A}{R} \int_{T_{FA}}^T \frac{dT}{T^2}$$

and

$$\ln y_A = \frac{-\Delta_{\text{fus}} H_A}{R} \left( \frac{1}{T} - \frac{1}{T_{FA}} \right)$$

For a given solute,  $\Delta_{\text{fus}} H_A$  and  $T_{FA}$  are fixed and are independent of the characteristics of the solvent. The mole fraction of  $A$  in the saturated solution depends only on temperature. Since  $\Delta_{\text{fus}} H_A > 0$  and  $T < T_{FA}$ , we find  $\ln y_A < 0$ . Therefore, we find that  $y_A < 1$ , as it must be. However,  $y_A$  increases, with  $T$ , implying that the solubility of a solid increases as the temperature increases, as we usually observe.

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