

## 16.14: Colligative Properties - Solubility of a Gas

A similar analysis yields an equation for the solubility of a gas in a liquid solvent as a function of temperature at a fixed pressure,  $P^\#$ . We refer to the gas component as  $A$  and the liquid component as  $B$ . We assume that solvent  $B$  is nonvolatile, so that the gas phase with which it is in equilibrium is essentially pure gaseous solute  $A$ . We again find that the properties of the solvent have no role in our model, and the solubility of gas  $A$  is the same in every solvent.

We assume that low concentrations of the solute obey [Henry's law](#) and choose the solution-phase standard state for solute  $A$  to be the pure hypothetical liquid  $A$  whose vapor pressure is  $\kappa_A$  at  $T$ . From [Section 16.4](#), we then have  $\tilde{a}_{A,\text{solution}} = y_A$ , so that  $d\ln \tilde{a}_{A,\text{solution}} = d\ln y_A$  at any temperature. Substituting into the general equation

$$d\mu_A = \bar{V}_A dP - \bar{S}_A dT + RT (d\ln \tilde{a}_A)$$

we have

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

The pressure of gas-phase  $A$  is constant at  $P^\#$ , and  $dP = 0$ . We choose the gas-phase activity standard state to be pure gas  $A$  at  $P^\#$  and  $T$ . Since this makes the activity of the pure gas unity at any temperature, we have  $d\ln \tilde{a}_{B,\text{gas}} = 0$ . Substituting, we have

$$d\mu_{A,\text{gas}} = -\bar{S}_{A,\text{gas}} dT$$

Any constant-pressure process that maintains equilibrium between gas-phase  $A$  and solution-phase  $A$  must involve the same change in the chemical potential of  $A$  in

each phase, so that  $d\mu_{A,\text{gas}} = d\mu_{A,\text{solution}}$ , and

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

so that

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

The difference  $\bar{S}_{A,\text{gas}} - \bar{S}_{A,\text{solution}}$  is the entropy change for the equilibrium—and hence reversible—process in which one mole of substance  $A$  originally in solution vaporizes into a gas phase consisting of essentially pure gas  $A$  while the system is at the constant pressure  $P^\#$ . Let us designate the enthalpy change for this reversible process at  $P^\#$  and  $T$  as  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}$ . Then, we have

$$\bar{S}_{A,\text{gas}} - \bar{S}_{A,\text{solution}} = \frac{\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}}{T}$$

so that

$$d\ln y_A = -\frac{\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}}{RT^2} dT$$

Since enthalpy changes are generally relatively insensitive to temperature, we expect that, at least over small ranges of  $y_A$  and  $T$ ,  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}$  is approximately constant. Since the vaporization process takes  $A$  from a state in which it has some of the characteristics of a liquid into a gaseous state, we can be confident that  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}} > 0$ . This conclusion implies that

$$\frac{d\ln y_A}{dT} < 0$$

Thus, our thermodynamic model leads us to the conclusion that the solubility of gas  $A$  decreases as the temperature increases. That the solubilities of gases generally decrease with increasing temperature is a well-known experimental observation. It stands in contrast to the observation that the solubilities of liquid or solid—at  $P^\#$  and  $T$ —substances generally increase with increasing temperature. Our analysis of gas solubility provides a satisfying theoretical interpretation for an experimental observation which otherwise appears to be counterintuitive.

The meaning of  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}$  is unambiguous. Our analysis enables us to measure it by experimentally measuring  $y_A$  as a function of  $T$ . We can estimate  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}}$  from another perspective: When we consider the “solution” in which  $y_A = 1$ , the vaporization process is the vaporization of liquid  $A$  into a gas phase of pure  $A$  at  $P^\#$  and  $T$ . Since we assume that  $A$  is stable as a gas at  $T$ , the boiling point of pure liquid  $A$  must be less than  $T$  at  $P^\#$  and the vaporization  $A$  must be a spontaneous process at  $P^\#$  and  $T$ . The enthalpy of vaporization datum which is most accessible for liquid  $A$  is that for the reversible vaporization at one atmosphere and the normal boiling point,  $T_B$ , which we designate as  $\Delta_{\text{vap}} H_A^\circ$ . If we stipulate that  $P^\#$  is one atmosphere; assume that our solubility equation remains valid as  $y_A$  increases from  $y_A \approx 0$  to  $y_A = 1$ ; and assume that the enthalpy of vaporization is approximately constant between the boiling point of  $A$  and  $T$ , we have  $\Delta_{\text{vap}} \bar{H}_{A,\text{solution}} = \Delta_{\text{vap}} H_A^\circ$ . Then,

$$d \ln y_A = - \frac{\Delta_{\text{vap}} H_A^\circ}{RT^2} dT$$

and

$$\int_1^{y_A} d \ln y_A = \int_{T_B}^T - \frac{\Delta_{\text{vap}} H_A^\circ}{RT^2} dT$$

so that

$$\ln y_A = \frac{\Delta_{\text{vap}} H_A^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_B} \right)$$

#### Check

Viewed critically, the accuracy of the approximation

$$\Delta_{\text{vap}} \bar{H}_{A,\text{solution}} \approx \Delta_{\text{vap}} H_A^\circ$$

is dubious. The assumptions we make to reach it are essentially equivalent to assuming that the cohesive forces in solution are about the same between  $A$  molecules as they are between  $A$  molecules and  $B$  molecules. We expect this approximation to be more accurate the more closely the solution exhibits ideal behavior. However, if solvent  $B$  is to satisfy our assumption that the solvent is nonvolatile, the cohesive interactions between  $B$  molecules must be greater than those between  $A$  molecules, and this not consistent with ideal-solution behavior.

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