

## Colligative Properties

There are several pedagogical advantages to teaching thermodynamics from the global point of view as formulated by Bent.<sup>1</sup> One is that little, if any, calculus is required. This is important for underclassmen who, although they have been exposed to calculus, are generally not yet facile with this tool. Another advantage is that it is not necessary to rely heavily on auxiliary thermodynamic functions, such as the Gibbs' and Helmholtz free energies, and thus the First and Second Laws are kept before the students at all times. This is also important for underclassmen, since the less time they have to spend on jargon and new vocabulary the more time they can spend on principles. A third advantage is that the very nature of the global approach makes it easy to recognize the various contributions to the total entropy and, therefore, to interpret the factors that are important in the achievement of equilibrium.

This paper applies a global analysis to colligative properties. It is the author's opinion that the material presented is suitable for advanced underclassmen as well as physical chemistry students.

### Osmosis

Osmotic pressure develops across a membrane which separates pure water and a water solution of a solute which cannot penetrate the membrane. The equilibrium which is finally achieved can be expressed as follows

$$\text{H}_2\text{O}(l, T, P, x = 1) = \text{H}_2\text{O}(l, T, P', x) \quad (1)$$

Pure water at temperature  $T$  and pressure  $P$  is in equilibrium with a water solution at temperature  $T$  and pressure  $P'$  and mole fraction  $X_{\text{H}_2\text{O}}$  of water. The final equilibrium situation is depicted in Figure 1.

To study the system at equilibrium consider the virtual transfer of one mole of pure water across the membrane to the solution side. Since, as is shown in Figure 1, there are only three parts to the universe in this problem, the First Law is written

$$\Delta E_\sigma + \Delta E_{wt} + \Delta E_\theta = 0 \quad (2)$$

where  $\sigma$  refers to the chemical system,  $wt$  refers to a weight which is raised or lowered in the surroundings, and  $\theta$  refers to the thermal surroundings.

From examination of eqn. (1) we can write

$$\Delta E_\sigma = \bar{E}_{\text{H}_2\text{O}}(T, P', x) - \bar{E}_{\text{H}_2\text{O}}(T, P, x = 1) = 0 \quad (3)$$

since the molar energy of a liquid is not a strong function of pressure and composition especially for dilute solutions. The bars over the  $E$ 's designate molar quantities.

The energy change of the weight is calculated as follows

$$\Delta E_{wt} = \Delta E_{wt_1} + \Delta E_{wt_2}$$

$$\Delta E_{wt} = P\Delta V + P'\Delta V'$$

$$\Delta E_{wt} = -P\bar{V}_{\text{H}_2\text{O}}(T, P) + P'\bar{V}_{\text{H}_2\text{O}}(T, P') = (P' - P)\bar{V}_{\text{H}_2\text{O}}(T, P') \quad (4)$$

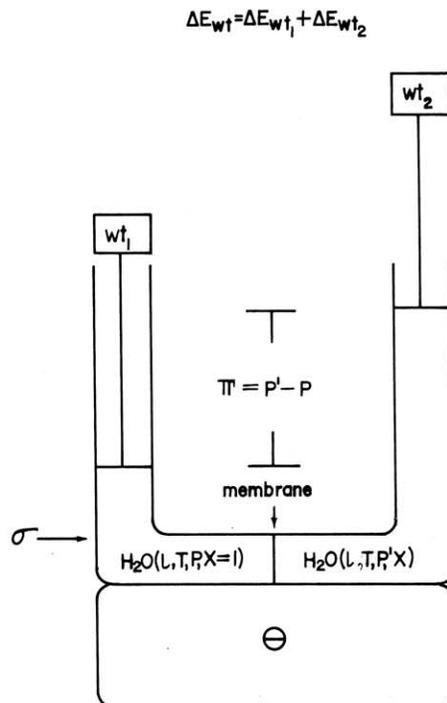


Figure 1. Osmosis.  $\sigma$  represents the chemical system;  $\theta$ , the thermal reservoir; and  $wt_1$  and  $wt_2$ , weights which are raised or lowered. In the actual experiment the pressure difference is due to columns of water of different heights.

Substituting eqns. (3) and (4) into eqn. (2) gives

$$\Delta E_\theta = -(P' - P)\bar{V}_{\text{H}_2\text{O}}(T, P') \quad (5)$$

the energy change in the thermal surroundings. The First Law demands that this term be negative since in the transfer of one mole of water across the membrane a weight rises in a gravitational field ( $\Delta E_{wt}$  is positive) at the expense of the thermal energy of the surroundings.

If the overall system is indeed at equilibrium, the virtual transfer of one mole of liquid water thru the membrane will not increase the entropy of the universe.

$$\Delta S_\sigma + \Delta S_\theta = 0 (\Delta S_{wt} = 0) \quad (6)$$

where by definition

$$\Delta S_\theta = \Delta E_\theta / T \quad (7)$$

The entropy change in the chemical system,  $\sigma$ , can be written

$$\Delta S_\sigma = \bar{S}_{\text{H}_2\text{O}}(T, P', x) - \bar{S}_{\text{H}_2\text{O}}(T, P, x = 1) \quad (8)$$

To proceed we assume ideal behavior for the solution on the right-hand side of the membrane. By this it is meant that the only contribution the presence of the solute makes to the molar entropy of water is a configurational term,  $-R \ln x_{\text{H}_2\text{O}}$ . Thus eqn. (8) can be written

<sup>1</sup> Bent, Henry A., "The Second Law," Oxford University Press, New York, 1965.

$$\Delta S_{\sigma} = \bar{S}_{\text{H}_2\text{O}}(T, P', x = 1) - R \ln x_{\text{H}_2\text{O}} - \bar{S}_{\text{H}_2\text{O}}(T, P, x = 1) = -R \ln x_{\text{H}_2\text{O}} \quad (9)$$

since the molar entropy of liquid water is not a strong function of pressure. Thus, the difference in molar entropy of water across the membrane is a configurational entropy term due to the presence of the solute on the right hand side of the membrane.

Equations (9), (7), and (5) can be substituted into eqn. (6) to give

$$-R \ln x_{\text{H}_2\text{O}} - \frac{(P' - P)\bar{V}_{\text{H}_2\text{O}}(T, P')}{T} = 0 \quad (10)$$

For every mole of water that passes through the membrane there is an increase in entropy in the chemical system of  $-R \ln x_{\text{H}_2\text{O}}$  because water has a higher molar entropy on the solution side of the membrane. However, the thermal entropy of the surroundings decreases due to weight-lifting done at expense of thermal energy of surroundings. When these terms cancel  $\Delta S_{\text{TOT}} = 0$  and equilibrium is achieved.

For dilute solutions it can be shown that equation (10) reduces to

$$\pi = C_{\text{solute}}RT \quad (11)$$

where  $\pi = P' - P$  and is the osmotic pressure.

### Raoult's Law

The global analysis of the equilibrium between a solution and its vapor provides a straight-forward derivation of Raoult's Law. To begin with we consider the equilibrium between a pure liquid and its vapor

$$\text{H}_2\text{O}(l, T, P^{\circ}, x = 1) = \text{H}_2\text{O}(g, T, P^{\circ}, x = 1) \quad (12)$$

where  $P^{\circ}$  is the equilibrium vapor pressure of the pure liquid at temperature  $T$ . The introduction of a non-volatile solute lowers the vapor pressure of the liquid such that, at the same temperature, the new equilibrium is

$$\text{H}_2\text{O}(l, T, P, x) = \text{H}_2\text{O}(g, T, P^{\circ}, x = 1) \quad (P < P^{\circ}) \quad (13)$$

For the vaporization of one mole of water under these conditions, the First Law reads (see Fig. 2)

$$\Delta E_{\sigma} + \Delta E_{\text{wt}} + \Delta E_{\theta} = 0$$

$$\Delta E_{\theta} = -[\bar{E}_{\text{H}_2\text{O}}^g(T, P, x = 1) - \bar{E}_{\text{H}_2\text{O}}^l(T, P, x)] - [P\bar{V}_{\text{H}_2\text{O}}^g(T, P) - P\bar{V}_{\text{H}_2\text{O}}^l(T, P)]$$

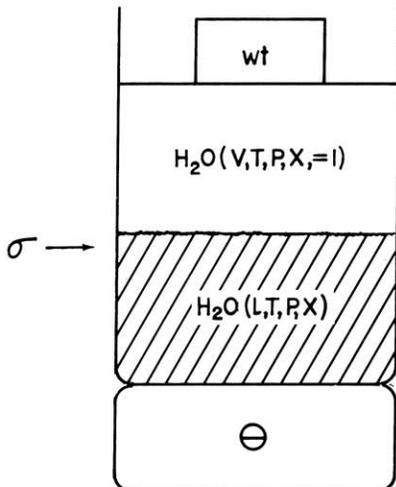


Figure 2. Liquid-vapor equilibrium.

or, since this is a constant pressure process

$$\Delta E_{\theta} = -\Delta \bar{H}_{\text{vap}}(T, P) \quad (14)$$

The Second Law statement for the equilibrium vaporization of one mole of water at equilibrium is

$$[\bar{S}_{\text{H}_2\text{O}}^g(T, P, x = 1) - \bar{S}_{\text{H}_2\text{O}}^l(T, P, x)] - \frac{\Delta \bar{H}_{\text{vap}}(T, P)}{T} = 0 \quad (15)$$

where the first term on the left is the entropy change of the chemical system and the second term is the entropy change of the thermal surroundings ( $\Delta S_{\text{wt}} = 0$ ). Again it is assumed that the solution is ideal and that the presence of the solute is accounted for by the addition of a configurational entropy term ( $-R \ln x_{\text{H}_2\text{O}}$ ) to the molar entropy of the liquid.

$$[\bar{S}_{\text{H}_2\text{O}}^g(T, P, x = 1) - \bar{S}_{\text{H}_2\text{O}}^l(T, P^{\circ}, x = 1) + R \ln x_{\text{H}_2\text{O}}] - \frac{\Delta \bar{H}_{\text{vap}}(T, P)}{T} = 0$$

Choosing  $(T, P^{\circ}, x = 1)$  as a reference state, this equation becomes

$$[\bar{S}_{\text{H}_2\text{O}}^g(T, P^{\circ}, x = 1) - R \ln P/P^{\circ} - \bar{S}_{\text{H}_2\text{O}}^l(T, P^{\circ}, x = 1) + R \ln x_{\text{H}_2\text{O}}] - \frac{\Delta \bar{H}_{\text{vap}}(T, P^{\circ})}{T} = 0 \quad (16)$$

since

$$\bar{S}_{\text{H}_2\text{O}}^g(T, P, x = 1) = \bar{S}_{\text{H}_2\text{O}}^g(T, P^{\circ}, x = 1) - R \ln P/P^{\circ}$$

$$\bar{S}_{\text{H}_2\text{O}}^l(T, P, x = 1) \approx \bar{S}_{\text{H}_2\text{O}}^l(T, P^{\circ}, x = 1)$$

$$\Delta \bar{H}_{\text{vap}}(T, P) = \Delta \bar{H}_{\text{vap}}(T, P^{\circ}) \quad (\text{ideal gas})$$

combining the first and third terms in the brackets on the left-hand side of eqn. (16) we can write

$$[\Delta \bar{S}_{\text{vap}}(T, P^{\circ}) - R \ln P/P^{\circ} + R \ln x_{\text{H}_2\text{O}}] - \frac{\Delta \bar{H}_{\text{vap}}(T, P^{\circ})}{T} = 0 \quad (17)$$

The first term on the left-hand side of this equation is the entropy of vaporization of pure water to pure water vapor at the equilibrium vapor pressure,  $P^{\circ}$ , at temperature  $T$ . The second term is a correction taking into account that the pressure of the vapor is  $P$  not  $P^{\circ}$  (the molar entropy of the gas is greater at  $P$  than  $P^{\circ}$ ). The third term takes into account the fact that the water is being vaporized from a solution which is not pure (the molar entropy of the water in the solution is greater than pure water) the entropy of the gas being unaffected as long as the solute is non-volatile. The final term on the left-hand side is the entropy change of the thermal surrounding for the vaporization as written in eqn. (13) assuming that the vapor is an ideal gas. Since the first and fourth terms in eqn. (17) cancel equilibrium is achieved when

$$R \ln P/P^{\circ} = R \ln x_{\text{H}_2\text{O}} \quad (18)$$

that is, when the entropy gain of the gas due to drop in pressure from  $P^{\circ}$  to  $P$  just matches the configurational entropy that is lost each time a mole of water is vaporized. Of course, eqn. (18) is nothing more than Raoult's Law

$$P = x_{\text{H}_2\text{O}}P^{\circ}$$

### Boiling Point Elevation

Since a non-volatile solute lowers a liquid's vapor pressure, it also elevates its normal boiling point. The global analysis of boiling point elevation is similar to that used in the previous section to derive Raoult's Law. The equilibrium between liquid and vapor at the normal boiling point is

$$\text{H}_2\text{O}(l, T, 1 \text{ atm}, x) = \text{H}_2\text{O}(g, T, 1 \text{ atm}, x = 1) \quad (19)$$

From a First Law analysis of the vaporization of one mole of  $\text{H}_2\text{O}$  from a water solution at atmospheric pressure and mole fraction  $x_{\text{H}_2\text{O}}$  we get

$$\Delta E_\theta = -\Delta \bar{H}_{\text{vap}}(T, 1 \text{ atm}) \quad (20)$$

For the equilibrium vaporization of one mole of water under these conditions the Second Law expression is similar to the Raoult's Law case

$$[\bar{S}_{\text{H}_2\text{O}}^g(T, 1 \text{ atm}, x = 1) - \bar{S}_{\text{H}_2\text{O}}^l(T, 1 \text{ atm}, x = 1) + R \ln x_{\text{H}_2\text{O}}] - \frac{\Delta \bar{H}_{\text{vap}}(T, 1 \text{ atm})}{T} = 0$$

which can be shortened to

$$[\Delta \bar{S}_{\text{vap}}(T, 1 \text{ atm}) + R \ln x_{\text{H}_2\text{O}}] - \frac{\Delta \bar{H}_{\text{vap}}(T, 1 \text{ atm})}{T} = 0 \quad (21)$$

Both  $\Delta \bar{S}_{\text{vap}}$  and  $\Delta \bar{H}_{\text{vap}}$  vary slowly as a function of temperature so that the following approximations can be made

$$\Delta \bar{S}_{\text{vap}}(T, 1 \text{ atm}) \approx \Delta \bar{S}_{\text{vap}}(T_b, 1 \text{ atm}) = \frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{T_b}$$

$$\Delta \bar{H}_{\text{vap}}(T, 1 \text{ atm}) \approx \Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})$$

where  $T_b$  is the normal boiling point of water. These equations can be substituted into eqn. (21) to give

$$\left( \frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{T_b} + R \ln x_{\text{H}_2\text{O}} \right) - \frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{T} = 0 \quad (22)$$

The entropy of vaporization of one mole of solution is less than the entropy of vaporization of one mole of pure water by the configurational term  $R \ln x_{\text{H}_2\text{O}}$  (the presence of a non-volatile solute increases the entropy of the liquid

but does not affect the entropy of the vapor). Therefore, at equilibrium  $\Delta S_\theta$  for the vaporization from solution will also be smaller and equilibrium is achieved at a temperature which is higher than the normal boiling point, since

$$\frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{T} < \frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{T_b} \text{ if } T > T_b$$

Equation (22) can be written in the form

$$\ln x_{\text{H}_2\text{O}} = \frac{\Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})}{R} \left( \frac{1}{T} - \frac{1}{T_b} \right) \quad (23)$$

which, for dilute solutions can be rearranged to

$$\Delta T = \left( \frac{RT_b^2 M}{1000 \Delta \bar{H}_{\text{vap}}(T_b, 1 \text{ atm})} \right) \times m$$

where  $\Delta T$  is the boiling point elevation,  $M$  is the molecular weight of the solvent and  $m$  is the molality of the solute.

### Ideal Solubility and Freezing Point Depression

The global approach to ideal solubility and freezing point depression is exactly the same as it was for boiling point elevation. If the global approach to colligative properties, as outlined here, is used in the classroom, the analysis of these last two colligative properties might be left as student exercises.

### Conclusions

Applying the global point of view to colligative properties is straight-forward. The starting point is always the First and Second Laws of Thermodynamics. This approach has, in addition, the virtue of being mathematically and conceptually simple. Using the global approach it is easy to keep track of what it is you are talking about and, therefore, easy to isolate the various entropy contributions that are important in the attainment of equilibrium.