

## Lecture 19: Dilute Solutions

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A solution is similar to the case of a mixture. A solution is called *dilute* if the concentration of solute is much less than the number of solvent molecules. In many ways the solute in a dilute solution behaves like an ideal gas. We can therefore predict many of the properties quantitatively.

## 19.1 Solvent and Solute

To make a prediction, we first need to know something about its chemical potentials. The chemical potential  $\mu_A$  is related to the Gibbs free energy by  $\mu_A = \partial G / \partial N_A$ . Suppose we start with a pure solvent of  $A$  molecules, then the Gibbs free energy is just  $N_A$  times the chemical potential.

$$G = N_A \mu_0(T, P) \quad (\text{in a pure solvent}) \quad (19.1)$$

where,  $\mu_0$  is the chemical potential of the pure solvent, a function of temperature and pressure.

Now imagine that we add a single B molecule to the system by holding  $T$  and  $P$  fixed, the change in  $G$  can be expressed as follows,

$$dG = dU + PdV - TdS \quad (19.2)$$

While  $dU$  and  $PdV$  won't depend on  $N_A$ , the  $TdS$  term is sensitive to such a change. The increase in  $S$  can be considered as proportional to  $N_A$

$$dS = k \ln N_A \quad (19.3)$$

$$dG = f(T, P) - kT \ln N_A \quad (\text{adding one molecule B}) \quad (19.4)$$

If we add two B molecules,

$$dG = 2f(T, P) - 2kT \ln N_A + kT \ln 2 \quad (\text{adding one molecule B}) \quad (19.5)$$

Note that we add the term of  $\ln 2$  due to the double counting of two B states.

$$G = N_A \mu_0(T, P) + N_B f(T, P) - N_B kT \ln N_A + N_B kT \ln N_B - N_B kT \quad (19.6)$$

This expression is valid when  $N_B \ll N_A$ . The solvent and solution chemical potential can be derived as follows

$$\mu_A = \left( \frac{\partial G}{\partial N_A} \right)_{T, P, N_B} = \mu_0(T, P) - \frac{N_B kT}{N_A} \quad (19.7)$$

$$\mu_B = \left( \frac{\partial G}{\partial N_B} \right)_{T, P, N_A} = \mu_0(T, P) - kT \ln(N_B / N_A) \quad (19.8)$$

As we would expect, adding more solute reduces the chemical potential of A and increases the chemical potential of B. Moreover, the results depend only on the ratio of  $N_B/N_A$ . We can therefore define a quantity as molality ( $m_B$ ).

$$\mu_B = \mu^0(T, P) - kT \ln m_B \quad (19.9)$$

## 19.2 Osmotic Pressure

Consider a solution that is separated from some pure solvent by a membrane that allows only solvent molecules to pass through. According to eq(19.11), the chemical potential of the solvent in the solution is less than that of the pure solvent. Particles tend to flow toward lower chemical potential, so the solvent molecules will spontaneously flow from the pure solvent into the solution. This flow of molecules is called **osmosis**. That osmosis should happen is counter-intuitive.

If you want to prevent osmosis from happening, the following condition must be met,

$$\mu_0(T, P_1) = \mu_0(T, P_2) - \frac{N_B kT}{N_A} \quad (19.10)$$

where  $P_1$  is the pressure on the side with pure solvent and  $P_2$  is the pressure on the side of solution. Assuming that these two pressures are not too different, we can approximate

$$\mu_0(T, P_2) \approx \mu_0(T, P_1) + (P_2 - P_1) \frac{\partial \mu_0}{\partial P} \quad (19.11)$$

$$(P_2 - P_1) \frac{\partial \mu_0}{\partial P} = \frac{N_B kT}{N_A} \quad (19.12)$$

To evaluate the derivative  $\frac{\partial \mu_0}{\partial P}$ , we use  $\mu_0 = G/N$ , so it is  $V/N$ . Therefore, the previous equation becomes,

$$P_2 - P_1 = \frac{N_B kT}{V} = \frac{n_B RT}{V} \quad (19.13)$$

This pressure difference is called the osmotic pressure, and the formula is called **van't Hoff's formula**. It says that the osmotic pressure is exactly the same as the pressure of an ideal gas of the same concentration as the solute. This is useful for biophysics studies.

## 19.3 Boiling and Freezing Points

Similar to the mixture of two phases, the concentration of solutes can shift the boiling and freezing points as well. Consider the case of a dilute solution at its boiling point, when it is in equilibrium with its gas phase (Fig. 19.1). Assuming

$$\mu_{A, \text{liq}}(T, P) = \mu_{A, \text{gas}}(T, P) \quad (19.14)$$

Using the previous learned relation,

$$\mu_0(T, P) - \frac{N_B kT}{N_A} = \mu_{\text{gas}}(T, P) \quad (19.15)$$

where  $\mu_0$  is the chemical potential of the pure solvent. Now, as in the osmotic \*\*\*

$$\mu_0(T, P_0) = \mu_{\text{gas}}(T, P_0) \quad (19.16)$$

$$\mu_0(T, P_0) + (P - P_0) \frac{\partial \mu_0}{\partial P} - \frac{N_B k T}{N_A} = \mu_{\text{gas}}(T, P_0) + (P - P_0) \frac{\partial \mu_{\text{gas}}}{\partial P} \quad (19.17)$$

$$(P - P_0) \frac{V}{N} - \frac{N_B k T}{N_A} = (P - P_0) \left( \frac{V}{N_{\text{gas}}} \right) \quad (19.18)$$

This can be reduced to

$$P - P_0 = \frac{-N_B}{N_A} P_0, \quad \frac{P}{P_0} = 1 - \frac{N_B}{N_A} \quad (19.19)$$

Alternatively, we could hold the pressure fixed and solve for the shift in temperature needed to maintain equilibrium in the presence of the solute. Let  $T_0$  be the boiling point of the pure solvent at  $P$ , so that

$$\mu_0(T_0, P) = \mu_{\text{gas}}(T_0, P) \quad (19.20)$$

In terms of the chemical potentials at  $T_0$ , it becomes,

$$\mu_0(T_0, P) + (T - T_0) \frac{\partial \mu_0}{\partial T} - \frac{N_B k T}{N_A} = \mu_{\text{gas}}(T_0, P) + (T - T_0) \frac{\partial \mu_{\text{gas}}}{\partial T} \quad (19.21)$$

Again the first term on each side cancels. Each  $\partial \mu / \partial T$  is just minus  $S$ , so

$$-(T - T_0) \left( \frac{S}{N} \right)_{\text{liq}} - \frac{N_B k T}{N_A} = -(T - T_0) \left( \frac{S}{N} \right)_{\text{gas}} \quad (19.22)$$

$$T - T_0 = \frac{N_B k T_0^2}{L} = \frac{n_B R T_0^2}{L} \quad (19.23)$$

With the results, let's compute the boiling temperature of seawater. A convenient quantity to consider is \*\*\*\*

$$T - T_0 = \frac{(1.2 \text{ mol})(8.3 \text{ J/mol} \cdot \text{K})(373 \text{ K})^2}{2260 \text{ kJ}} = 0.6 \text{ K} \quad (19.24)$$

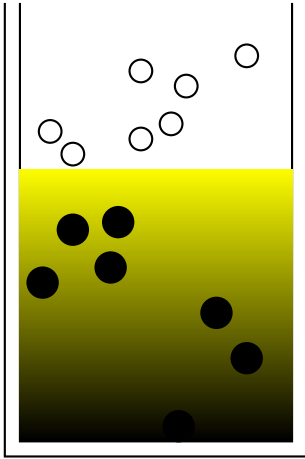


Figure 19.1: The presence of a solute reduces the boiling point of the solvent.