

Aqueous Solutions

Solutions

A solution is a mixture containing at least two kinds of pure substances. Although we usually think of solutions as being liquid, a solution can exist in any of the three states of matter. We can have solutions of gas in gas (e.g. air), gas in liquid (e.g. soda pop), gas in solid (e.g. ice), liquid in liquid (e.g. ethanol and water), solid in liquid (e.g. brine), or solid in solid (e.g. alloys).

In most solutions, one material predominates and this is called the solvent, with the other compounds being called solutes, although this convention is arbitrary and only used for convenience. When the components of a solution are in different states of matter, the solvent is considered to be the one which does not undergo a change of state upon mixing.

Aqueous solutions are important for cryobiology since the freezing of biological systems always involves solutions containing electrolytes, non-electrolytes, polymers, and gases. During the phase change that occurs with freezing, the concentration and distribution of the solutes is altered, sometimes accompanied by irreversible chemical reactions.

Concentration:

The composition of a solution is described by the concentration of its constituents. There are two primary ways of expressing concentration:

- Molarity (M) - the number of moles of solute in 1 litre of solution;
- Molality (m) - the number of moles of solute associated with 1000g of solvent.

Molarity is based on the volume of solution whereas molality is based on the weight of solvent. The difference becomes most noticeable when temperature effects are considered. Because the volume of liquids can expand or contract with changes in temperature, molarity can change with changing temperature. The weight of solvent, on the other hand, is constant with temperature, so molality gives a measure of concentration that is independent of temperature.

A more fundamental expression of the concentration of a solution uses the mole fraction (that is, the fraction of molecules on the interval 0- 1). The mole fraction of solute is given by:

$$X_s = \frac{n_s}{n_0 + n_s} \quad (4.1.1)$$

And the mole fraction of solvent is:

$$X_0 = \frac{n_0}{n_0 + n_s} \quad (4.1.2)$$

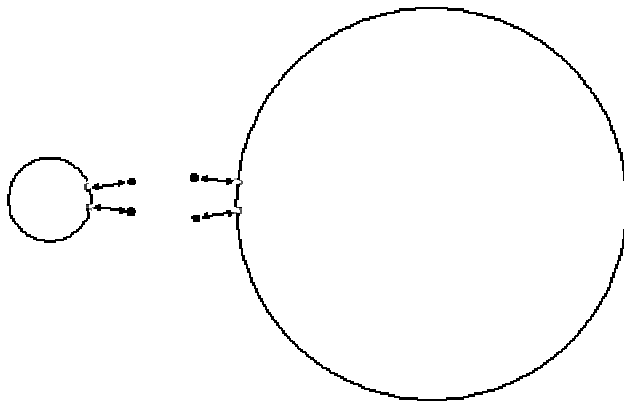
With $X_s + X_0 = 1$

Solubility:

A property that any particular combination of solute and solvent have is the solubility. This is the amount of solute that can be associated with a given amount of solvent in the context of a solution. Most solids show a well defined saturation point in liquids where no more solid can be dissolved; the ration of solute to solvent at this point defines the solubility. In general, solubilities in liquids increase with temperature (hence the solubility is a temperature-dependent property) although there are some exceptions.

If a saturated solution is made at a certain temperature and then the temperature of the solution decreases, the solubility of the solution will be exceeded. The solution becomes supersaturated and exists in a metastable state. The solute will precipitate out of solution, usually forming crystals in the liquid.

Even in crystalline form, solute molecules continually leave and join the crystal surface, going back and forth from solution to the solid phase. This has the effect of increasing the average crystal size, since small crystals have a high surface energy while large crystals have a small surface energy. The constant movement between crystal and solution tends to minimize the total surface energy of all the crystals present in the solution.



surface energy proportional to curvature

Figure 4.1.1

Colligative Properties:

The properties that solutions exhibit which are characteristic of the solution, that arise from the behavior of the collection rather than from the behavior of individual components are called colligative properties. Vapor pressure, boiling point elevation and freezing point depression are three such properties which depend upon the concentration of the solutions rather than the chemical properties of the constituents.

Vapor Pressure and Raoult's Law:

Let's consider a closed container with pure water in it and vapor above the liquid. If we think about the liquid molecules near the surface, there will be a distribution of energies. When a particular molecule with a high energy happens to be moving toward the interface, at the surface it will feel a force trying to restrain it to the liquid (due to the intermolecular bonds). If it's energy is high enough to overcome this restraining force, then it will escape the liquid and enter the gas phase (evaporation). We can see immediately that some work is done to accomplish this as the intermolecular bonds must be broken for the molecule to leave the liquid. Likewise, since work must be done, the molecule will lose energy as it passes to the gas phase. This has the effect of slowing it down so that, even though we started with an energetic molecule, near the upper end of the energy distribution, it will lose that extra energy and pass into the gas phase with the average kinetic energy (i.e. the temperature of the gas and liquid are the same).

The water molecules in the gas phase above the water may either strike the sides of the container or the surface of the water. If we assume that all those molecules which strike the surface of the water are captured by the intermolecular bonds (condensation) then we can see that the number of molecules which strike the water is a function of the velocity of the molecules (i.e. the temperature). Thus we can see that there will be an equilibrium established in which a certain number of molecules exist above the liquid in the gas phase. The pressure that this gas exerts on the sides of the container is called the vapor pressure of the liquid. If we use the ideal gas law then we have

$$P_{V_w} = \frac{RT}{V} \quad (4.1.3)$$

where P_{V_w} is the vapor pressure above pure water and V bar is the molal volume of water.

If a solute is added to the liquid then it follows that any molecule that was traveling toward the surface with a high enough energy to escape to the gas but encountered a solute molecule would be reflected back into the liquid. Thus the fraction of molecules which leave the surface is reduced in proportion to the mole fraction of water (X_w). The vapor pressure above an ideal solution will then be

$$P_{V_s} = X_w \frac{RT}{V} \quad (4.1.4)$$

Combining these equations gives

$$P_{Vs} = P_{Vw} \cdot X_w \quad (4.1.5)$$

Which is known as Raoult's Law.

A quantity called the water activity is often used as well. It is analogous to the chemical potential and is defined as:

$$a_w = P_{Vs} \cdot P_{Vw} \quad (4.1.6)$$

The water activity is always less than one for solutions. Water always flows from regions of high activity to low activity.

Freezing Point Depression:

In the section on the freezing of water we will derive an equation for the minimum radius of an ice crystal that is stable at a given temperature

$$r = \frac{2\sigma T_f}{L_f \Delta T} \quad (4.1.7)$$

Where s is the surface tension, T_f the freezing point, L_f the latent heat of fusion and ΔT the difference between the temperature and the freezing point. A similar argument can be used to derive an equation for the vapor pressure above a drop with a given curvature (both are variations on the Kelvin equation)

$$\ln \frac{P_{Vs}}{P_{Vw}} = \frac{V}{RT} \cdot \frac{2\sigma}{r} \quad (4.1.8)$$

Equating the two gives us

$$\ln \frac{P_{Vs}}{P_{Vw}} = \frac{VL_f \Delta T}{RT_f^2} \quad (4.1.9)$$

and since

$$\ln \frac{P_{Vs}}{P_{Vw}} = -\ln X_w \approx X_s \quad (4.1.10)$$

we arrive at an expression for the freezing point depression

$$\Delta T = \frac{RT_f^2}{VL_f} X_s \quad (4.1.11)$$

If $n_w \gg n_s$ then we can make the simplifying assumption

$$X_s = \frac{n_s}{n_w + n_s} \approx \frac{n_s}{n_w} \approx \frac{n_s M_w}{1000V} \quad (4.1.12)$$

where M_w is the molecular weight of water. Thus we arrive at the common expression for the freezing point depression of an ideal dilute solution (substituting c for n_s/V).

$$\Delta T = cK_f \quad (4.1.13) \quad \text{where} \quad K_f = \frac{RT_f^2 M_w}{1000L_f} \quad (4.1.14)$$

For water, K_f is $1.86^\circ\text{C}/\text{mol}$, so for aqueous solutions, the freezing point depression is given by 1.86 times the molality of solutes. Measurement of the freezing point depression is reasonably easy (just supercool the solution and nucleate ice, then the latent heat of fusion brings the temperature up to the freezing point) thereby providing a simple method of measuring the concentration of solutions.

Boiling Point Elevation:

The boiling point of a liquid is the temperature at which the vapor pressure of the liquid just equals the ambient pressure of the environment. At this temperature, the thermal energy of the molecules of the liquid exceed the energy of the intermolecular bonds that hold the liquid together and the liquid boils. Since solutes lower the vapor pressure of a solution, the temperature required to raise the vapor pressure to the ambient pressure is higher than than for the pure solvent. The equation for the boiling point elevation in dilute solutions is analogous to that for the freezing point depression:

$$\Delta T_b = \frac{RT_0^2}{\Delta H_{vap}} X_s \quad (4.1.15)$$

Where ΔH_{vap} is the molal heat of vaporization. As before, this can be rewritten as:

$$\Delta T_b = cK_b \quad (4.1.16)$$

For water, $K_b = 0.512^\circ\text{C}/\text{mol}$.

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