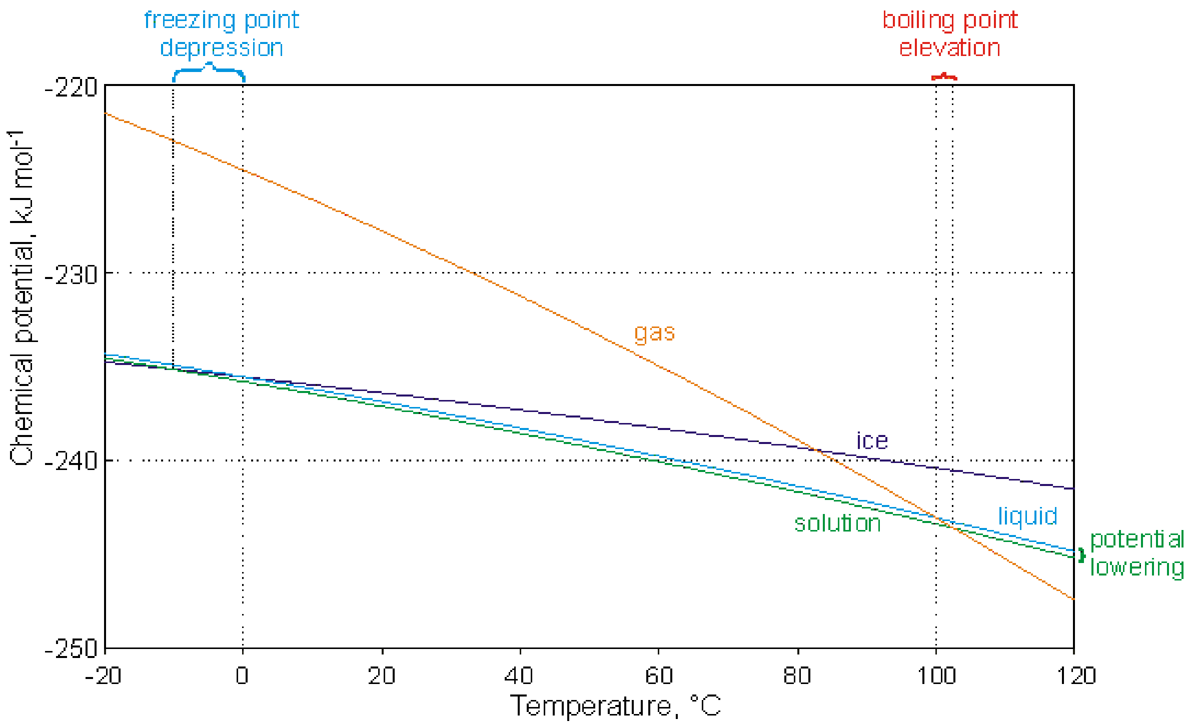
Colligative properties of water

- **Overview of colligative properties** : **mole fraction** : **molarity, molality, % w/w and % w/v**
- **Vapor pressure lowering** : **$CaCl_2$**
- **Freezing point depression** : **examples** : **Glucose** : **Urea** : **Ethanol** : **NaCl** : **$CaCl_2$**
- **Boiling point elevation** : **Glucose**
- **Osmotic pressure**
- **Self-generation of osmotic pressure at interfaces**

Overview of colligative properties

The colligative properties of solutions consist of freezing point depression, boiling point elevation, vapor pressure lowering and osmotic pressure.[n] These properties ideally depend on changes in the entropy of the solution on dissolving the solute, which is determined by the number of the solute molecules or ions but does not depend on their structure. The rationale for these colligative properties is the increase in entropy on mixing solutes with the water. This extra entropy provides extra energy available in the solution which has to be overcome when ice or water vapor (neither of which contains a non-volatile solute)[l] is formed. It is available to help break the bonds of the ice causing melting at a lower temperature and to reduce the entropy loss when water condenses, so encouraging the condensation and reducing the vapor pressure. Put another way, the solute stabilizes the water in the solution relative to pure water. The entropy change reduces the chemical potential(μ_w)[a] by $-RTLn(x_w)$ (that is, the negative energy term $RTLn(x_w)$ is added to the potential) where x_w is the mole fraction[b]of the 'free'[d] water ($0 < x_w < 1$). Note that x_w may be replaced by the water activity (a_w) in this expression. Dissolving a solute in liquid water thus makes the liquid water more stable whereas the ice and vapor phases remain unchanged as no solute is present in ice crystals and no non-volatile solute is present in the vapor. The colligative properties of materials encompass all liquids but on this web page we concentrate on water and aqueous solutions. Deviations from ideal behavior[i]provide useful insights into the interactions of molecules and ions with water.



The above figure is based on an ideal solution where $x_w = 0.9$ with $x_S = 0.1$ (that is, 6.167 molal [c]), freezing point depression is at -11.47 °C (that is, at 6.167 x 1.8597 K), boiling point elevation is at 103.16 °C (that is, at 6.167 x 0.5129 K), the vapor pressure is 0.9 x that of pure water and the chemical potential changed by an amount equal to RTLn(0.9) (that is, 8.314 x 273.15 x -0.10536 = -239.28 J mol^{-1} at 0 °C); see below for an explanation of terms and the derivation of the equations. The small change of the chemical potential of ice with temperature gives rise to a larger freezing point depression than the boiling point elevation. Thus, solutions have higher boiling points and lower freezing points than pure water.

Vapor pressure lowering

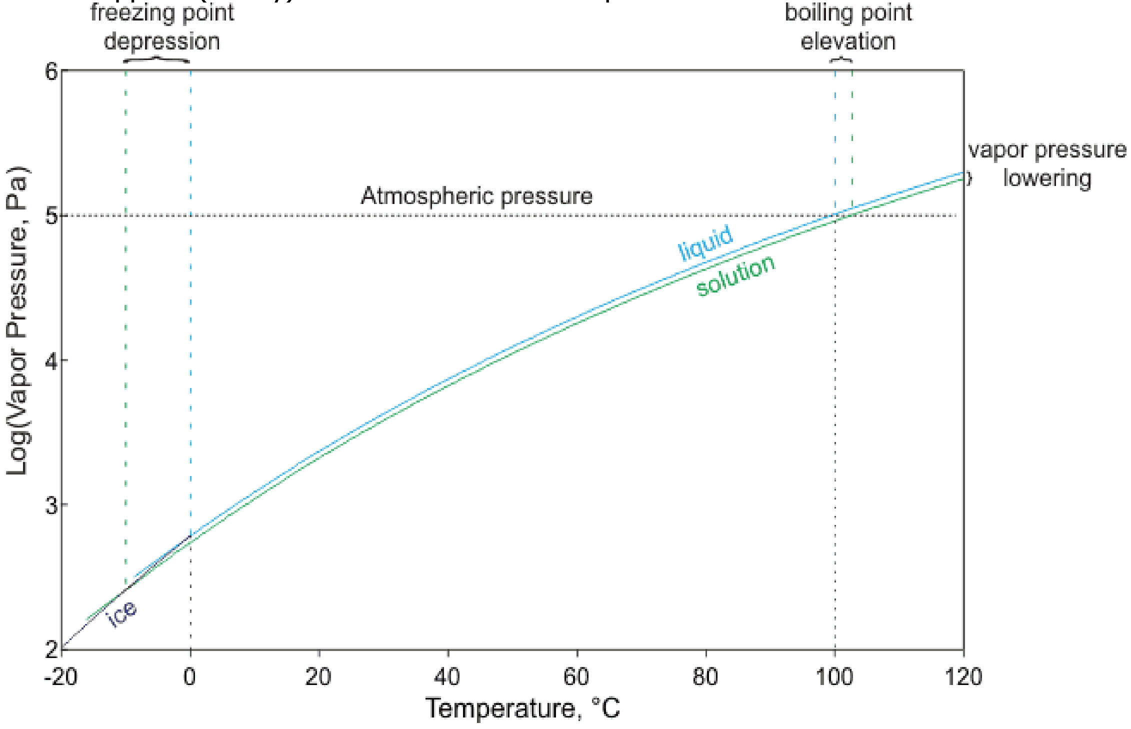
The partial pressure of water vapor (vapor pressure) is the pressure of gaseous water. The saturation vapor pressure is the equilibrium value of this vapor pressure which, in a given mixture of gasses such as air, is the same regardless of the mixture’s composition and depends only on temperature and on the energy required for vaporization. It is commonly found in textbooks and elsewhere on the Web that the vapor pressure is lowered due to the presence of other molecules 'blocking' the surface or that it depends on the volume fraction of materials. These explanations are completely false and highly misleading as they lead to the erroneous conclusion that the vapor pressure lowering may be dependent on molecular size rather than energetic entropic effects. Also, the surface of water should not be considered as identical to the bulk aqueous liquid phase. The correct explanation for the vapor pressure lowering is that the presence of solute increases the entropy of the solution (a randomly disbursed mixture having greater entropy than a single material); such entropy rise increasing the energy required for removing solvent molecules from the liquid phase to the vapor phase.

(1)

In the presence of a solute,

$$P_{solute} = x_w P_{pure\ liquid} = (1 - x_S)\ P_{pure\ liquid}$$

where P_{solute} is the vapor pressure over a solution containing the solute (here assumed non-volatile) and $P_{pure\ liquid}$ is the vapor pressure over the pure liquid. This equation is also known as Raoult's law and may also be applied (ideally) to mixtures of volatile liquids.



The above figure is based on an ideal solution where $x_w = 0.9$ with $x_S = 0.1$ (as in the top figure), the vapor pressure is 0.9 x that of pure water.

Raoult's law may be simply derived,

(2)
As above, in a solution,

$$\mu^{solution} = \mu^{liquid} + RTLn(x_w)$$

The vapor phase is in equilibrium with the liquid phase.

(3)

Therefore,

$$\mu^{liquid} = \mu^{vapor}_{P_{pure\ liquid}}$$

(4)

and

$$\mu^{solution} = \mu^{vapor}_{P_{solute}}$$

Assuming ideal gas behavior (a good approximation at these low pressures),

(5)

$$\mu^{vapor}_{P_{solute}} = \mu^{vapor}_{P_{pure\ liquid}} + RT\,Ln\left(\frac{P_{solute}}{P_{pure\ liquid}}\right)$$

(6)

Hence,

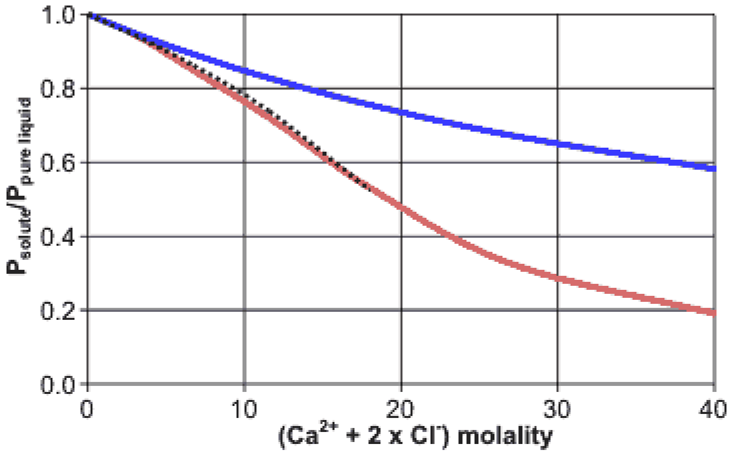
$$\mu^{liquid} + RTLn(x_w) = \mu^{vapor}_{P_{pure\ liquid}} + RT\,Ln\left(\frac{P_{solute}}{P_{pure\ liquid}}\right)$$

which cancels down to give,
(7)

$$x_w = P_{solute}/P_{pure\ liquid} \quad \text{or} \quad P_{solute} = x_w P_{pure\ liquid}$$

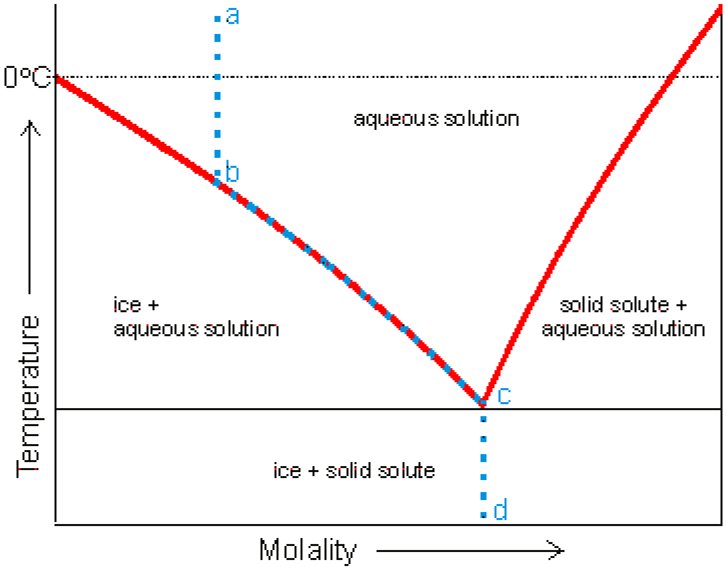
This is Raoult's law. As with other colligative properties, Raoult's law is also applicable to polymers, except at high enough concentrations as to cause significant molecular overlap [1101].

$CaCl_2$



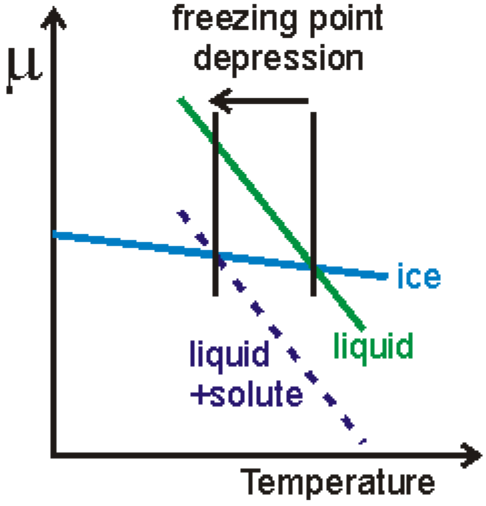
Opposite shows the vapor pressure depression of $CaCl_2$solutions at 100 °C (data from [1121]). The upper blue line shows the 'ideal' behavior whereas the lower red line shows the actual vapor pressure depression. The black dotted line shows the 'ideal' behavior corrected for the bound water of hydration (5.9 water molecules bound to each $CaCl_2$ unit), which is somewhat less than is bound at lower temperaturesas found by freezing point depression. At high molalities there is considerable deviation from this 'corrected' line as the water bound to each $CaCl_2$ unit reduces when much less water is available (for example, only 3.4 water molecules bound to each $CaCl_2$ unit at 13.5 m $CaCl_2$; 60 % w/w).

Freezing point depression



When a solute is dissolved in water, the melting point of the resultant solution may be described using a phase diagram, as opposite. The bold red lines show the phase changes. A solution at **a** on cooling will not freeze at 0 °C but will meet the melting point line at a lower freezing point **b**. If no supercooling takes place[k] some ice will form resulting in a more concentrated solution, freezing at an even lower temperature. This will continue (following the blue dotted line until the eutectic point **c** is reached. Further cooling will result in solidification of the remaining solution with the mixed solid cooling to **d**. The eutectic point is at the lowest temperature that the solution can exist at equilibrium and is at the point where the ice line meets the solubility line of the solid solute (or one of its solid hydrates), shown on the right.

Although the eutectic should be independent of the original concentration, ESR studies with spin probes show that interactions between solutes may cause variation at initially low concentrations [1540].



In an equilibrium mixture of pure water and pure ice at the melting point (273.15 K) the chemical potential of the ice (μ^{ice}) must equal the chemical potential of the pure water (μ^{liquid}), that is, $\mu^{ice} = \mu^{liquid}$. With solute present, the chemical potential of the water is reduced by an amount -RTLn(x_w). There will be a new melting point where $\mu^{ice} = \mu^{solution}$ and,

$$\mu^{solution} = \mu^{liquid} + RT\,Ln(x_w) \qquad (8)$$

$$\mu^{ice} = \mu^{liquid} + RT\,Ln(x_w) \qquad (9)$$

where x_w is the mole fraction of the water, R is the gas constant (= 8.314472 J mol^{-1} K^{-1}) and T is the new melting point of ice in contact with the solution. Note that x_w may be replaced by a_w (the water activity) in this equation. The chemical potential of the ice is not affected by the solute which dissolves only in the liquid water and is generally completely excluded from the ice lattice. The process of melting is also called fusion. The enthalpy change during this process ΔH_{fus} is $H^{liquid} - H^{solid}$.[f] Thus,

(10)

$$RT\,Ln(x_w) = \mu^{ice} - \mu^{liquid} = -\Delta G_{fus}$$

$$Ln(x_w) = -\Delta G_{fus}/RT$$

(11)

As ΔG = ΔH - TΔS, at constant pressure,

$$\frac{\partial(\Delta G_{fus})}{\partial T} = -\Delta S_{fus}$$

(12)
and,

$$\frac{\partial\left(\Delta G_{fus}/T\right)}{\partial T}=\frac{1}{T}\left(\frac{\partial\Delta G_{fus}}{\partial T}\right)-\frac{1}{T^{2}}\Delta G_{fus}=-\frac{T\Delta S_{fus}+\Delta G_{fus}}{T^{2}}=\frac{-\Delta H_{fus}}{T^{2}}$$

(This is the Gibbs-Helmholtz equation)

Therefore, differentiating *Ln*(x_w) = -ΔG_{fus}/RT we get,

(13)

$$\frac{\partial Ln(x_w)}{\partial x_w}=-\frac{\partial\left(\Delta G_{fus}/T\right)}{\partial T}\times\left(\frac{\partial T}{\partial x_w}\right)$$

(14)

Therefore,

$$\frac{1}{x_w}=\frac{\Delta H_{fus}}{RT^{2}}\left(\frac{\partial T}{\partial x_w}\right)$$

(15)

$$\int_{1}^{x_w}\frac{dx_w}{x_w}=\int_{T_m}^{T}\frac{\Delta H_{fus}}{RT^{2}}dT$$

(16)

$$Ln(x_w)=\int_{T_m}^{T}\frac{\Delta H_{fus}}{RT^{2}}dT$$

Solving the right hand side and replacing *Ln*(x_w) by *Ln*(1-x_S) and ignoring the small temperature dependence of ΔH_{fus}, [g]

[250] (17)

$$Ln(1-x_S)=\frac{\Delta H_{fus}}{R}\left(\frac{1}{T_m}-\frac{1}{T}\right)$$

Ignoring the small temperature dependence of ΔH_{fus} introduces a small error (**a**), see below. The corrected value for ΔH_{fus}may later be obtained from a plot of Ln(1-x_S) versus (1/T_m-1/T).
If x_S << 1 then Ln(1-x_S) = - x_S (This introduces a small error (**b**), see below)[e]

(18)

and,

$$x_S = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right) = \frac{\Delta H_{fus}}{R}\left(\frac{T_m - T}{T \times T_m}\right)$$

The freezing point lowering ΔT is (T_m - T), a positive value. If T is close to T_m then $TxT_m = T_m^2$. This introduces a small error (**c**), see below).

(19)[h]

Therefore,

$$\Delta T = \frac{x_S R T_m^{\ 2}}{\Delta H_{fus}}$$

As x_S is the mole fraction of the solute = moles solute/(moles water + moles solute), at low x_S it may be approximated by moles solute/moles water = molality x molar mass of water = $m_S M_w$ (where m_S is the molality = moles per kg water, and M_w is the molar mass of water = 0.018015268 kg mol^{-1}).

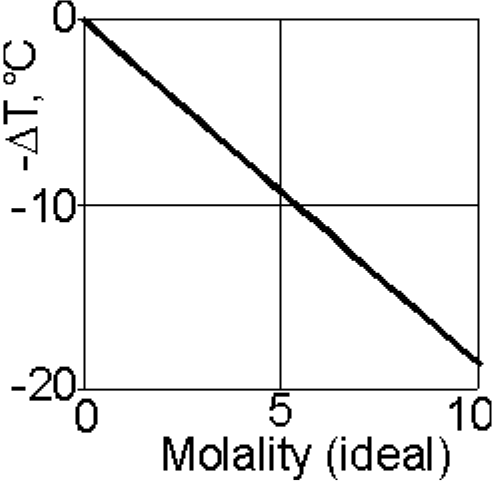
With this approximation,
(20)

$$\mathbf{\Delta T = m_S K_f}$$

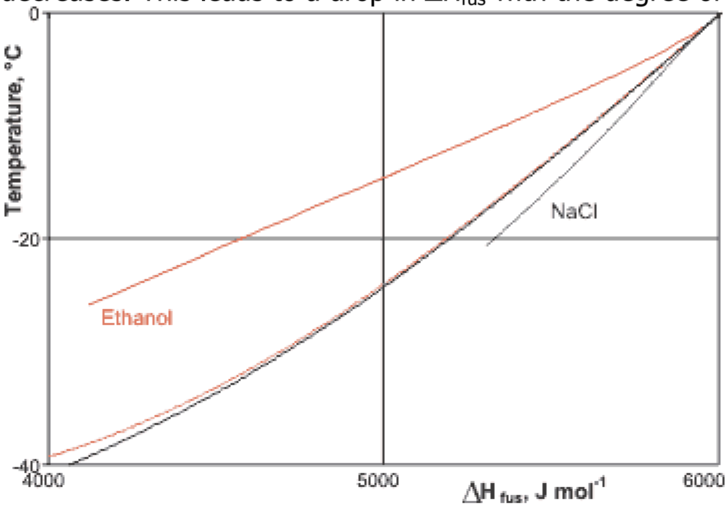
(21)
This is the commonly used cryoscopic equation,

$$K_f = \frac{M_w R T_m^{\ 2}}{\Delta H_{fus}}$$

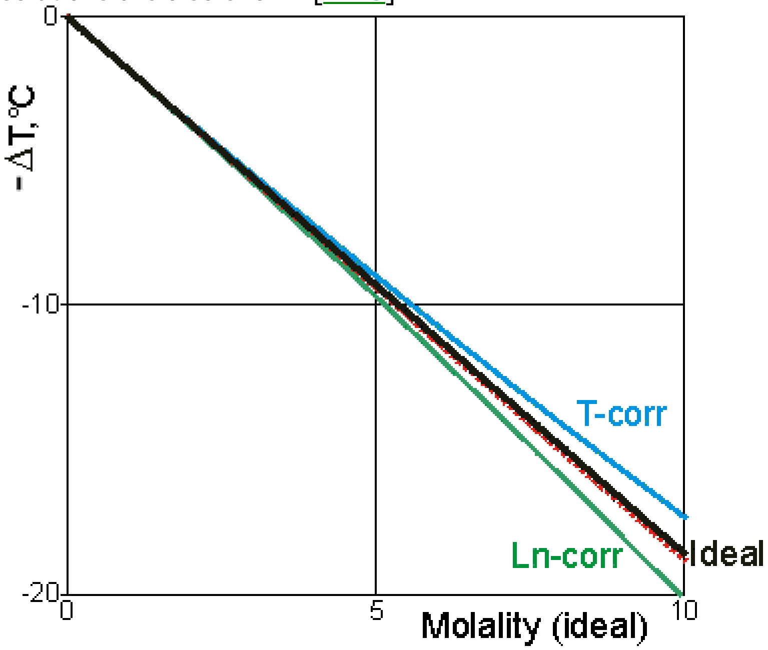
where K_f (the cryoscopic constant) for water is
where K_f for water is and calculated to be 1.8597 K kg mol^{-1} using R = 8.314472 J mol^{-1} K^{-1}, T_m = 273.15 K, and ΔH_{fus}= 6009.5 J mol^{-1}.



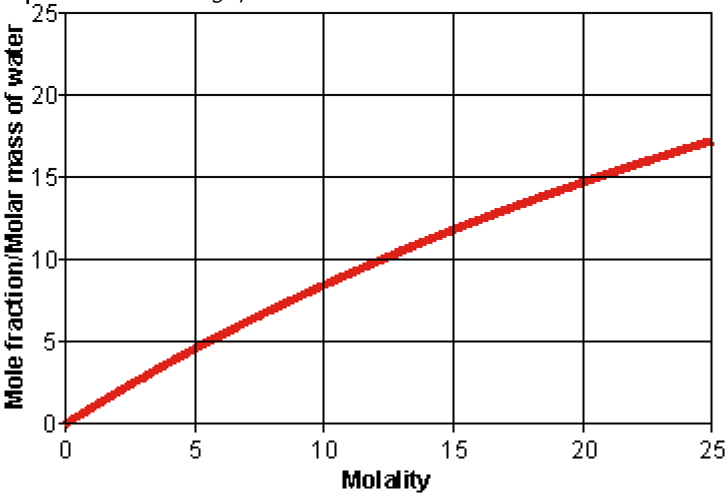
The equation $\Delta T = m_S K_f$ (shown opposite) thus makes several assumptions. The assumption (**a**) concerning the constancy of ΔH_{fus} clearly introduces some error. For example, it is well known that the specific heat of pure water increases considerably on supercooling whereas that of ice decreases. This leads to a drop in ΔH_{fus} with the degree of supercooling [1748].



The effect is shown opposite where the data for the enthalpy of fusion of ice used is from [906] and [76] for the upper central line and from Dorsey and Angell *et al* [1098] for the lower central line. In practice, however, the changes occurring in solution [1098] will be somewhat less as the solutes will destroy much of the aqueous structuring responsible for the large specific heat increases of the liquid phase on cooling. However there is also heat lost or gained from the solution on concentration because of the solute concentrations. The overall latent heats of fusion of ethanol and NaCl solutions are also shown [1475] .



The assumptions (**b**, error due to the Ln(1-x) approximation[e] shown by the green 'Ln-corr' curve, and **c**, due to the temperature approximation shown by the blue 'T-corr' curve) operate in different directions and mostly compensate for each other to only produce small net errors in ΔT (shown as the dotted red line opposite, indicating the actual 'ideal' behavior). Thus, there is only a net 2% error, for using these two approximations, in 10 molal solution for the ideal behavior using the equation $\Delta T = m_S K_f$.



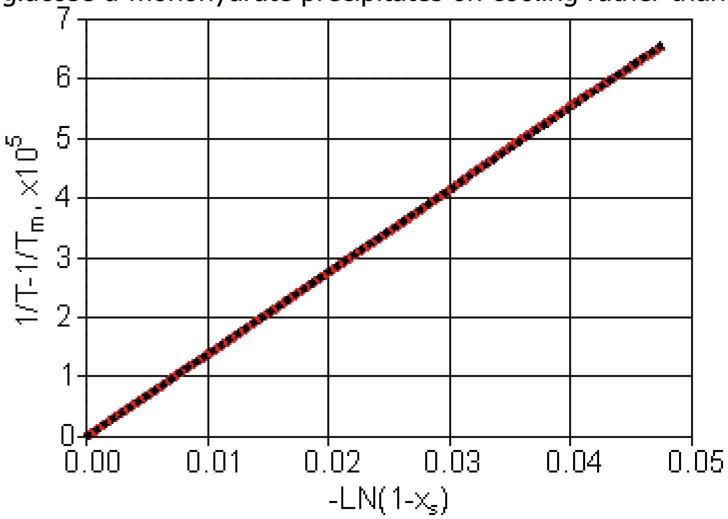
The error introduced by using the molality (m_S) rather than the mole fraction (x_S) may be significant in solutions greater than a few molal and is shown opposite. At higher molality, the expected freezing point depression using the molality equation ($\Delta T = m_S K_f$) is greater than using the mole fraction equation ($\Delta T = x_S K_f / M$). This effect is partially compensated by the effect of the Ln(1-x) approximation explained above.

In reality, deviations from 'ideal' behavior occur through solute-solute and solute-solvent interactions so introducing a partial dependence on the identity of the solute, (for example, see [1012]): (a) solutes may interact (salts forming ion pairsor larger clusters), lowering their effective concentration, (b) solutes may bind variable amounts of water [1100], depending on both their identity and concentration and the identity and concentration of other solutes, so removing water from the 'free' water pool that freezes [445]. As such water is removed from the 'free' (freezable) water pool[d] with addition of solute, addition of incremental amounts of solute has a progressively greater lowering affect on the freezing point. Freezing point depression may thus be used to determine the 'hydration' number of ions and such values are greater than those obtained by boiling point elevation, indicating the greater hydration of ions at low temperatures (for example, see [1064]). It is important to note that hydration numbers also vary with concentration in addition to the method of determination, temperature and pressure. Colligative properties are applicable to all solutes, including polymers, except at high enough concentrations as to cause significant molecular overlap [1101].

Freezing point depression examples

Glucose

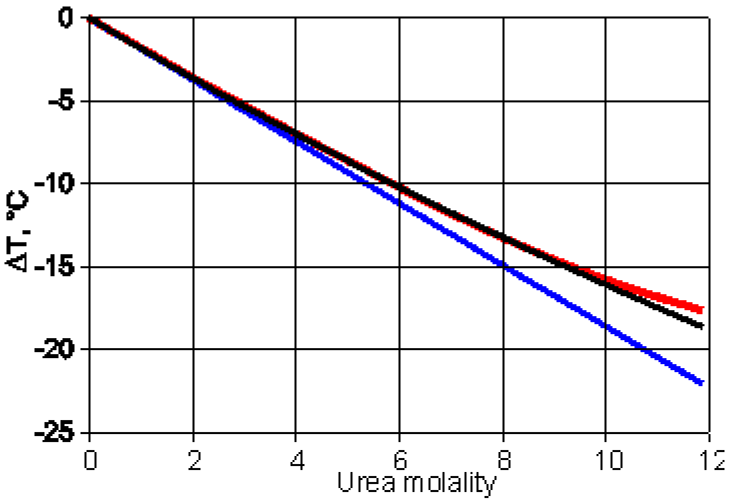
The upper blue line follows the 'ideal' colligative equation, $\Delta T = m_S K_f$. for glucose ($C_6H_{12}O_6$). The red line follows the experimental freezing point curve [70], hardly deviating from the relationship obtained directly from the unapproximated colligative equations above (black line) where allowance has been made for bound water of hydration (2.8 water molecules bound to each glucose molecule)[i] and the changes in enthalpy of fusion with temperature (here the fitted ΔH_{fus} is 6016 J mol^{-1}). The eutectic for glucose solutions is at 2.5 m and -5 °C. At higher concentrations solid glucose α-monohydrate precipitates on cooling rather than ice forming.



The equation for the straight line relationship is

$$(1/T - 1/T_m) = 0.001382 \times -Ln(1-x_S)$$

($R^2 = 0.99997$) giving a value for ΔH_{fus} of 6016 J mol^{-1}.

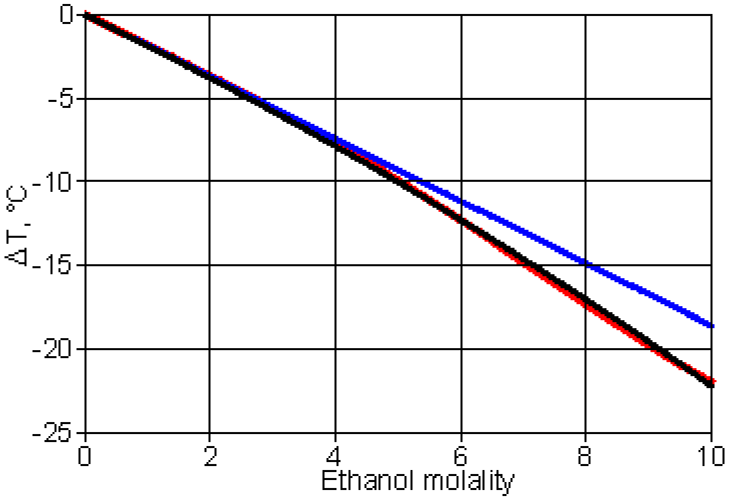


Urea

The lower blue line follows the 'ideal' colligative equation, $\Delta T = m_S K_f$. for urea (H_2NCONH_2). The red line follows the experimental freezing point curve [70], deviating from the relationship obtained directly from the unapproximated colligative equations above (black line) at higher molality where no bound water of hydration is found[i] but allowance has been made for the dimerization of the urea (that is, urea + urea $\rightleftharpoons$ (urea)$_2$) with equilibrium constant 0.0007. Further deviation occurs at higher molality due to the multiple association of urea molecules [364]. The fitted enthalpy of fusion (ΔH_{fus}) is 6022 J mol^{-1} here.

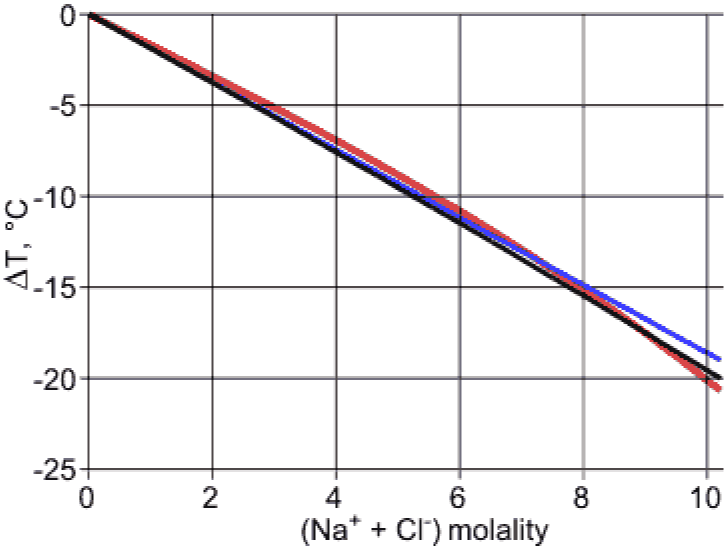
Note that mid-infrared pump-probe spectroscopy studies indicate that one molecule of water may be more tightly bound to each molecule of urea [1130]. This may occur together with the above equilibria.

Ethanol



The upper blue line follows the 'ideal' colligative equation, $\Delta T = m_S K_f$. for ethanol (CH_3CH_2OH). The red line follows the experimental freezing point curve [70], hardly deviating from the relationship obtained directly from the unapproximated colligative equations above (black line) where allowance has been made for bound water of hydration (1.8 water molecules bound to each ethanol molecule) and the changes in enthalpy of fusion with temperature (here the fitted ΔH_{fus} is 6092 J mol^{-1}). There is considerable deviation at higher molalities, however, as ethanol forms hydrogen bonded chains and solidclathrate I and II hydrates (at around -63 °C) rather than ice [1102], and with solutions eventually behaving as a solution of water in ethanol rather than ethanol in water.

There are recent interesting papers on the increased hydrogen bonding in alcoholic drinks [1119] and the formation of azeotropes [1746] and 'peculiar points' (possible formation of molecular complexes) [2024].

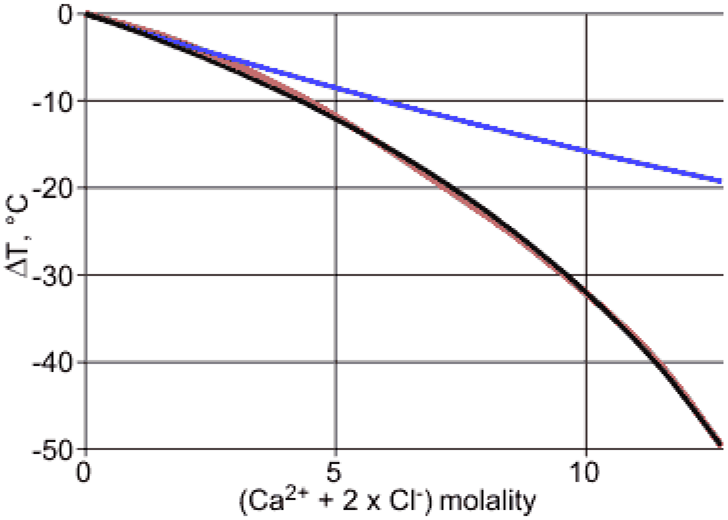


NaCl

The molality is that of the Na^+ plus Cl^- ions. The blue line (upper at higher molality) follows the 'ideal' colligative equation, $\Delta T = m_S K_f$. The red line (upper at lower molality) follows the experimental freezing point curve [70], deviating slightly from the relationship obtained directly from the unapproximated colligative equations above where allowance has been made for bound water of hydration (2.3 water molecules bound to each NaCl unit)[i] and the changes in enthalpy of fusion with temperature (here the fitted ΔH_{fus} is 6085 J mol^{-1}). The actual freezing point depression line (red) shows some deviations away from the theoretical line (black), particularly at lower molality, due to ion pair (probably separated by bound water) formation.
A minimum in the degree of dissociation of NaCl has been found to be about 0.78 at an ionic molality of about 3 [1108]. Such minima occur with most strong electrolytes and may be explained as the increased ionic concentration interferes with the individual water separated ion pair formation.

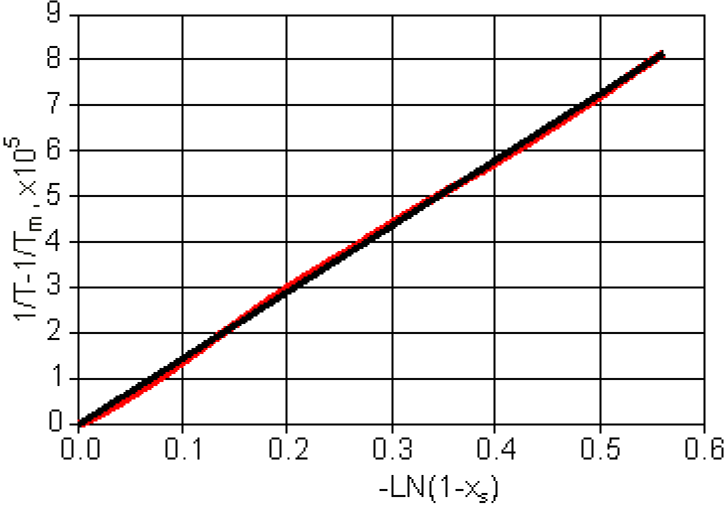
The eutectic point for NaCl aqueous solution occurs at -21.1 °C at ionic molality of 10.34 m (5.17 m NaCl, 23.2 % w/w). At higher concentrations up to 6.0 m NaCl (26.1 % w/w at -0.01 °C) solid $NaCl.2H_2O$ precipitates on cooling rather than ice forming and at higher temperatures there is the solubility line for unhydrated NaCl showing a slight increase in solubility with increasing temperature.

$CaCl_2$



The molality is that of the Ca^{2+} plus Cl^- ions. The upper blue line follows the 'ideal' colligative equation, $\Delta T = m_S K_f$. The red line follows the experimental freezing point curve [70], deviating slightly from the relationship obtained directly from the unapproximated colligative equations above where allowance has been made for bound water of hydration (9.1 water molecules bound to each $CaCl_2$ unit)[i] and the changes in enthalpy of fusion with temperature (here the fitted ΔH_{fus} is 5736 J mol^{-1}). The actual freezing point depression line (red) shows some deviations away from the theoretical line (black), particularly at lower molality, due to ion pair (probably separated by bound water) formation, as with NaCl above.

The eutectic point for $CaCl_2$ aqueous solution occurs at -50 °C at ionic molality of 12.7 (4.24 m $CaCl_2$, 32 % w/w) (variously reported at -54.23 °C at 3.83 m $CaCl_2$ 29.85% w/w [1121]). At higher concentrations up to 8.8 m $CaCl_2$(49 % w/w, at +28.9 °C) solid $CaCl_2.6H_2O$ precipitates on cooling rather than ice forming. At increasingly higher solution concentrations there are solubility curves for $CaCl_2.4H_2O$, $CaCl_2.2H_2O$ and $CaCl_2.H_2O$.

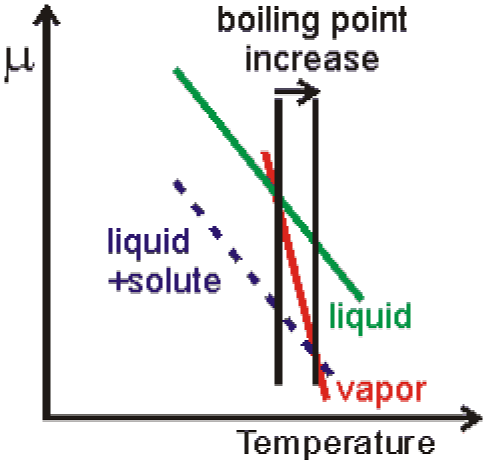


The equation for the straight line relationship is

$$(1/T - 1/T_m) = 0.001450 \times -Ln(1-x_S)$$

(R^2 = 0.9992) giving a value for ΔH_{fus} of 5736 J mol^{-1}. The deviations at low molality due to solvent separated ion pairs mentioned above can be seen at low -Ln(1-x) values, where the experimental data line (red) dips below the theoretical straight line (black). Work similar to this has been published [1064].

Boiling point elevation

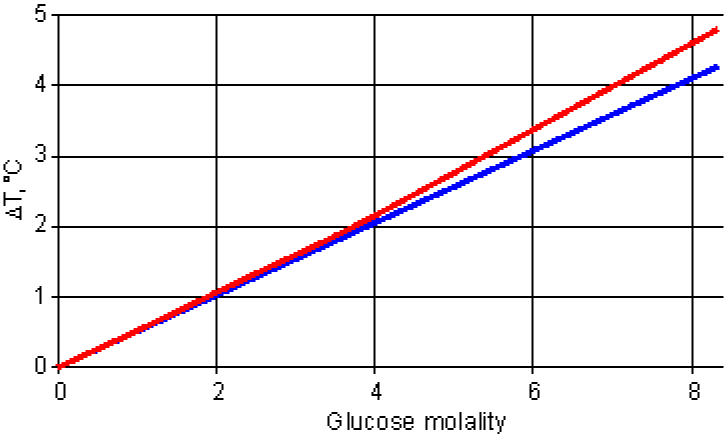


The equations for boiling point elevation can be derived in a way similar to those of freezing point depression above. The theoretical expression for the ebullioscopic constant (K_b) is

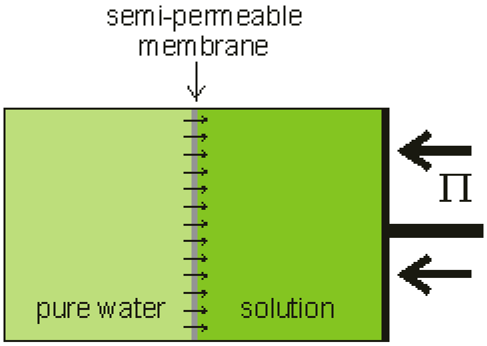
$$K_b = \frac{M_w R T_b^2}{\Delta H_{vap}} \qquad (22)$$

where M_w is the molar mass of water (kg mol^{-1}), R is the gas constant, T_b is theboiling point of water and ΔH_{vap} is the enthalpy of vaporization of water.[f] This results in K_b = 0.5129 K kg mol^{-1}. As molecules tend to bind less water at higher temperatures, boiling point elevation is less affected than freezing point depression by any such reduction in 'free' water [1064].

Glucose



The lower blue line follows the 'ideal' colligative equation, ΔT = $m_S K_b$. for glucose ($C_6H_{12}O_6$). The red line follows the experimental boiling point curve. The colligative equations may be best fitted making allowance for the smaller bound water of hydration (1.1 water molecules bound to each glucose molecule) than is found in the freezing point depression above. and the changes in enthalpy of vaporization with temperature (here the fitted ΔH_{vap} is 40.4 kJ mol^{-1}).



Osmotic pressure

When pure liquid water is separated by a membrane, permeable to water but not solute, from a solution containing a solute, water will pass from the pure water side until sufficient extra pressure (п) is caused or applied to the solution side [1872]. Note that osmotic pressure is an equilibrium thermodynamic effect and gives no information concerning the rate of passage of the water, which depends primarily on the properties of the membrane [1873].[m]

At equilibrium the chemical potential of the water must be the same on both sides of the semipermeable membrane.

(23)

$$\mu_{P}^{liquid} = \mu_{P+\Pi}^{solution}$$

The effect of the solute may be included as above.

(24)

$$\mu_{P+\Pi}^{solution} = \mu_{P+\Pi}^{liquid} + RTLn(x_w)$$

The change in chemical potential with pressure may be included.

(25)

$$\mu_{P+\Pi}^{liquid} = \mu_{P}^{liquid} + \int_{P}^{P+\Pi} V_m dP$$

Combining equations 23, 24 and 25 and then assuming the molar volume of water (V_m, m^3 mol^{-1}) varies little within the likely pressure range.

(26)

$$-RTLn(x_w) = \int_{P}^{P+\Pi} V_m dP = \Pi V_m$$

[250] (27)

Hence,

$$\Pi = -k_p\ T\ Ln(1-x_s)$$

where k_p is the piezoscopic constant (= R/V_m).

When x_s is low the following approximation is valid

(28)

$$\mathrm{Ln}(x_w) = \mathrm{Ln}(1 - x_s) = - x_s$$

(29)

$$\Pi V_m = x_s RT$$

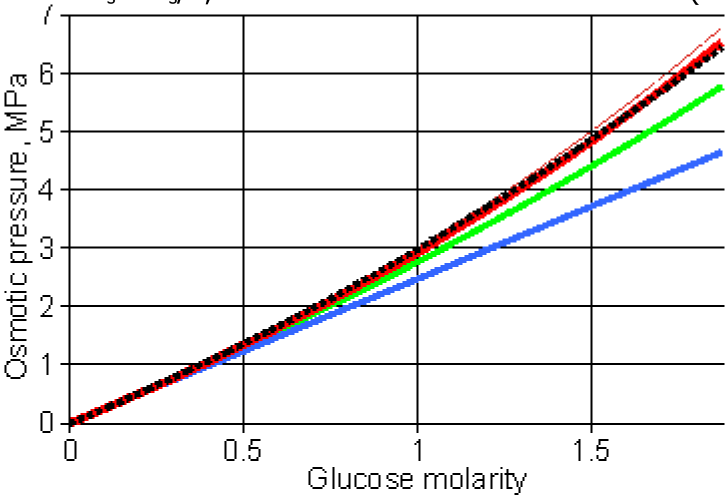
(30)
At low x_s,

$$x_s = n_s/n_w$$

where n_s is the number of moles of solute and n_w is the number of moles of water. As the molar volume approximately equals V/n_w,
the Van't Hoff equation (31)

$$\Pi = M_s RT$$

where $M_s = n_s/V$, the molar concentration of the solute (normally, moles m^{-3}, if in SI units).



Opposite shows the osmotic behavior of glucose solutions. The lower blue line follows the 'ideal' colligative equation, $\Pi = M_s RT$. The thick red line follows the osmotic pressure as calculated from the experimental freezing point data [70]. The middle green line shows the osmotic pressure calculated from the 'ideal' colligative equation, $\Pi = M_s RT$ but correcting the concentration errors made by assuming $\mathrm{Ln}(1 - x_s) = - x_s$ and $x_s = n_s/n_w$ (but not the error in the molar volume of water). The dotted black line is a best fit to the equation,

$$\Pi = RT(M_s + AM_s^2) \qquad (32)$$

a commonly used form of approximation [1104], where $A = 0.2\ M^{-1}$ in this case; most of the 'A' parameter being due to the approximations used and not due to non-ideality. Note that at low osmotic pressures, up to about five atmospheres pressure (0.5 MPa) the ideal colligative equation holds well.

Although osmosis and simple diffusion are distinct unrelated phenomena [2100], osmotic pressure has been considered, by some, as due to the 'diffusion' of water from a region of high 'free' water concentration to a region of lower 'free' water concentration (e.g. one with higher salt content). A diffusion-based theory for osmotic pressure has been described [1315], which involves a number of assumptions and gives the equation $\Pi = M_s RT \times \left(\frac{x_w V^2}{1 + x_s V}\right)$ where x_w and x_S are the mole fractions of water and solute and V is the volume (in liters) of solution containing one liter of water. This equation contains no empirical parameters (such as A above) and gives a good fit; it is shown as the top thin dashed red line for glucose above. It is noteworthy that this equation includes the experimentaly determined volume (V) term that has some dependency on the size of the solute.

Proteins may remove much of the 'free' water[d] from inside cells causing much intracellular water to be osmotically unresponsive. As an example, one molecule of bovine serum albumin may bind 5000-43000 molecules of water [1103].

The osmotic behavior of polyelectrolytes depends on the concentration relative to that concentration at which the molecules overlap in solution [1493].

Interfaces can also generate osmotic pressure without the reqirement for dissolved solutes [1772, 2057].

Footnotes

[a] The chemical potential (μ) is a term first used by Willard Gibbs and is the same as the molar Gibbs energy of formation, ΔG_f, for a pure substance. For materials in a mixture $\mu_i = \left(\frac{\partial G}{\partial n_A}\right)_{P,T,n_B}$ where the substance changing is A with number of molecules n_A and n_B represents the number of molecules of all other materials present.

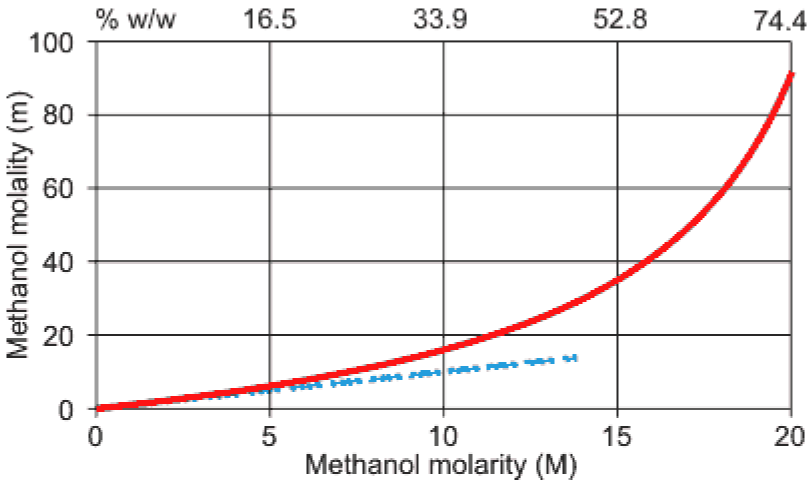
[b] The mole fraction of water (x_w) is that fraction of the molecules (and/or ions) present that are water molecules, (that is, x_w = moles water/(moles water + moles solute). When considering colligative properties, these water molecules must be 'free',[d] (that is, x_w = moles 'free' water/(moles 'free' water + moles solute). The mole fraction of a solute is the fraction of the molecules (and/or ions) present that is that solute (that is, x_S= moles solute/(moles water + moles solute). At low solute concentrations, x_S may be approximated by moles solute/moles water = molality x molar mass of water = $m_S M$ (where m_S is the molality[c] and M is the molar mass of water = 0.018015268 kg mol^{-1}). Note that 'moles' here refers to independent species such as molecules or ions. Care should be taken to correct concentration terms when the solution consists of a mixture of solutes where x_w = moles water/(moles water + moles solutes), or more exactly x_w = moles 'free' water/(moles 'free' water + moles solutes).[d]

[c] Molality (m) is defined as the number of gram-moles per kilogram water. Molarity (M) is defined as the number of gram-moles per liter of solution. Care should be taken to differentiate these terms. Conversion of molarity to molality and vice versa is often incorrectly described. The formulae are

$$M = \frac{1000m\rho}{1000 + m \times MWt}$$

and

$$m = \frac{1000M}{1000\rho - M \times MWt}$$

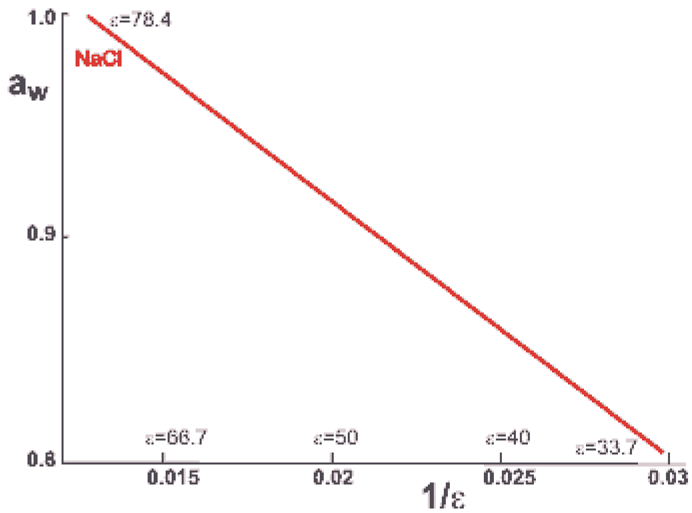


where ρ is the experimentally determined density in g mL^{-1} and MWt is the relative molecular mass of the solute. Allowance must be made for other solutes (and co-ions) present.

Opposite shown red (for methanol) are the very different values equivalent concentrations may have when expressed as molality or molarity. The lower blue dashed line shows the relationship as the concentrations tend to zero. Molality is always numerically greater than the molarity. Note that % w/w varies non-linearly with both molarity and molality.

Molarity is often used as it is easy to measure out volumes but such solutions are often less accurately prepared and dispensed due to the difficulties in attaining accurate volumes and the changes in volume that occur with temperature changes. Solutions with known molalities, prepared by weighing, are generally more precisely and accurately known. Often, molarity is used for chemical reactions where the number of moles of reagent present is simply calculated (moles = molarity x volume in liters), whereas molality should be used when physical or thermodynamic determinations are made, such as the above colligative properties. Other concentration units, such as % w/w (g per 100 g) and % w/v (g per 100 mL) should be avoided wherever possible. By-volume dilutions of by-weight concentrations (or vice versa) should never be made as the final concentrations may only be determined using a knowledge of the densities of the solutions concerned. Note that theSI unit of concentration is mol m^{-3} with molarity (M) and molal (m, to be replaced by mol kg^{-1}) being recommended for discontinuance by SI; recommendations that have not been generally accepted.

[d] Wherever water is present in solution it may be considered as being either 'bound' or 'free', although there will be a transitional water between these states. When considering the colligative properties, 'water' is considered bound to any solute when it has a very low entropy compared with pure liquid water. This occurs, for example, when salts form strongly bound hydration shells [1494], with the hydration shells of some ions (for example, Mg^{2+}) giving clear Raman spectra in solution [1503]. Such water should be considered part of the solute and not part of the dissolving 'free' water. The molality of a solution as prepared is given above,[c] but the effective molality of a hydrated solute should not include the bound water within the kilogram of dissolving water [250]. In contrast to the molality, bound water makes no difference to the numerical value of the molarity.



As the 'bound' water contributes little to the dielectric relaxation processes at low frequencies, the dielectric drops in solutions and may be used to estimate the 'bound' water. The reciprocal dielectric constant (1/ε) increases linearly as the water activity drops over wide ranges of salt solutions [1220]. However, as the proportionality is dependent on the salt composition, the hydrated salt must contribute significantly to the dielectric effect.

[e] The term Ln(1 - x) may be expanded in terms of a Maclaurin series

$$\mathrm{Ln}(1 - x) = -(x + x^2/2 + x^3/3 + x^4/4 + x^5/5 + x^6/6 + x^7/7 + ...)$$

This series quickly converges for values of x close to zero.

[f] The (latent) heat of fusion (ΔH_{fus}) is the amount of thermal energy required to convert the solid form into the liquid form, at constant temperature and pressure. The (latent) heat of vaporization (ΔH_{vap}) is the amount of thermal energy required to convert the liquid form into the gaseous form, at constant temperature and pressure.

[g] Experimentally, the (latent) heat of fusion of the solution (ΔH) appears to vary linearly with the mole fraction of the solute (x_s) (that is, $\Delta H = (1 - kx_s).\Delta H_{fus}$ where k is a constant for that particular solute and ΔH_{fus} is the (latent) heat of fusion of pure water, see [1123]) and thus with melting point temperature. Although presented differently, this relationship gives identical equations to the above analysis where k equals the number of moles of hydrating water per mole solute molecules or ions. The similarity is unsurprising given that the bound water does not freeze and therefore does not contribute to the total heat of fusion.

[h] Raoult recognized that the freezing point depression was determined by the mole fraction in 1882 [1286].

[i] The term 'ideal' indicates adherence to a particular equation; it does not indicate any more basic truth.

[j]. Reference [250] gives hydration values calculated with unchanging enthalpy of fusion of ice: glucose 2.8 H_2O/mol bound using the data up to 1.8 molal; urea -0.2 H_2O/mol bound using the data up to 7.84 molal; NaCl 4.0 H_2O/mol bound using the data up to the eutectic concentration (reported

10.4 molal ions concentration); $CaCl_2$ 11.2 H_2O/mol bound using the data up to 8.54 molal ions concentration.

[k] Some solutes, such as hydrophilic polymers like polyvinyl alcohol, increase the chance of supercooling [1498].

[l] In contrast to liquid water, ice (ice 1h) is a very poor solvent.

[m] There is often confusion in the literature between the thermodynamic rationale and the kinetic process for osmosis. The thermodynamics of the process (the colligative property) simply describes the tendency for the process to occur but does not describe the mechanism or the rate of the flow of water in any osmotic process, apart from its direction. Clearly, the (net) rate of water flow depends on the relative rates of flow in the opposite directions. This, in turn, will depend on the ease with which the water molecules may leave the compartments on each side of the membrane (dependent on the mole fraction of 'free' water; the water activity) and the ease with which they can pass through the membrane. Water molecules leaving the lower-water-activity compartment will require more energy as they cause the formation of a localised even lower activity water in their wake. Therefore only higher energy water molecules can leave this compartment; necessarily a smaller amount than travel in the opposite direction.

[n] Osmotic pressure can also apply to gasses [2100].

Source: http://www1.lsbu.ac.uk/water/collig.html