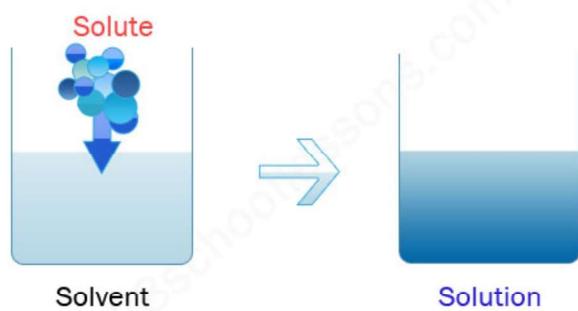


The thermodynamic description of mixtures

- We will investigate the thermodynamic properties of non-electrolyte homogeneous mixtures.
- In homogeneous mixtures, or solutions, all components that make up the mixture are uniformly distributed throughout the mixture.
- The component in smaller abundance is called the **solute** and that in larger abundance is the **solvent**.



Concentration

- The **molar concentration**, $[J]$ or c_J , of a solute J in a solution (more formally, the “amount of substance concentration”) is the chemical amount of J divided by the volume of the solution:

$$[J] = \frac{n_J}{V}$$

Amount of
J (mol)
↓
Volume of
solution (L)

- Molar concentration is typically reported in moles per liter (mol/L or molar).

Concentration

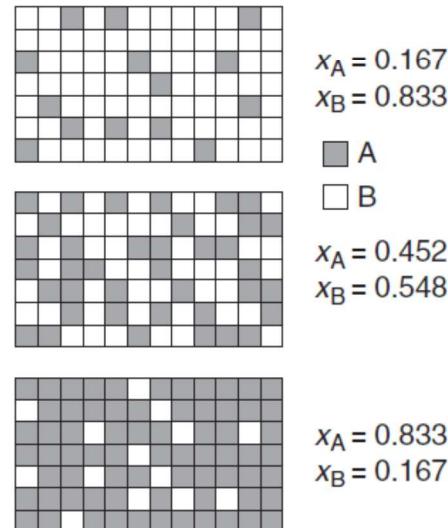
- A useful measure of concentration of a gas J in a mixture is its **mole fraction**, the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture.
- In a mixture that consists of n_A A molecules, n_B B molecules, and so on (where the n_J are amounts in moles), the mole fraction of J (where J = A, B, . . .) is

$$x_J = \frac{n_J}{n}$$

Amount of J (mol)
Total amount of molecules (mol)

- where $n = nA + nB + \dots$
- For a **binary mixture**, one that consists of two species, this general expression becomes

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B} \quad x_A + x_B = 1$$



- **Self-exercise:** Calculate the mole fractions of N_2 , O_2 , and Ar in dry air at sea level, given that 100.0 g of air consists of 75.5 g of N_2 , 23.2 g of O_2 , and 1.3 g of Ar.

Dalton's Law

- To be able to assess the contribution that each component of a gaseous mixture makes to the total pressure, John Dalton carried out a series of experiments that led him to formulate what has become known as **Dalton's law**:
 - The pressure exerted by a mixture of perfect gases is the sum of the pressures that each gas would exert if it were alone in the container at the same temperature:
$$p = p_A + p_B + \dots$$
- For any type of gas (perfect or not) in a mixture, the **partial pressure**, p_J , of the gas J is defined as
$$p_J = x_J p$$
 - where x_J is the mole fraction of the gas J in the mixture.
 - In this expression, p is the pressure that the gas J would exert if it were alone in the container at the same temperature.
 - Dalton's law is strictly valid only for mixtures of perfect gases, but it can be treated as valid under most conditions we encounter.

- A **partial molar property** is the contribution (per mole) that a substance makes to an overall property of a mixture.
- The most important partial molar property for our purposes is the **partial molar Gibbs energy**, G_J , of a substance J, which is the contribution of J (per mole of J) to the total Gibbs energy of a mixture.
- We can calculate the total Gibbs energy of the mixture by using the partial molar Gibbs energies of two substances A and B in a mixture by:

$$G = n_A G_A + n_B G_B$$

- To gain insight into the significance of the partial molar Gibbs energy, consider a mixture of ethanol and water.
- Ethanol has a particular partial molar Gibbs energy when it is pure (and every molecule is surrounded by other ethanol molecules), and it has a different partial molar Gibbs energy when it is in an aqueous solution of a certain composition (because then each ethanol molecule is surrounded by a mixture of ethanol and water molecules).

- The partial molar Gibbs energy is so important in chemistry that it is given a special name and symbol. From now on, we shall call it the **chemical potential** and denote it μ (mu).

$$G = n_A \mu_A + n_B \mu_B$$

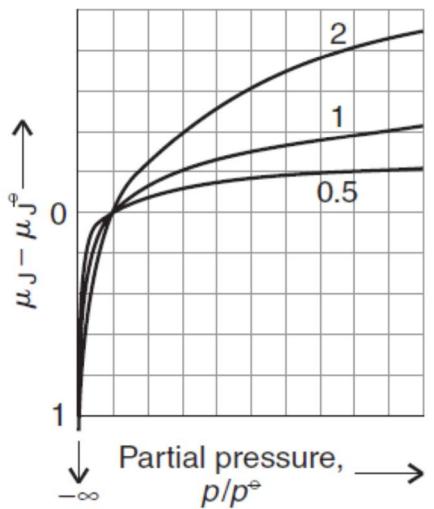
- where μ_A is the chemical potential of A in the mixture and μ_B is the chemical potential of B.
- μ_J is a measure of the ability of J to bring about physical and chemical change.
- A substance with a high chemical potential has a high ability to drive a reaction or some other physical process forward.

Chemical Potential of Ideal Gas Mixtures

- To make progress, we need an explicit formula for the variation of the chemical potential of a substance with the composition of the mixture.

$$\mu_J = \mu_J^\ominus + RT \ln p_J$$

- Figure illustrates the pressure dependence of the chemical potential of a perfect gas predicted by this equation.
- Note that the chemical potential becomes negatively infinite as the pressure tends to zero, rises to its standard value at 1 bar (because $\ln 1 = 0$), and then increases slowly (logarithmically, as $\ln p$) as the pressure is increased further.



The variation with partial pressure of the chemical potential of a perfect gas at three different temperatures (in the ratios 0.5:1:2).

- *The higher the partial pressure of a gas, the higher its chemical potential.*
- Chemical potential can be thought of as an indication of the potential of a substance to be active chemically: the higher the partial pressure, the more active chemically the species.
- In this instance the chemical potential represents the tendency of the substance to react when it is in its standard state (the significance of the term) plus an additional tendency that reflects whether it is at a different pressure.
- A higher partial pressure gives a substance more chemical “punch,” just like winding a spring gives a spring more physical punch (that is, enables it to do more work).

- Suppose that the partial pressure of a perfect gas falls from 1.00 bar to 0.50 bar as it is consumed in a reaction at 25°C. What is the change in chemical potential of the substance?

$$\begin{aligned}\mu_j &= \mu_j^\theta + RT \ln p_j \\ \mu_{j1} &= \mu_j^\theta + RT \ln p_{j1} = \mu_j^\theta + RT \ln 1 \\ \mu_{j2} &= \mu_j^\theta + RT \ln p_{j2} = \mu_j^\theta + RT \ln 0.5\end{aligned}$$

$$\begin{aligned}\Delta\mu_j &= \mu_{j1} - \mu_{j2} = RT \ln 1 - RT \ln 0.5 \\ &= 0 - [8.314 \text{ J / mol K} \times 298.15 \text{ K} \times (-0.69)] \\ \Delta\mu_j &= -1.7 \text{ kJ / mol}\end{aligned}$$

- The molar Gibbs energy of a pure substance is the same in all the phases at equilibrium.
- We can use the same argument to show that *a system is at equilibrium when the chemical potential of each substance has the same value in every phase in which it occurs.*
- We can think of the chemical potential as the pushing power of each substance, and equilibrium is reached only when each substance pushes with the same strength in any phase it occupies.

Chemical Potential of Ideal solutions

- We can anticipate that the chemical potential of a species ought to increase with concentration, because the higher its concentration, the greater its chemical “punch.”
- In the following, we use J to denote a substance in general, A to denote a solvent, and B a solute.
- **We transform equations that work for gases into equations that work for liquids.**
- The key to setting up an expression for the chemical potential of a solute is the work done by the French chemist Francois Raoult (1830–1901), who spent most of his life measuring the vapor pressures of solutions. He measured the **partial vapor pressure**, p_J , of each component in the mixture, the partial pressure of the vapor of each component in dynamic equilibrium with the liquid mixture, and established what is now called **Raoult’s law**:
- The partial vapor pressure of a substance in a liquid mixture is proportional to its mole fraction in the mixture and its vapor pressure when pure:

$$p_J = x_J p_J^*$$

- where p_J^* is the vapor pressure of the pure substance.

Ideal Solutions

- For example, when the mole fraction of water in an aqueous solution is 0.90, then, provided Raoult's law is obeyed, the partial vapor pressure of the water in the solution is 90% that of pure water.
- This conclusion is approximately true whatever the identity of the solute and the solvent.
- A hypothetical solution of a solute B in a solvent A that obeys Raoult's law throughout the composition range from pure A to pure B is called an **ideal solution**.

- The molecular origin of Raoult's law is the effect of the solute on the entropy of the solution.
- In the pure solvent, the molecules have some entropy due to their random motion; the vapor pressure then represents the tendency of the system and its surroundings to reach a higher entropy.
- When a solute is present, the molecules in the solution are more dispersed than in the pure solvent, so we cannot be sure that a molecule chosen at random will be a solvent molecule.
- Because the entropy of the solution is higher than that of the pure solvent, the solution has a lower tendency to acquire an even higher entropy by the solvent vaporizing.
- In other words, the vapor pressure of the solvent in the solution is lower than that of the pure solvent.

- No mixture is perfectly ideal, and all real mixtures show deviations from Raoult's law.
- However, the deviations are small for the component of the mixture that is in large excess (the solvent) and become smaller as the concentration of solute decreases.
- We can usually be confident that Raoult's law is reliable for the solvent when the solution is very dilute.
- More formally, Raoult's law is a *limiting law* (like the perfect gas law) and is strictly valid only at the limit of zero concentration of solute.

Chemical Potential of the solvent

- The theoretical importance of Raoult's law is that, because it relates vapor pressure to composition and we know how to relate pressure to chemical potential, we can use the law to relate chemical potential to the composition of a solution.

$$\mu_A = \mu_A^* + RT \ln x_A$$

- where A* is the chemical potential of pure A.

If the pressure is 1 bar, μ_A^* can be identified with the standard chemical potential of A, μ_A^θ

Chemical potential of a solute in a solution

- The chemical potential of the solute has its pure value when it is present alone ($x_B = 1$, $\ln 1 = 0$) and a smaller value when dissolved (when $x_B < 1$, $\ln x_B < 0$).

$$\mu_B = \mu_B^* + RT \ln x_B$$

- These expressions are valid, in very dilute solutions.

Gibbs Energy of mixing

- Is mixing to form an ideal solution spontaneous? To answer this question, we need to discover whether ΔG is negative for mixing.

$$\Delta G = nRT\{x_A \ln x_A + x_B \ln x_B\}$$

- where $n = n_A + n_B$ and the x_j the mole fractions in the mixture.

$$\Delta S = -nR\{x_A \ln x_A + x_B \ln x_B\}$$

- Calculate the (molar) Gibbs energy of mixing when the two major components of air (nitrogen and oxygen) are mixed to form air. The mole fractions of N₂ and O₂ are 0.78 and 0.22, respectively. Is the mixing spontaneous?

$$\Delta G = nRT \{x_A \ln x_A + x_B \ln x_B\}$$

$$\Delta G = 1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} [0.22 \ln 0.22 + 0.78 \ln 0.78]$$

$$\Delta G = -1.30 \text{ kJ}$$

- Self exercise:** Calculate the molar entropy.

The crucial feature is that because x_A and x_B are both less than 1, the two logarithms are negative ($\ln < 0$ if $x < 1$), so $\Delta G < 0$ at all compositions. Therefore, *mixing is spontaneous for ideal solutions in all proportions.*

Ideal Dilute Solutions

- Raoult's law provides a good description of the vapor pressure of the *solvent* in a very dilute solution, when the solvent A is almost pure.
- However, we cannot in general expect it to be a good description of the vapor pressure of the solute B because a solute in dilute solution is very far from being pure.
- In a dilute solution, each solute molecule is surrounded by nearly pure solvent, so its environment is quite unlike that in the pure solute, it is very unlikely that the vapor pressure of the solute will be related in a simple manner to the vapor pressure of the pure solute.
- However, it is found experimentally that in dilute solutions, the vapor pressure of the solute is in fact proportional to its mole fraction, just as for the solvent.
- Unlike the solvent, though, the constant of proportionality is not in general the vapor pressure of the pure solute.
- This linear but different dependence was discovered by the English chemist William Henry (1774–1836) and is summarized as **Henry's law**:
- The vapor pressure of a volatile solute B is proportional to its mole fraction in a solution:

$$p_B = x_B K_B$$

- where K_B is the Henry's law constant.

- The molar concentration depends on the partial pressure:

$$[J] = K_H p_J$$

- Henry's constant, K_H , is commonly reported in moles per cubic meter per kilopascal ($\text{mol m}^{-3} \text{ kPa}^{-1}$).
- This form of the law and these units make it very easy to calculate the molar concentration of the dissolved gas, simply by multiplying the partial pressure of the gas (in kilopascals) by the appropriate constant.

Table 3.2 Henry's law constants for gases dissolved in water at 25°C

	$K_H / (\text{mol m}^{-3} \text{ kPa}^{-1})$
Carbon dioxide, CO ₂	3.39×10^{-1}
Hydrogen, H ₂	7.78×10^{-3}
Methane, CH ₄	1.48×10^{-2}
Nitrogen, N ₂	6.48×10^{-3}
Oxygen, O ₂	1.30×10^{-2}

- The concentration of O_2 in water required to support aerobic aquatic life is about 4.0 mg L^{-1} . What is the minimum partial pressure of oxygen in the atmosphere that can achieve this concentration?
 - Strategy:** Determine the partial pressure of oxygen that, according to Henry's law corresponds to the concentration specified.

$$[J] = K_H p_J$$

$$p_{O_2} = \frac{[O_2]}{K_H}$$

$$\begin{aligned}[O_2] &= \frac{4.0 \times 10^{-3} \text{ g L}^{-1}}{32 \text{ g mol}^{-1}} = \frac{4.0 \times 10^{-3}}{32} \frac{\text{mol}}{\text{L}} = \frac{4.0 \times 10^{-3}}{32 \times 10^{-3}} \frac{\text{mol}}{\text{m}^3} \\ &= \frac{4.0}{32} \text{ mol m}^{-3}\end{aligned}$$

$$p_{O_2} = \frac{(4.0/32) \text{ mol m}^{-3}}{1.30 \times 10^{-2} \text{ mol m}^{-3} \text{ kPa}^{-1}} = 9.6 \text{ kPa}$$

The partial pressure of oxygen in air at sea level is 21 kPa, which is greater than 9.6 kPa, so the required concentration can be maintained under normal conditions.

- What partial pressure of methane is needed to dissolve 21 mg of methane in 100 g of benzene at 25°C ($K_B = 5.69 \times 10^4$ kPa)?

$$n_{\text{methane}} = 21 \times 10^{-3} \text{ g} / 16.04 \text{ g mol}^{-1} = 0.0013 \text{ mol}$$

$$n_{\text{benzene}} = 100 \text{ g} / 78.11 \text{ g mol}^{-1} = 1.2802 \text{ mol}$$

$$n = n_{\text{methane}} + n_{\text{benzene}} = 0.0013 + 1.2802 = 1.2815 \text{ mol}$$

$$p_B = x_B K_B$$

$$P_{\text{methane}} = (0.0013 / 1.2815) \times 5.69 \times 10^4 \text{ kPa} = 57,7 \text{ kPa}$$

Gas solubility and breathing

- We inhale about 500 cm³ of air with each breath we take.
- The influx of air is a result of changes in volume of the lungs as the diaphragm is depressed and the chest expands, which results in a decrease in pressure of about 100 Pa relative to atmospheric pressure.
- Expiration occurs as the diaphragm rises and the chest contracts and gives rise to a differential pressure of about 100 Pa above atmospheric pressure.
- The total volume of air in the lungs is about 6 L, and the additional volume of air that can be exhaled forcefully after normal expiration is about 1.5 L. Some air remains in the lungs at all times to prevent the collapse of the alveoli.

- A knowledge of Henry's law constants for gases in fats and lipids is important for the discussion of respiration.
- The effect of gas exchange between blood and air inside the alveoli of the lungs means that the composition of the air in the lungs changes throughout the breathing cycle.
- Alveolar gas is in fact a mixture of newly inhaled air and air about to be exhaled.
- The concentration of oxygen present in arterial blood is equivalent to a partial pressure of about 40 Torr (5.3 kPa), whereas the partial pressure of freshly inhaled air is about 104 Torr (13.9 kPa).
- Arterial blood remains in the capillary passing through the wall of an alveolus for about 0.75 s, but such is the steepness of the pressure gradient that it becomes fully saturated with oxygen in about 0.25 s.

- If the lungs collect fluids (as in pneumonia), then the respiratory membrane thickens, diffusion is greatly slowed, and body tissues begin to suffer from oxygen starvation.
- A hyperbaric oxygen chamber, in which oxygen is at an elevated partial pressure, is used to treat certain types of disease.
- Carbon dioxide moves in the opposite direction across the respiratory tissue, but the partial pressure gradient is much less, corresponding to about 5 Torr (0.7 kPa) in blood and 40 Torr (5.3 kPa) in air at equilibrium.
- However, because carbon dioxide is much more soluble in the alveolar fluid than oxygen is, equal amounts of oxygen and carbon dioxide are exchanged in each breath.

Real Solutions

- No actual solutions are ideal, and many solutions deviate from ideal-dilute behavior as soon as the concentration of solute rises above a small value.
- In thermodynamics we try to preserve the form of equations developed for ideal systems so that it becomes easy to step between the two types of system.
- This is the thought behind the introduction of the **activity**, a_j , of a substance, which is a kind of effective concentration.
- For ideal solutions, $a_j = x_j$, and the activity of each component is equal to its mole fraction.
- For ideal-dilute solutions, $a_B = [B]$, and the activity of the solute is equal to the numerical value of its molar concentration.

- For *non-ideal* solutions we write
 - *For the solvent:* $a_A = \gamma_A x_A$
 - *For the solute:* $a_B = \gamma_B [B]$
- where γ (gamma) in each case is the **activity coefficient**. Activity coefficients depend on the composition of the solution, and we should note the following:
 - Because the solvent behaves more in accord with Raoult's law as it becomes pure, $\gamma_A \rightarrow 1$ as $x_A \rightarrow 1$.
 - Because the solute behaves more in accord with Henry's law as the solution becomes very dilute, $\gamma_B \rightarrow 1$ as $[B] \rightarrow 0$.

- The expression becomes:

$$\mu_J = \mu_J^\ominus + RT \ln a_J$$

- It is true at *all* concentrations and for both the solvent and the solute.

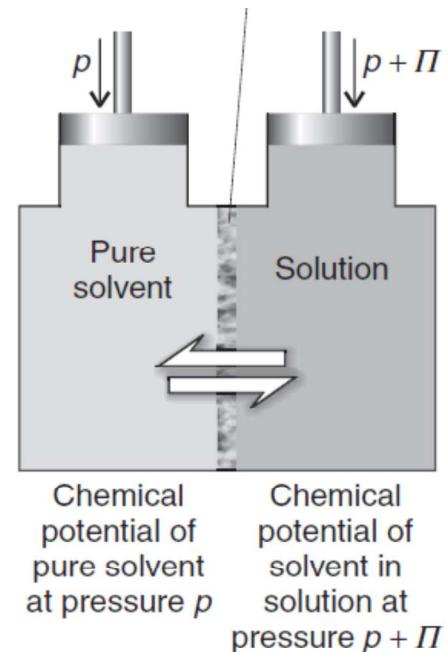
Osmotic Pressure

- An ideal solute has no effect on the enthalpy of a solution in the sense that **the enthalpy of mixing is zero**.
- However, it does affect the entropy, $\Delta S > 0$ when two components mix to give an ideal solution.
- We can therefore expect a solute to modify the physical properties of the solution.
- Apart from lowering the vapor pressure of the solvent, which we have already considered, a nonvolatile solute has three main effects:
 - (i) It raises the boiling point of a solution, (ii) it lowers the freezing point, and (iii) it gives rise to an osmotic pressure.
- The osmotic pressure of a solution is proportional to the concentration of solute.

Osmotic Pressure

- The phenomenon of **osmosis** is the passage of a pure solvent into a solution separated from it by a semipermeable membrane.
- A **semipermeable membrane** is a membrane that is permeable to the solvent but not to the solute.
- The membrane might have microscopic holes that are large enough to allow water molecules to pass through, but not ions or solutes.
- The **osmotic pressure**, Π (uppercase pi), is the pressure that must be applied to the solution to stop the inward flow of solvent.

$$\Pi V \approx n_B RT$$

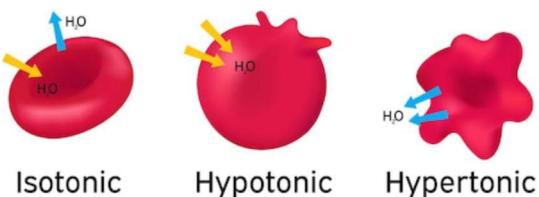


- Since $nB/V = [B]$,

$$\Pi \approx [B]RT$$

Osmosis in biology

- Osmosis helps biological cells maintain their structure. Cell membranes are semipermeable and allow water, small molecules, and hydrated ions to pass, while blocking the passage of biopolymers synthesized inside the cell.
- The difference in concentrations of solutes inside and outside the cell gives rise to an osmotic pressure, and water passes into the more concentrated solution in the interior of the cell, carrying small nutrient molecules.
- The influx of water also keeps the cell swollen, whereas dehydration causes the cell to shrink.
- These effects are important in everyday medical practice. To maintain the integrity of blood cells, solutions that are injected into the bloodstream for blood transfusions and intravenous feeding must be *isotonic* with the blood, meaning that they must have the same osmotic pressure as blood.
- If the injected solution is too dilute, or *hypotonic*, the flow of solvent into the cells, required to equalize the osmotic pressure, causes the cells to burst and die by a process called *hemolysis*.
- If the solution is too concentrated, or *hypertonic*, equalization of the osmotic pressure requires flow of solvent out of the cells, which shrink and die.



Dialysis

- Osmosis also forms the basis of **dialysis**, a common technique for the removal of impurities from solutions of biological macromolecules.
- In a dialysis experiment, a solution of macromolecules containing impurities, such as ions or small molecules (including small proteins or nucleic acids), is placed in a bag made of a material that acts as a semipermeable membrane and the filled bag is immersed in a solvent.
- The membrane permits the passage of the small ions and molecules but not the larger macromolecules, so the former migrate through the membrane, leaving the macromolecules behind.
- In practice, purification of the sample requires several changes of solvent to coax most of the impurities out of the dialysis bag.

