Why isn’t anything a gas? How come molecular compounds can exist as liquids or even solids?

It is understandable why ionic compounds such as sodium chloride or magnesium oxide form solids. Chemical bonding in ionic compounds is not restricted to a few ions but extends in three dimensions. A lattice results that often produces macroscopic crystals of considerable size, sometimes as big as cars*

*In the Sonata Dessert, Northern Mexico, caves have been discovered with anhydride and selenite crystals up to 6 m in length.

But how can water be a liquid at room temperature and solidify at 273.15 K. A water molecule consists of three atoms only. Two hydrogen atoms that are covalently bound to one oxygen atom. The O-H bond length together with the density of liquid water suggests that the water molecules are at close proximities (liquids and solids are not compressible!). To separate the molecules and essentially produce steam we would have to heat the water to its boiling point. Work needs to be done to separate the water molecules. What kind of forces form the liquid water in the first place and what is the origin of these forces?

Van der Waals Forces

The weak forces that exist between molecules are called van der Waals forces. Van der Waals forces are one to two orders of magnitude weaker (typically between 2 and 35 kJ/mol) then chemical bonds that hold atoms together (typically 150-900 kJ/mol for covalent bonds). No covalent bonds are broken when boiling water!

Dipole-Dipole interactions:

Polar species have a permanent dipole moment (μ) and can align in a way that minimizes the energy of the molecules. Such dipole-dipole interactions are electrostatic in nature and are always present in polar species. Strong dipoles can cause small molecular compounds to have high boiling and melting points. For example: Ammonia (NH₃) a polar molecule with 10 electrons has a boiling point of 240 K whereas methane (CH₄) a non-polar molecule with 10 electrons has a much lower boiling point of 111 K.

Figure above: Dipole-dipole interaction (dashed line) between two permanent dipoles in liquid hydrogen chloride (boiling point -85 °C).
**Induced Dipole Interaction**

Electrons in a non-polar species may be displaced momentarily resulting in an *instantaneous dipole*. This can result in an *induced dipole* in nearby molecules, causing a short lived attraction between the molecules called a *dispersion* or *London force*.

![Figure 4.1](image1)

**Figure 4.1.** Electrons in an argon atom are distributed symmetrically around the nucleus (top left and bottom left). Spontaneously and without any cause the electron charge density in the argon atom may be distorted temporarily polarizing the atom (top right and bottom right).

**Figure 4.2.** The temporarily polarized argon atom (top left) can *induce* a temporary dipole in a neighboring argon atom (top right) if *and only if* the atoms are in close proximity. This results in a short lived attraction between the temporary dipole and the induced dipole (bottom). It is important to note that even though the polarization is short lived it is constantly occurring and if many atoms (or molecules) are in close proximity the induced dipole might “spread” to many more neighbors’ long after the original temporary dipole has vanished.

Dispersion forces are usually much weaker than dipole-dipole interaction but they are possessed by all molecular matter polar or not and can contribute very significantly to physical properties if the molecules are easily polarizable. Polarizability is affected by the *size* of the molecule (the more electrons the greater the polarizability) and by the *shape* of the molecule. Small compact spherical species are harder to polarize than long, cigar-shaped molecules.
More interactions exist between larger molecules. The larger the molecules the more electrons, the greater the attraction. Careful it is not gravity! Its polarizability. It is much easier to polarize a many electron species such as a krypton atom or an octane molecule than a helium atom for example which only has two electrons.

**Class exercise:**

Satisfy yourself that both methane and octane are non-polar molecules by giving a three dimensional drawing of the molecules.

The enthalpy of vaporization for octane at room temperature is 42 kJ/mol. How does this compare to the work done to lift one mole of octane by one meter.
**Summary:** Week forces exist between all molecules called van der Waals forces. Even though these forces are much weaker than those responsible for chemical bonding they are strong enough to influence a wide variety of physical and chemical properties. The following table lists different intermolecular forces all known as van der Waals forces and their approximate strengths:

<table>
<thead>
<tr>
<th>Type of intermolecular force</th>
<th>Strength of force</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion - dipol</td>
<td>20-50 kJ/mol</td>
<td>Solvated ions e.g. [Na(H₂O)₆]⁺</td>
</tr>
<tr>
<td>Dipole-dipole</td>
<td>10-35 kJ/mol</td>
<td>Solid and liquid water</td>
</tr>
<tr>
<td>Induced dipole-dipole</td>
<td>3-8 kJ/mol</td>
<td>Acetone-hexane mixture</td>
</tr>
<tr>
<td>Induced dipole-induced dipole</td>
<td>3-5 kJ/mol</td>
<td>Dispersion forces in liquid argon</td>
</tr>
</tbody>
</table>

Comparing molecules of vastly different molecular mass: the larger molecule will have the higher melting and boiling point.

When comparing molecules of similar molecular mass generally the more polar molecule will have a higher melting and boiling point.

When comparing isomers (molecules with the same molecular formula but a different shape) antenna or road shaped molecules will have a higher melting and boiling point compared to more compact molecules.

**Class exercise:**

Arrange in order of decreasing boiling point: He, Ne, Cl₂, (CH₃)₂CO, O₂, O₃

*Examples how intermolecular interactions affect chemical properties are found in enzymes which activate substrates and speed up reaction that would otherwise take too long or would not occur at all by binding the substrate in a tight “pocket”. This holds the molecule in place and directs the bond to be cleaved or modified toward the enzymes active site. The mechanism of holding the substrate in place often involves a multitude of different van der Waals forces.

A simpler example is the acidity of aqueous solutions of Iron(III) chloride. When FeCl₃ is dissolved in water the solution tests acidic indicating the presence of excess H⁺. How can this be?

\[
\text{FeCl}_3 + n\text{H}_2\text{O} \leftrightarrow [\text{Fe(H}_2\text{O)}_6]^{3+} + 3[\text{Cl(H}_2\text{O)}_6]^{-}
\]

The very high positive charge on the iron ion strongly attracts the partially negative charged oxygen in water. This causes some of the electron charge density on oxygen (and from the O-H bond) to shift to iron which in turn weakens (or activates) the O-H bond. The result is an equilibrium in which some O-H bonds in water are cleaved producing OH⁻ which reduces the overall charge on the solvated ion from +3 to +2 and yields a proton which is responsible for the acidic pH (Figure 4.4.).

\[
[\text{Fe(H}_2\text{O)}_6]^{3+} \rightleftharpoons [\text{Fe(OH)(H}_2\text{O)}_5]^{2+} + \text{H}^+ 
\]
Hydrogen bonding

When comparing trends in boiling points of element hydrides of groups 14 to those of group 15-17 an astonishing observation is made. We would expect dispersion forces and thus the boiling point to increase as the number of electrons in a molecule increases. Group 14 element hydrides follow this prediction nicely (Figure 4.5.). For group 15, 16 an 17 there seems to be an irregularity for the smallest element hydrides namely ammonia, water and hydrogen fluoride (Figures 4.6.- 4.8.)
The effect seems to be most pronounced in group 16 with water being a liquid at room temperature whereas all higher element hydrides of group 16 are gasses.

- The anomalous boiling points of NH$_3$, H$_2$O and HF are a result of **hydrogen bonding**, a specially strong type of intermolecular force (strong dipole-dipole interaction).

- **Hydrogen bonding results when a hydrogen atom on a highly electronegative atom is attracted to a highly electronegative atom (usually F, O and N) on an adjacent molecule.**

- Hydrogen bond energies are between 15 and 40 kJ mol$^{-1}$

**Class exercise:**

Draw two water molecules hydrogen bonded. Use solid single lines for covalent bonding as usual and use dotted lines for hydrogen bonds. Be sure to draw the molecules in their actual shape and align them properly.

Just a reminder: It is the hydrogen bonds that break when water boils **not** the covalent O-H bonds within the molecule!
Consequences of Polarity

The consequences of the anomalous melting and boiling point for water are far reaching. We have grown used to the fact that ice floats but this is actually remarkably unusual. Almost all solids sink in their own liquid. (e.g. adding paraffin wax to molten paraffin or adding solid lead to a lead bath).

The reason that ice is less dense than water lays in hydrogen bonding. Ice is rigid and highly ordered to maximize the number of hydrogen bonds that can form. When ice melts, about 25% of the hydrogen bonds break. The molecules no longer restricted to orient themselves in the lattice can pack more densely. As liquid water is heated it expands like most liquids and thus water has the anomaly of having a density maximum at 4°C.

This is of tremendous importance for aquatic life. In the summer a Lake might warm up significantly but as warm water is less dense then cooler water it raises and layers the surface of the lake. The bottom of a deep lake will remain cool at a temperature near 4°C (Figure 4.10). During severe cold a lake freezes and the ice forms an insulating floating blanket. This helps to insulate the lake from the atmosphere and although the ice might be up to a metre thick the water below will not freeze and the bottom of the lake will be about 4°C providing a stable environment year round (Figure 4.9). If ice would sink the lake would freeze solid as ice would continuously be forming and sinking.

Vapour pressure and Boiling Point

Even below the boiling point at any given temperature there is a certain amount molecules that overcome the intermolecular forces and form a vapour over the liquid. Temperature is the average kinetic energy so there are always a few fast ones that can escape. You can literally feel that it is the fast, more energetic molecules that are leaving the liquid phase when you return to shore from a swim on a windy day. Your skin will feel very cool as water evaporates taking heat with it. This also explains why clothes dry on a cloth line even though the temperature is well below the boiling point of water.

Vapour pressure increases with temperature and at the normal boiling point of the liquid the vapour pressure equals the surrounding atmospheric pressure. Vapour bubbles form from within the liquid. We say the liquid boils.
Class exercise:

Which of the following liquids would have the higher vapour pressure? Explain!

![Molecular structures of two liquids with the same formula C₂H₆O.]

You might have noticed that the two molecules above have the same molecular formula: C₂H₆O. The two molecules are said to be isomers have the same molecular formula but a different bonding arrangement of the atoms.

Class exercise:

Which liquid would be more suitable for the construction of a barometer gasoline or mercury? Justify your answer!

Class exercise:

Look at the cartoon below. Pictures three pieces of clothing made from three different types of fabric below. You probably know from experience which material when hung up wet on a cloth line will dry fastest and which one most slowly.

Figure 4.11. Polypropylene, Nylon and Cotton fabrics on a cloth line (from left to right)
Now look at the picture representing the molecular structure of a small section of each polymer. Do not let the complexity of these structures discourage you from justifying your answers above. Why do the fabrics above have such different drying times.

Figure 4.12. Molecular structure of sections of the polypropylene, nylon and cellulose polymers
Solubility, miscibility and immiscibility

We discussed the strength of ionic bonds and learned that it takes 800°C to melt the lattice of a sodium chloride crystal. Yet ordinary salt placed in ordinary water will dissolve at room temperature. How can water overcome the strong ionic bonds that hold the oppositely charged ions together in the crystal lattice?

Remember the behaviour of polar molecules between capacitor plates. When the field was off the molecules oriented randomly but with the field turned on molecules align with the field. This weakens the field and the effect is greater for small highly polar molecules. The dielectric constant of a medium describes how much the field is weakened by a substance between the plates. Water has a relative dielectric constant \( \varepsilon_r \) of 80.1 meaning relative to vacuum water weakens the electric field by almost 2 orders of magnitude. Now envision a molecular capacitor as in sodium chloride. Replace the plates by point charges of the sodium and the chloride ions. When water enters the space between the two point charges the electric field and thus the ionic bond is hugely weakened and the ionic crystal falls apart. We say sodium chloride dissolves.

When ionic salts such as NaCl dissolve in water, the polar water molecules surround the ions. This process is known as solvation. The solvation of the ions effectively screens anions and cations from their charges and hinders the reformation of solid sodium chloride.

\[
\text{NaCl(s) + 12 H}_2\text{O (l)} \rightarrow \left[\text{Na(H}_2\text{O)}_6\right]^+ \left[\text{Cl(H}_2\text{O)}_6\right]^-
\]

If plenty of water is available six water molecules coordinate each ion in an octahedral fashion. The solubility of sodium chloride at room temperature is quite high 36 g NaCl dissolve in 100 g of water.

At this point all water is essentially used up in solvation (on average 4.5 water molecules per ion) and no more sodium chloride dissolves. We say the solution is saturated.

So why are not all ionic compounds water soluble? Some ionic compounds especially those with small and/or highly charged ions form ionic solids with tremendously high lattice energies. The weakening of the electrostatic attraction between ions in crystals such as alumina, magnesia or lead sulfide by water molecules is not strong enough. These compounds are insoluble in water.

Octane does not dissolve sodium chloride. It’s relative dielectric constant of \( \varepsilon_r \) 1.94 suggests that cannot appreciably lower the electrostatic attraction between the oppositely charged ions. Even without knowledge of \( \varepsilon_r \) we would not have anticipated the non-polar octane to dissolve the very polar NaCl.

Polar substances tend to dissolve in polar solvents, e.g. sugar in water.

Nonpolar substances tend to dissolve in nonpolar solvents, e.g. oil in petrol.

The more similar the intermolecular attractions, the more likely one substance is to be soluble in another. In other words: “like dissolves like.”

Paint thinners for example remove paint, greasy stains, tar or pitch. They do not mix well with water!
Soap, a special case!

Soaps are essentially salts of fatty acids (long chain carboxylic acids) which consist of a long non-polar hydrocarbon tail and a very polar head group. Pictured below are the sodium salts of stearic acid ($\text{C}_{18}\text{H}_{35}\text{O}_2\text{Na}$) and acetic acid for comparison. The two have the same functional group differing only in the length of the hydrophobic hydrocarbon tail.

![Soap molecule](image)

The lipophilic hydrocarbon tail of the molecule interacts well with the lipid (represented as oil droplet) while the hydrophilic polar head group interacts with the polar water thus aiding in the emulsification of fats and oils in aqueous solutions.

Class Exercise:

Explain the fact that a saturated solution of HCl in water is 37 % at RT (e.g. 37 g HCl dissolve in enough water to produce 100 g hydrochloric acid) but a saturated solution of hydrogen in water is only a few ppm in oxygen.
Surface tension

You probably are familiar with the unusual abilities of the water strider which can walk across water without breaking through the surface. I have also seen much denser objects such as copper and even gold flakes float on the surface of water despite their much greater densities.

The reason for surface tension is an unbalance of forces between molecules in the bulk (within the liquid) and molecules at the surface.

Molecules within the liquid have more neighbours to which they are attracted through intermolecular forces then molecules on the surface. This places an interior molecule at lower energy than a surface molecule. Consequently as many molecules as possible enter the bulk phase of the liquid.

This explains the tendency of liquids to minimize their surface as seen in spherical rain drops.
Surface tension is a measure of the energy required to increase the surface area of a liquid. Since intermolecular forces decrease with increasing temperature, surface tension also decreases with increasing temperature.

When a liquid is brought in contact with a solid surface two extreme situations can be observed. The liquid can spread out and wet the surface like an oil drop on a glass plate or it can remain a spherical droplet like mercury on glass. If a liquid wets a surface depends on two different interactions:

- **cohesive forces** (forces within the molecules holding the droplet together)
- **adhesive forces** (forces between the molecules of the liquid and the surface)

If cohesive forces are strong when compared with adhesive forces a drop remains its shape. If cohesive forces are comparable in strength with adhesive forces the liquid will wet the surface since it can interact equally strong with the surface.

When you read a burette or fill a volumetric flask to the mark you are instructed to read the bottom of the meniscus. The meniscus, the concave shaped surface of the water is created by strong adhesive forces between water and the glass surface. No meniscus is observed in a polyethylene graduate cylinder filled with water. Adhesive forces between water and polyethylene are much weaker. A negative (or convex) meniscus is observed between mercury and glass (cohesive forces actually result from strong metallic bonding between Hg atoms). Cohesive forces in liquid mercury are much stronger than adhesive forces between mercury and glass.

![Figure 4.14. Concave meniscus, no meniscus and convex meniscus.](image)

**Class exercise:**

How does an understanding of adhesive and cohesive forces assist you in understanding the phenomena of capillary action?
Adhesive forces can be quite strong. Capillary forces inside a stone, concrete or dry wall structure can soak up water from a ditch in the basement to several feet.

Caulking prevents fluids from entering crucial cracks or seams because very strong adhesive forces exist between the silicon and the wall, tile, or glass surface. If caulking is applied to a wet surface a thin film of water will prevent silicon from sticking to the wall properly (weak adhesive forces between water and silicone). For certain applications e.g. polysulfide caulking gas pumps on gas stations workers can only proceed above the dew point to ensure there is no thin water film on the concrete.

**Class exercise:**

Which of the two liquids would you expect to have the higher surface tension?

![Chemical structures](image)

When designing a waterproofed coat a material like nylon or polyester would be beneficial because water does not wet the surface of these non-polar polymers. You all have seen the formation of droplets that run down rather then soak in to a new rain jacket.

This property is very desirable when the jacket is in use but unwanted when it needs to be washed. Soaps hugely reduce the surface tension of water allowing it to wet non-polar surfaces and thus assist in the cleaning process (See emulsifying properties of soap).

Impregnating a fabric is essentially applying a non-polar coating to a fairly polar fibre such as cotton, linen or canvas which would otherwise soak water up like a sponge and retain it.

**Flotation**

The mining industry is often challenged to extract a few percent of economically valuable ore minerals from enormous amounts of waste rock. A hugely important process that is based on the ability of water to wet the surfaces of different solids differently is flotation. Desired minerals such as metallic sulfides and oxides (often transition metal) are often less hydrophilic (more hydrophobic) than the minerals which comprise the rock that hosts these ores (clay and other silicates like feldspars and quartz or carbonate minerals in limestones). After grinding the mined ore-bearing rock to a fine powder it is suspended in water with some soapy surfactant additives (Xanthates) and turned into a frothing convecting foam by injecting compressed air and stirring in cells. The water will completely wet the
hydrophilic (polar) waste rock particles which will settle under the influence of gravity. The water only partially wets the hydrophobic sulfide minerals. This allows air bubbles become attached to these particles and even though they are much denser the attached air bubbles allow them to be carried to the surface where they are skimmed off as froth.

**Viscosity**

Viscosity is the resistance of a liquid to flow. Interactions between molecules create an internal friction, which slows the passing of molecules with respect to each other. You are all familiar with the slow flow rate of highly viscose fluids such as honey or maple syrup. The viscosity of an oils is a key parameter. As the temperature decreases intermolecular interactions increase and thus viscosity increases as well. This is especially important in colder climate where oils can become to viscose for transmissions and engines to function properly. Silicone oils have the advantage over mineral oils that their viscosity does not vary as strongly with temperature. They are also non-flammable.

**Class exercise:**

Predict which compound is very likely to be the most and the least viscose. Justify your answer.

![Chemical structures](image-url)
**Henries' Law**

Just like other solutes, gas molecules can dissolve in solvents creating solutions. The solubility of the gas depends on the nature of the gas, the solvent, the temperature and the pressure. In general, the solubility of gases in water increases with increasing mass. Larger molecules have stronger dispersion forces. The table below lists the molar solubility of a few non polar gasses.

<table>
<thead>
<tr>
<th>gas</th>
<th>Number of electrons</th>
<th>Solubility (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen, N₂</td>
<td>14</td>
<td>0.38 ×10⁻⁵</td>
</tr>
<tr>
<td>Oxygen, O₂</td>
<td>16</td>
<td>1.36 ×10⁻⁵</td>
</tr>
<tr>
<td>Argon, Ar</td>
<td>18</td>
<td>1.48 ×10⁻⁵</td>
</tr>
<tr>
<td>Krypton, Kr</td>
<td>36</td>
<td>2.25 ×10⁻⁵</td>
</tr>
</tbody>
</table>

**Henry's Law states that the solubility of a gas is directly proportional to its pressure:** \( S_g = k \times p_g \)

Where

- \( S_g \) is the solubility of the gas;
- \( k \) is the Henry's law constant for that gas in that solvent;
- \( p_g \) is the partial pressure of the gas above the liquid.

**Class exercise:**

Calculate the molar solubility of CO₂ in water that has been carbonated with 405.3 kPa pressure above the liquid (equilibrium pressure) at 25 °C.

The Henry's law constant for CO₂ in water at 25 °C is 3.06 ×10⁻⁴ mol/(L kPa)

What volume of CO₂ gas could be given off (approximately) if 1 L of the solution above is depressurized?
Although Henry’s law seems to be a very simple and useful law a practical problem arises. The constant $k$ not only varies from gas to gas but it also varies from solvent to solvent and with temperature.

To carbonate beverages they are pressurized with CO$_2$ giving the desired “fizz” when you open them and expose them to the lower atmospheric pressure. You all know what happens when you shake a carbonated bottle (that has also been out of the fridge for a while). It seems to boil and spill out because the gas is released to fast.

What happens to a highly carbonated lake when it is “shaken” through an earthquake or a land slide? Although geologically quite rare there are a number of crater lakes in Africa which are fed carbon dioxide through volcanic vents.

The table bellow lists the concentration of CO$_2$ and O$_2$ as well as pH as a function of depth (pressure) in Lake Nyos which “exploded” in 1984 killing 1400 people and 3000 cattle by sending an asphyxiating cloud of CO$_2$ down the valley. Carbon dioxide is colorless and odourless and although it is not as poisons as carbon monoxide it is toxic at higher concentrations.

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>p (atm)</th>
<th>pH</th>
<th>O$_2$ (mg/L)</th>
<th>CO$_2$ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>8.7</td>
<td>8.1</td>
<td>39</td>
</tr>
<tr>
<td>15</td>
<td>1.5</td>
<td>6.9</td>
<td>6.1</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>6.3</td>
<td>2.3</td>
<td>42</td>
</tr>
<tr>
<td>50</td>
<td>4.8</td>
<td>5.5</td>
<td>0</td>
<td>370</td>
</tr>
<tr>
<td>100</td>
<td>9.6</td>
<td>5.3</td>
<td>0</td>
<td>550</td>
</tr>
<tr>
<td>150</td>
<td>15</td>
<td>5.2</td>
<td>0</td>
<td>690</td>
</tr>
<tr>
<td>200</td>
<td>19</td>
<td>5</td>
<td>0</td>
<td>1100</td>
</tr>
<tr>
<td>208</td>
<td>20</td>
<td>5</td>
<td>0</td>
<td>1200</td>
</tr>
</tbody>
</table>

**Temperature effects on the solubility of gasses.**

The solubility of gases **decreases with increasing Temperature**. Carbonated soft drinks are more “bubbly” if stored in the refrigerator. In contrast: warm lakes and rivers have less O$_2$ dissolved in them than cool lakes and rivers.
It is important to note, that the opposite is generally true for the solubility of solid solutes in liquid solvents which in most cases increases with increasing temperature. Sugar and salt dissolve much more readily and to a much greater extend in hot water rather than cold water.

**Colligative Properties**

It is not surprising to find that solutes effect the properties of solutions. For example if a nonvolatile solute is dissolved in a solvent the vapour pressure over the solution will be lower when compared to the vapor pressure of the pure solvent. What is surprising to find is that the lowering of the vapour pressure only depends on the number of solute particles present not on their identity. Thus the addition of 1 mol of sugar to 1 L of water should lower the vapour pressure of the solution to the same extend as would the addition of one mole of the non volatile glycol to the same amount of water.

A property which changes as a function of the number of solute particles and is independent of the identity of those solute particles is known as **colligative property**. Among colligative properties are:

- Vapour pressure lowering
- Boiling point elevation
- Melting point depression
- Osmotic pressure
**Lowering of the vapour pressure: Raoult’s Law**

Because of solute-solvent intermolecular attraction, higher concentrations of nonvolatile solutes make it harder for solvent to escape to the vapour phase. More solvent molecules are “tied up” in engaging in solvent-solute interaction. *A salted road dries slower than non salted road!*  

![Diagram showing comparison of vapour pressure](Picture Brown LeMay)

Therefore, the vapour pressure of a solution is lower than that of the pure solvent (at the same temperature). This means it is harder to boil the solution.

Raoult’s Law: \( p_A = X_A \times p^\circ_A \)

where

- \( p_A \) is the vapour pressure of the solution
- \( X_A \) is the mole fraction of the solvent *A* *not the solute!* (e.g. number of moles of solvent divided by the sum of the number of moles of solutes and solvent)
- \( P^\circ_A \) is the normal vapour pressure of the pure solvent *A* at that temperature

**Class exercise:**

What is the vapour pressure of a solution of 1 mol of sucrose in 15 mol of water at 25 °C?

\( p^\circ_{\text{H}_2\text{O}} (25 \text{ C}) = 31.26 \text{ mbar} \)
**Class exercise:** Applying Raoult’s law to ideal solutions of volatile liquids

The vapour pressure of pure benzene and pure toluene at 25 °C are 95.1 and 28.4 mm Hg respectively. A solution is prepared in which the mole fractions of benzene and toluene are both 0.5. What are the partial pressures of benzene and toluene above this solution? What is the total vapour pressure of the mixture?

**Predicting vapour compositions (How distillation works)**

What is the composition of the vapour in equilibrium with the benzene toluene mixture in our example above (25 °C) ?

---

Liquid vapour equilibrium for benzene-toluene mixtures at 25 °C (not to scale)

1. Vapour pressure of toluene, 2. vapour pressure of benzene, 3. total vapour pressure, 4. vapour composition
Osmosis

Some substances form semi permeable membranes, allowing some smaller particles to pass through, but blocking other larger particles.

In biological systems most semi permeable membranes allow water to pass through, but solutes are not free to do so.

In osmosis, there is net movement of solvent from the area of higher solvent concentration to lower solvent concentration.

The pressure required to stop osmosis, known as osmotic pressure, \( \pi \), is

\[
\pi = MRT
\]

where \( M \) is the molar concentration of the solute

\( R \) is the universal gas constant:

\[
R = 8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1} \quad \text{or} \quad 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \quad \text{(when working with atm)}
\]

\( T \) is the temperature in Kelvin.
Class exercise:

Calculate the osmotic pressure of a 0.15 M NaCl at 25 °C. Careful! It looks so simple.

Osmotic pressures can be huge. They are powerful enough to deliver water in tree tops of 80m and more, let roots of trees crack and uplift concrete and cause serious medical conditions.

We are prevailed upon by nutritionists to keep well hydrated and drink an average of 3-4 L of water a day. Most of us do not. During extremely strenuous exercise like running a marathon in the heat replacing water is essential. Sometimes though runners drink too much water replacing the fluid but not the electrolytes that were lost. This causes the sodium ion concentration in the blood to decrease. If levels become dangerously low osmosis forces water to flows from the blood in to brain cells which consequently expand. This condition can be fatal.

Osmosis can be reversed by applying a pressure greater than the osmotic pressure to the membrane. This is applied in desalination plants where seawater is converted to drinking water in countries along the Persian sea where freshwater from rivers and lakes is scarce or simply not available and energy is cheap.

If the osmotic pressure is the same on both sides of a membrane (i.e., the concentrations are the same), the solutions are isotonic. This is of uttermost importance when administering IV medication.

Class exercise:

Explain what happens in the pickling of cucumbers?