COLLIGATIVE PROPERTIES

Definition: A **COLLIGATIVE PROPERTY** is a property whose value depends only on the ratio of the number of moles of ***solute*** particles to moles of ***solvent*** particles**,** and ***not*** on their chemical identities**.**

There are three immediate consequences of this definition:

i) The more concentrated the solute, the greater the effect on the property.
ii) If two solutes have equal concentrations, the solute that produces more particles will have a greater effect on the property.
iii) All solutes have the same effect on the property, provided the solutes either do not ionize in solution or produce ions to the same extent in solution.

We will look at four colligative properties:

- Vapour pressure depression,
- Boiling point elevation,
- Freezing point depression, and
- Osmotic pressure.

A. VAPOUR PRESSURE DEPRESSION

It is experimentally observed that dissolving a solute such as NaCl(s) in water decreases the vapour pressure (VP) of the water. (The reason for vapour pressure depression involves a concept called entropy, which will be covered in Chemistry 12.)

EXAMPLE: At 20°C, the vapour pressure of water is 2.34 kPa. If NaCl is dissolved in 1.00 L of water at 20°C, the following vapour pressures are found for water:

Dissolving 1.00 mol of NaCl : 2.26 kPa (VP is depressed by 0.08 kPa)
Dissolving 2.00 mol of NaCl : 2.18 kPa (VP is depressed by 0.16 kPa)

EXAMPLE: At 50°C, the vapour pressure of water is 12.34 kPa. Dissolving the three substances below in 1.00 L of water at 50°C produces the following vapour pressures for water:

Dissolving 95.2 g (1.00 mol) of $MgCl_2$: $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2\,Cl^{-}(aq)$: 11.71 kPa
Dissolving 87.7 g (1.50 mol) of NaCl: $NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$: 11.71 kPa
Dissolving 180.2 g (3.00 mol) of urea: urea(s) → urea(aq) : 11.71 kPa

These substances give identical results because they all produce 3.00 mol of particles in solution.

As can be seen, the drop in vapour pressure is not very large, but is easily measurable.

If two miscible liquids are mixed, the vapour pressures of both liquids decrease.

EXAMPLE: Acetone and methanol are miscible molecular liquids. At 25°C, the VP of pure acetone is 30.59 kPa and the VP of pure methanol is 16.92 kPa. When 1.00 mol of both acetone and methanol are mixed together, the VP of the acetone drops to 15.30 kPa and the VP of the methanol drops to 8.46 kPa. As a result, the total VP of the mixture is:

$$VP_{TOT} = 15.30\text{ kPa} + 8.46\text{kPa} = 23.76\text{ kPa}$$

Notice that this value is half-way between the VP values of the pure liquids. As the moles of acetone, say, increases, relative to the moles of methanol, the total VP gets closer to the VP of pure acetone. Similarly, if the moles of methanol increases relative to the moles of acetone, the total VP gets closer to the VP of pure methanol.

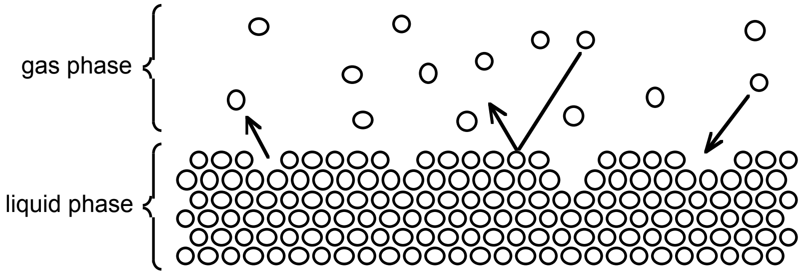
EXERCISES:

1. Arrange the following solutions in order of increasing vapour pressure depression:
   1 M KBr, 1 M $Al_2(SO_4)_3$, table sugar, 1 M $CaCl_2$, 2 M $MgCl_2$
2. Which liquid, 1 M KCl or pure water, has the greater initial evaporation rate and why?
3. Ethanol and ethyl acetate are miscible molecular liquids. At 25°C, the VP of pure liquid ethanol is 7.83 kPa and the VP of pure liquid ethyl acetate is 12.63 kPa. Mixture A contains 1.00 mol of each liquid and a vapour pressure of 10.23 kPa. Mixture B contains 3.00 mol of ethanol and 1.00 mol of ethyl acetate, and has a combined vapour pressure of 9.03 kPa. Which mixture has the higher VP of ethanol, and why?
4. You have 3 different aqueous solutions, each having 10.0 g of a substance dissolved in 100 mL of water. The dissolved substances are:
   KBr , LiCl and $Al_2(SO_4)_3$
   List the solutions of the 3 substances in order from highest to lowest vapour pressure.
5. What mass of NaBr must be dissolved in 100 mL of water to produce the same vapour pressure as 23.0 g of $Mg(NO_3)_2 \cdot 2H_2O$ dissolved in the same volume of water?
6. You make up a sugar solution and accidentally spill both a few drops of water and a few drops of sugar solution on a clean kitchen counter. Within half an hour, the water droplets have completely evaporated, whereas the droplets of sugar solution remain sticky for a much longer time. Why does the sugar solution remain sticky for so long?

B. BOILING POINT ELEVATION

At a given temperature, two separate processes occur in a liquid.

a) Molecules in the liquid are knocked out of the liquid by energetic neighbouring molecules, leaving a "hole" or "cavity" in the smooth surface of the liquid.
b) Molecules in the gas phase dart about in random directions. Sometimes the gas molecules head in the direction of the liquid and either
   i) rebound off a molecule at the liquid surface, or
   ii) enter a cavity and become part of the liquid again.



When a liquid is first introduced into a closed vessel, there are no molecules from the liquid in the gas phase. However, there is a small probability that a given molecule at the liquid's surface will enter the gas phase and therefore, as time passes, the number of molecules in the gas phase increases and the pressure increases.

Once in the gas phase, there is a very small probability that a given molecule will be "aimed" in precisely the correct direction so as to allow it to re–enter the liquid phase. However, as the number of gas phase molecules continues to rise, there is an increasing ***total*** probability that ***some*** molecules will re–enter the liquid. Eventually, gas molecules enter the liquid as often as liquid molecules enter the gas phase. At this point the gas pressure ceases to rise and stays at some constant value known as the **VAPOUR PRESSURE.** Note that **some** liquid must be present in order to know that the gas phase has become SATURATED with gas molecules from the liquid.

Since evaporation occurs when molecules in the liquid gain enough energy to escape into the gas phase, the greater the temperature of the liquid, the greater the average kinetic energy of the molecules in the liquid. The greater the kinetic energy, the greater the evaporation rate and the greater the vapour pressure. Therefore:

The higher the temperature, the greater the vapour pressure.

Now, the total gas pressure in the space immediately above the surface of an **open** vessel of water is due to a mixture of air and water vapour. Therefore

$$P_{TOTAL} = P_{WATER} + P_{AIR}$$

where: P_{WATER} = the vapour pressure of water
P_{AIR} = the pressure due to the air molecules.

But this total pressure equals the pressure of the atmosphere pushing down on the vessel's surface since the vessel is open to the air.

$$P_{ATM} = P_{TOTAL} = P_{WATER} + P_{AIR}$$

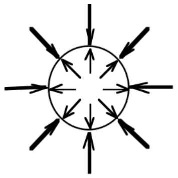
When water is heated, P_{WATER} increases. But P_{ATM} ***cannot*** be changed in an open container, so that if P_{WATER} is increasing just above the surface of the liquid, then P_{AIR} ***must*** be decreasing. That is, the water vapour starts to displace the air.

Eventually, a maximum water temperature is achieved when

$$P_{WATER} = P_{ATM}$$

which implies that $P_{AIR} = 0$ just above the liquid; that is, the air molecules above the liquid have been displaced by water molecules. But, if $P_{WATER} = P_{ATM}$ then **molecules all through the liquid** have enough KE to overcome the downward pressure from the atmosphere (which forces them to stay in the liquid) and go directly into the gas phase. As a result, gas "bubbles" appear all through the liquid and the liquid **BOILS.**

When $P_{WATER} < P_{ATM}$, some highly energetic molecules below the liquid surface have sufficient KE to separate from their neighbours and form a microscopic gas bubble (see figure at right), but the greater pressure of the atmosphere crushes the bubble out of existence and thus no bubbles are seen to form.



When $P_{WATER} = P_{ATM}$, the pressure generated within the bubble (which equals P_{WATER}) matches the pressure of the atmosphere bearing down on the liquid and the gas bubble remains in existence. Note that if a bubble forms at the bottom of the liquid, the weight of the water above the liquid causes a small additional increase in the pressure bearing down on the bubble, so that a slightly greater temperature is required to maintain sufficient vapour pressure within the bubble and prevent it from being compressed out of existence.

As the low–density bubble slowly rises up through the higher–density liquid, the pressure on the outside of the bubble decreases (less water is pushing down on it) and the bubble **expands** against the lowered external pressure. This explains why BUBBLES EXPAND AS THEY RISE UP THROUGH A LIQUID. (You may have seen this expansion of rising bubbles if you have looked closely at a glass of soda pop.)

Boiling occurs when the VP of a liquid equals the total pressure pushing down on the surface of the liquid. There are two different ways in which we can change the boiling temperature.

i) Change the total pressure pushing down on the liquid.

EXAMPLE: When lava erupts from a deep ocean trench, the enormous pressure created by a depth of several kilometers of ocean water over the lava means the water that boils when it contacts the red-hot lava may be at 600-700^{o}C.

ii) Lower the vapour pressure of the liquid by dissolving a solute in the liquid. As with all colligative properties, the more solute particles in solution, the lower the vapour pressure.

EXAMPLE: You heat water in a pot in preparation for making spaghetti. When the water is boiling, as seen by the bubbles on the bottom of the pot, you add some salt. Almost immediately, the boiling stops. The addition of the salt reduces the vapour pressure of the water so that more heat is required to raise the temperature of the water and increase the VP until it again equals atmospheric pressure. (This does not take a long time because the rise in boiling point elevation from the small amount of salt added is quite small.)

EXERCISES:

7. On a mountain top the atmospheric pressure is 70 kPa**.** Would water boil at a higher or lower temperature than $100^{O}C$ on top of the mountain? Why?

8. The lowest exposed land on Earth is the shoreline of the Dead Sea, which is bordered by Jordan and Israel. Would the boiling temperature of water be more or less than $100^{O}C$ on the Dead Sea shoreline? Why?

9. Automobile radiators usually contain a mixture of water and antifreeze (either ethylene glycol, which is poisonous to pets or propylene glycol, which is safe for pets). What benefit will the antifreeze have in a hot climate where overheating of automobile engines can be a problem?

C. FREEZING POINT DEPRESSION

Experiments show that if a solute is dissolved in a pure solvent, the freezing temperature of the resulting solution is lower than that of the pure solvent.

EXAMPLE: Dissolving 4.00 mol of $CaCl_2$ in 1.00 L of water produces a solution having a freezing point of $-22.3^{O}C$ and a boiling point of $106.1^{O}C$.

Note:
- Freezing point depression ($-22.3^{O}C$, above) and boiling point elevation ($6.1^{O}C$, above) have different values.
- Adding a solute to a pure liquid effectively expands the temperature range over which the solvent remains in the liquid phase. (Water normally has a liquid range of $100^{O}C$ but in the above example the liquid range is $128.4^{O}C$.)

Some organisms living in cold environments take advantage of freezing point depression by having substantial concentrations of various compounds in their blood and tissues. These compounds act as a form of antifreeze, allowing the organisms to survive (and sometimes thrive) in conditions where the surroundings are at a temperature below $0^{O}C$.

EXERCISES:

10. Arrange the following solutions from highest to lowest freezing temperature:
1 M KBr, 2 M KBr, 1 M $Al_2(SO_4)_3$, 1 M table sugar, 1 M $CaCl_2$, 2 M $MgCl_2$

11. You have 3 different aqueous solutions, each having 20.0 g of a substance dissolved in 100 mL of water. The dissolved substances are:
KCl , LiBr and Na_2SO_4
List the solutions of the 3 substances in order from highest to lowest freezing temperature.

12. Why do some communities put common salt, NaCl, on roads in the winter, especially before or during a snowstorm? What chemical advantage might $MgCl_2$ have over NaCl in some cases?

D. OSMOTIC PRESSURE

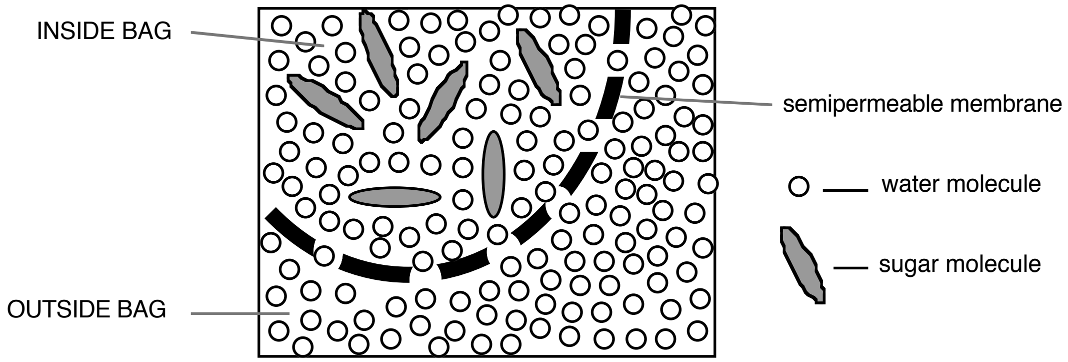
Definitions: A **SEMIPERMEABLE MEMBRANE** allows the free passage of certain types or sizes of molecules or ions through the membrane, but blocks the passage of other molecules or ions.

OSMOSIS is the passage of solvent molecules through a semipermeable membrane.

DIALYSIS is the selective passage of certain sizes of molecules or ions through a semipermeable membrane. (OSMOSIS is restricted to passage of solvent molecules.)

[In contrast, **DIFFUSION** is the mixing of one substance with another by random movement when they are either in direct contact with each other or are separated by a permeable membrane.]

OSMOSIS, DIALYSIS and DIFFUSION are based on simple probability. Here, we examine the probabilities underlying the process of osmosis. Consider two molecules of water in the diagram below, one of which is inside a semipermeable "bag" and one of which is outside.



Both water molecules have the same probability of passing through a "hole" in the "bag". However, because sugar molecules occupy much of the solution inside the "bag", there is a greater concentration of water molecules outside the bag than inside. Hence, there is a greater overall probability that a water molecule will enter the bag than leave the bag. This means there will be a net **inflow** of water molecules into the bag, creating a substantial pressure increase within the bag. This pressure is called the **OSMOTIC PRESSURE.** Under certain conditions, it is possible to generate osmotic pressures much greater than 10,000 kPa.

The colligative nature of osmosis becomes clear if you consider that the more ions a compound can break into, the larger the ion concentration on one side of a semipermeable membrane (and therefore the smaller the resulting concentration of water molecules) and the greater the probability that more water molecules will enter than leave the “bag”. You can think of what happens during osmosis of aqueous solutions this way:

> **Water** flows from the side having a **lower** concentration of dissolved particles to the side having a **higher** concentration.

(If the process continued indefinitely, the concentrations on both sides of the semipermeable membrane would become equal.)

Experimentally, it is found that osmotic pressure is proportional to the molarity of particles (at low concentrations).

Some applications of osmotic pressure are as follows:

In biology, osmosis affects the way cells behave in different environments.

An **isotonic** environment has the same particle concentration as the inside of a cell, and hence the same water concentration, so internal cell pressure is unchanged (and the cell remains the same size) .

A **hypertonic** solution has a larger concentration of particles than the interior of a cell, and therefore a lower concentration of water, so there is a net flow of water molecules out of the cell and into the environment, and the cell decreases in volume.

A **hypotonic** solution has a lower concentration of particles than are found inside the cell, and therefore a higher concentration of water, so there is a net flow of water molecules out of the environment and into the cell, and the cell increases in volume.

Water surrounding the root systems of trees creates an osmotic pressure as it enters the sap-filled interior of root hairs. The semipermeable cell walls admit water and dissolved minerals into the root hair's interiors, which have a high concentration of dissolved molecules. The resulting pressure causes water to ascend tens of meters up the tree, where it is respired out through leaves or needles.

If sufficient external pressure is applied to a semipermeable membrane, water can be pushed from higher to lower concentrations of particles (in other words, the flow of water across the membrane is reversed). This process is called **reverse osmosis** and is used to purify drinking water: impure water on one side of the membrane and pure water on the other. Desalination of sea water requires reverse osmosis pressures over 3000 kPa to overcome the osmic pressure of sea water.

Some people with kidney disease are treated with kidney dialysis. In this procedure, the patient's blood is passed through a semipermeable membrane having pore sizes that allow water and waste products to pass out of the blood but prevent red blood cells from passing through. The red blood cells are then returned to the patient, free from waste products.

EXERCISES:

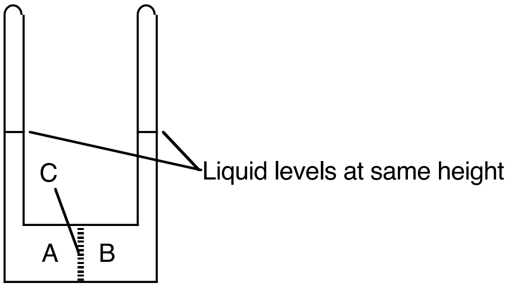
13. You have the following compounds, diluted to 1.00 L:
    i) 50.0 g of sucrose, $C_{12}H_{22}O_{11}$,
    ii) 50.0 g of KCl,
    iii) 100.0 g of urea, $CO(NH_2)_2$ [molecular],and
    iv) 25.0 g of $MgCl_2$.

    You also have four osmosis apparatus. Each apparatus consists of two side-by-side compartments separated by a semipermeable membrane. Into one compartment of each apparatus is placed 0.450 M NaCl(aq) and the four test solutions are poured into the remaining compartments.
    a) Which test solution will create the greatest osmotic pressure, from the test solution side to the side containing 0.450 M NaCl?
    b) Which solution(s) will have a net flow of water molecules from the 0.450 M NaCl side to the test solution side?

14. Adding sugar to jam and jelly creates a hypertonic sugar solution relative to the solution inside bacterial cells. Bacterial cell walls are semipermeable membranes. What happens to a bacterium that happens to be in contact with jam or jelly?

15. The cell walls of red blood cells are semipermeable membranes. What happens to red blood cells being studied by a biochemist when she places them in a hypotonic solution?

16. You have the following apparatus:



Side A contains 0.50 M NaCl, side B contains 0.4 M $MgCl_2$ and C is a semipermeable membrane. What would you expect to see one day after the apparatus is set up, and why?