CHEM1011 INTERMOLECULAR FORCES: WEEKS 6-7

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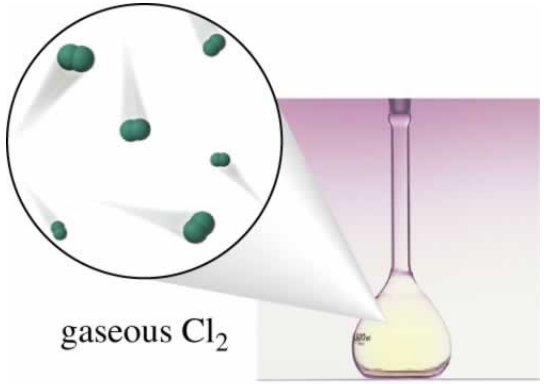
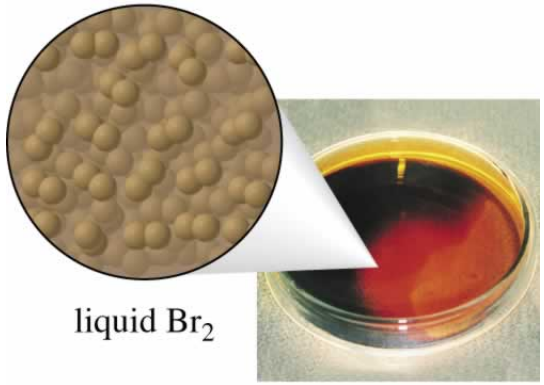
IM Forces: Weeks 6-7

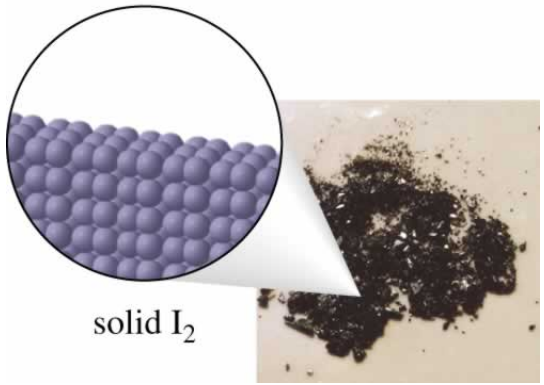
Content	Blackman Book	Learning Objectives
Intermolecular forces Dipole-dipole, dispersion forces, hydrogen bonds	6.7, 6.8	Identify the types of intermolecular forces present between particular species Relate the strength of intermolecular forces to properties such as dipole moment and polarizability
Deviations from ideal gas laws; van der Waals equation; a and b constants		Use the van der Waals equation to calculate the pressure of a non-ideal gas Explain the origin and size of *a* and *b* constants
States of matter. Comparison of properties of solids, liquids, and gases; Solids – types (atomic, molecular, ionic, metallic, network, crystalline vs amorphous) Liquids – general description; viscosity and surface tension	7.1-7.3	Classify solids as ionic, molecular, or metallic based on their properties Relate viscosity and surface tension to intermolecular forces
Properties of solutions; energy changes on dissolution, solubility, 'like dissolves like', Raoult's law, ideal and non ideal solutions; positive and negative deviations from Raoult's law. Distillation.	10.1, 10.3 10.5	Understand the process of dissolution at the molecular level Predict the relative solubility of a substance in a range of solvents

Intermolecular forces

- The states of matter adopted by chemical substances and the physical behaviour of the various states of matter depend ultimately upon the strength and nature of forces between atoms and molecules in the substance.

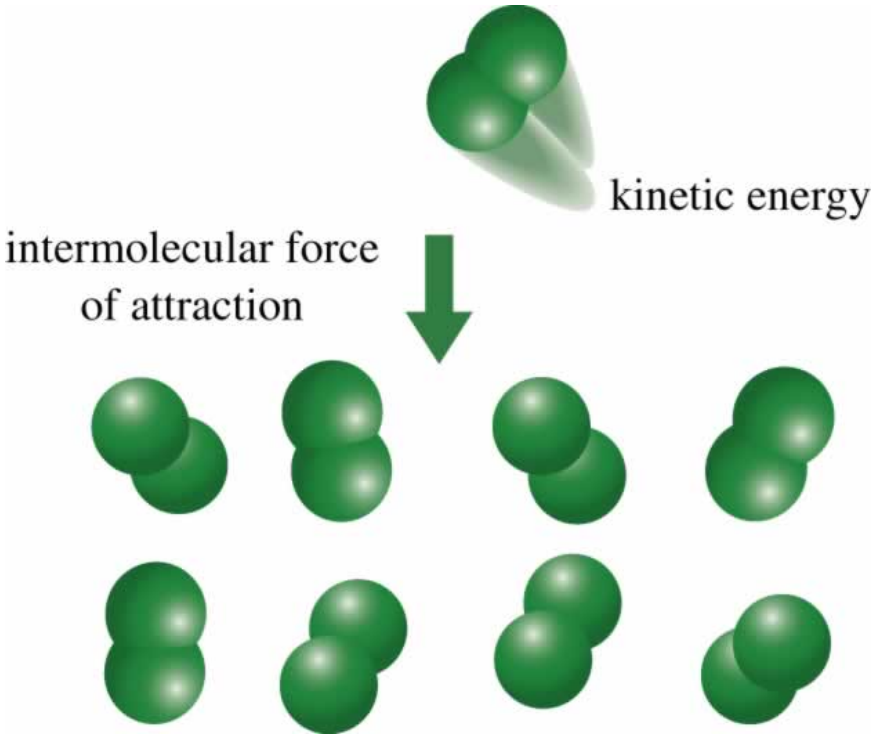


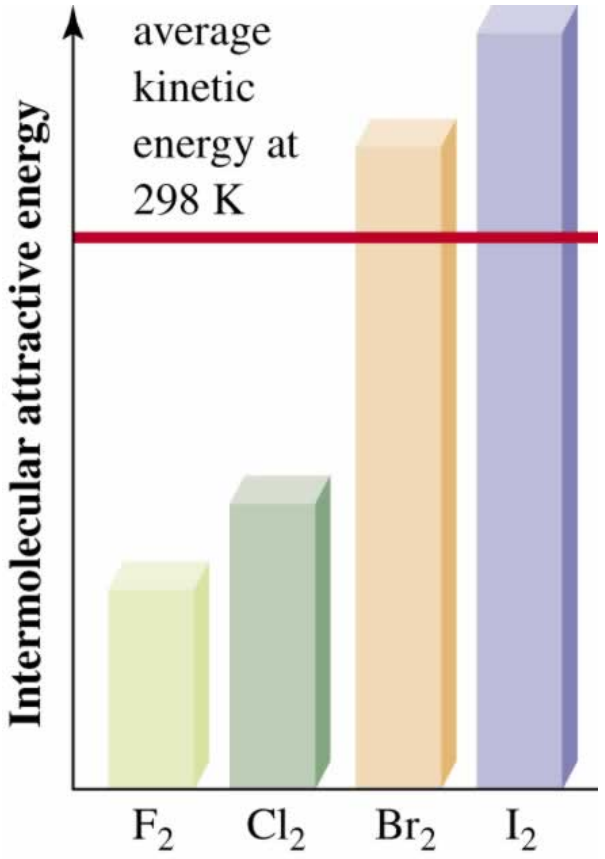




Intermolecular forces

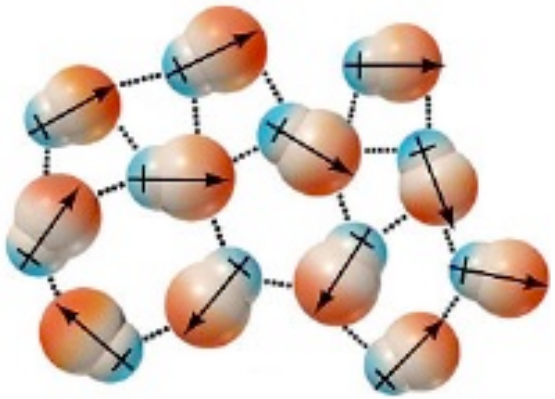
"A substance exists in a condensed phase (solid or liquid) when its molecules have too little average kinetic energy to overcome intermolecular forces of attraction"





Intermolecular forces

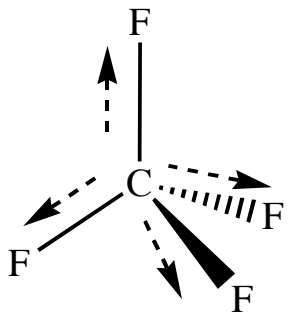
- Molecules are small groups of atoms that have strong bonds between the atoms in the molecule, but weak bonding at the surfaces between molecules.
- There are three basic types of intermolecular forces:
- **1. Dipole-dipole forces**
- **2. Dispersion forces (London)**
- **3. Hydrogen bonding**

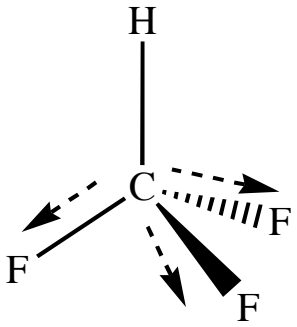


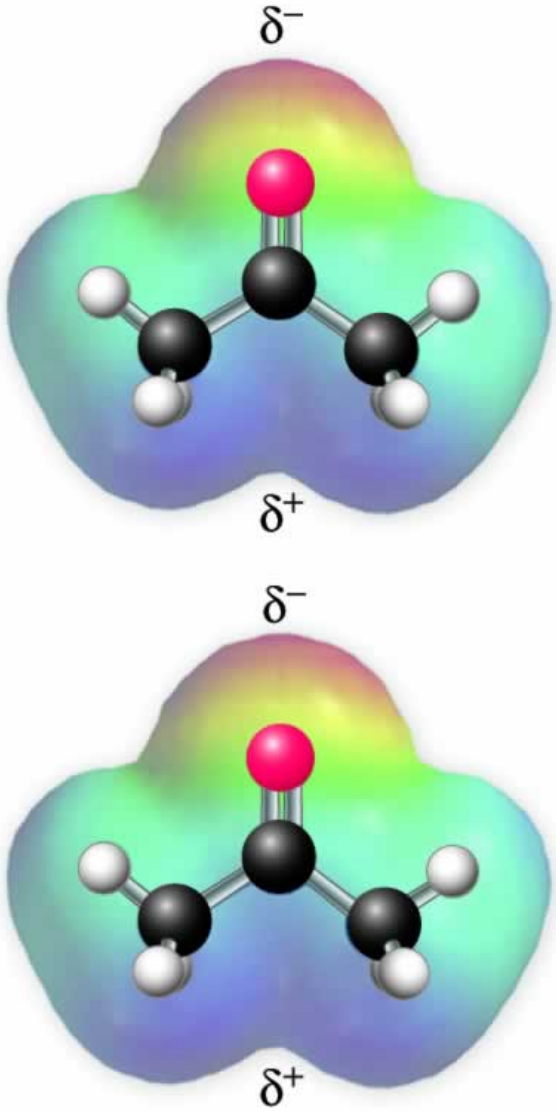
Dipolar attractions in a liquid.

Dipole-dipole forces

- Two molecules with permanent dipole moments will attract each other by the approach of their oppositely charged ends.
- Such molecules will align themselves to maximize this type of interaction.
- e.g. The boiling point of CF_4 (no permanent dipole) is –128°C, whereas the b.p. of CHF_3 (with a permanent dipole) is –84.4°C.







acetone

CH_3COCH_3

Intermolecular forces

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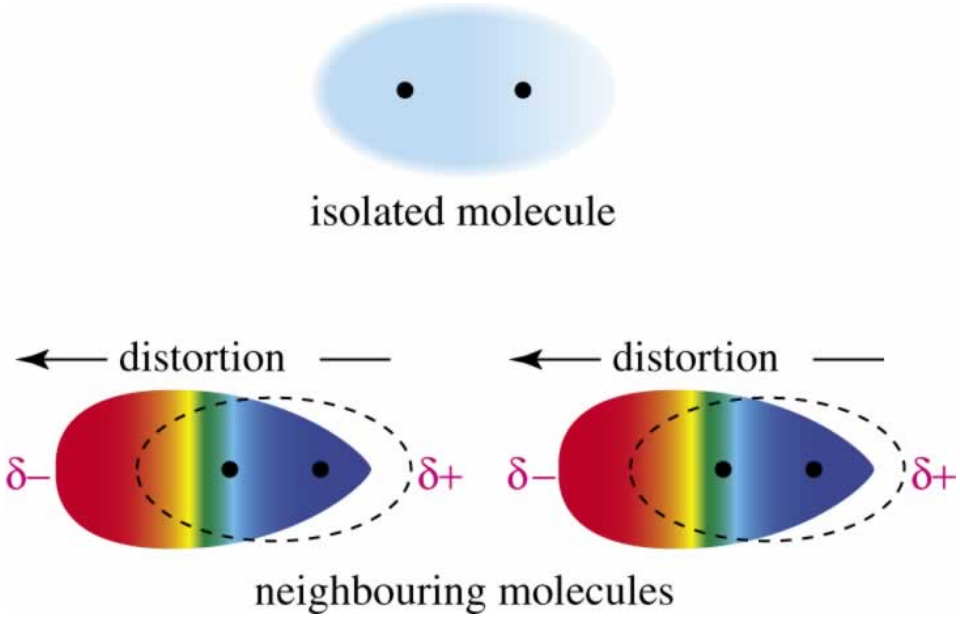
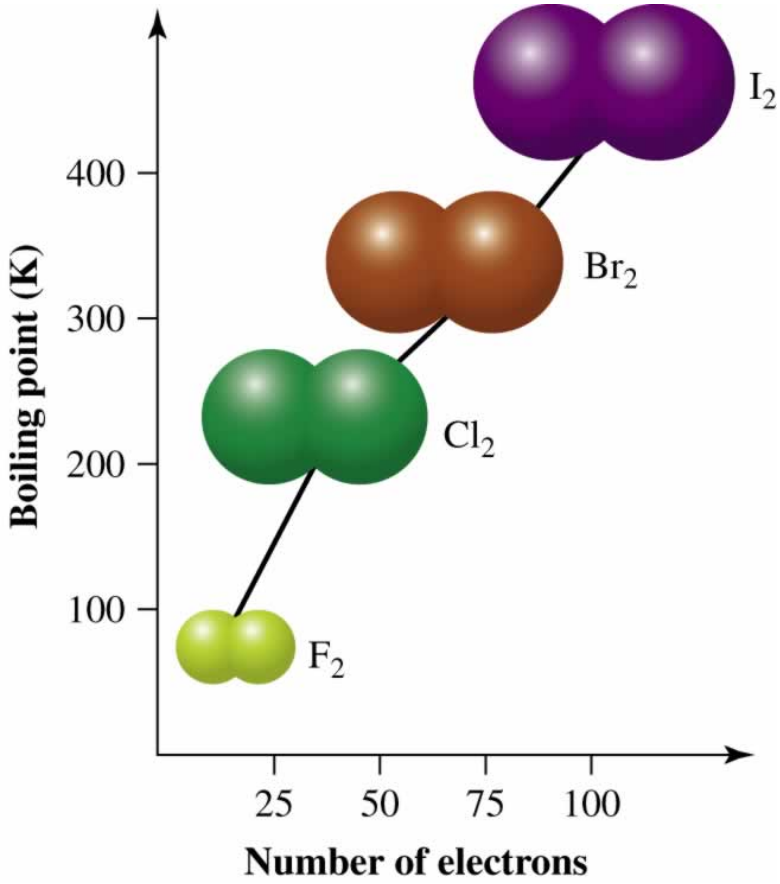
Dispersion forces (London forces)

- A molecule with no permanent dipole can become temporarily polar when polarity in nearby (e.g. colliding) molecules induce its electron cloud to redistribute and become unsymmetrical. The polarity induced on the molecule enhances the polarity of the neighbouring molecules, giving a feed-back increase in the attraction.



Dispersion forces (London forces)

- Dispersion forces occur between all molecules and are not dependent upon the orientation of the molecules, as permanent dipole attractions are.
- Dispersion forces usually have a strength similar to permanent dipole forces.
- The strength of dispersion forces depend upon the ease with which the electron cloud of a molecule can be distorted. This is called the **polarisability** of the molecule.
- Large atoms with many electrons are easily polarised and give higher dispersion forces.
- Atoms with many electrons have many protons (and neutrons) in their nucleus — so dispersion forces increase with increased molar mass of a molecule.



Dispersion forces (London forces)

- Thus, the boiling points of the noble gases follow the order: He < Ne < Ar < Kr < Xe < Rn

  –269 < –246 < –186 < –152 < –108 < –62 °C

- Thus, the boiling points of the halogens follow the order:

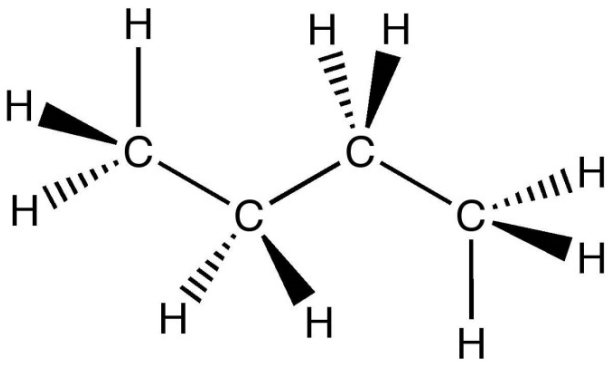
  $F_2 < Cl_2 < Br_2 < I_2$.

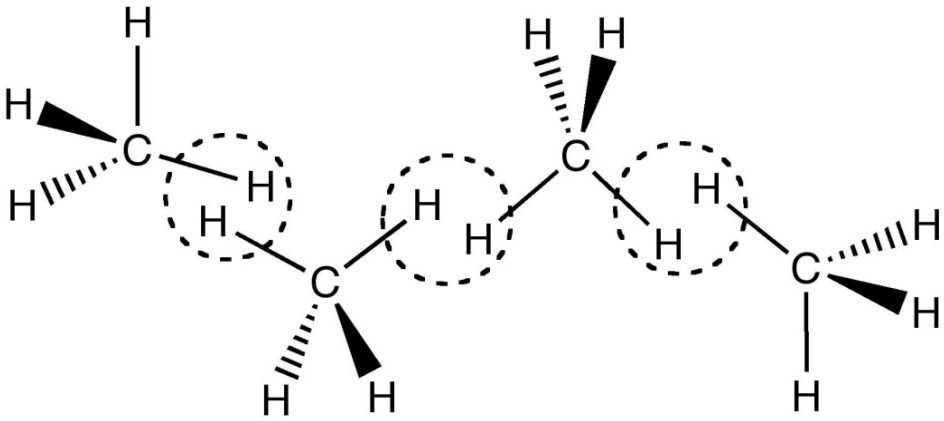
  –188 < –34 < 59 < 184 °C

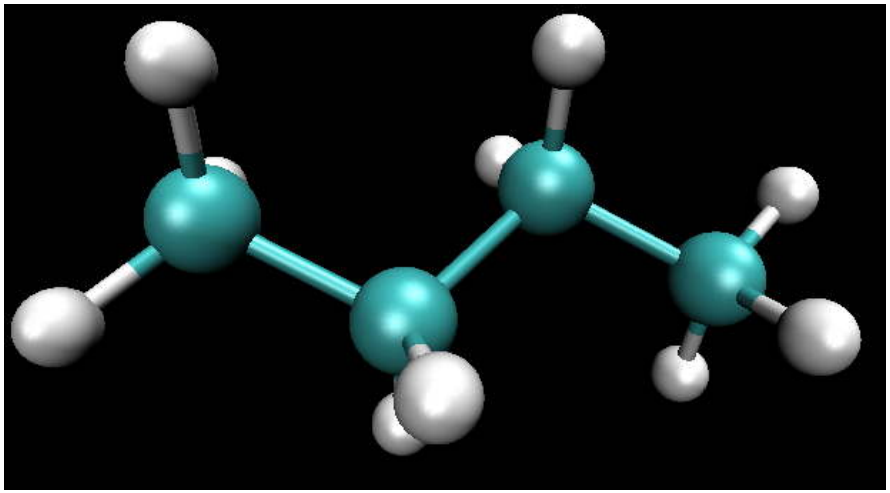
- The halogenomethanes boiling points follow the order: $CF_4 < CCl_4 < CBr_4 < CI_4$.

  –128 < 77 < 190 < decomp. °C

Dispersion forces in alkanes

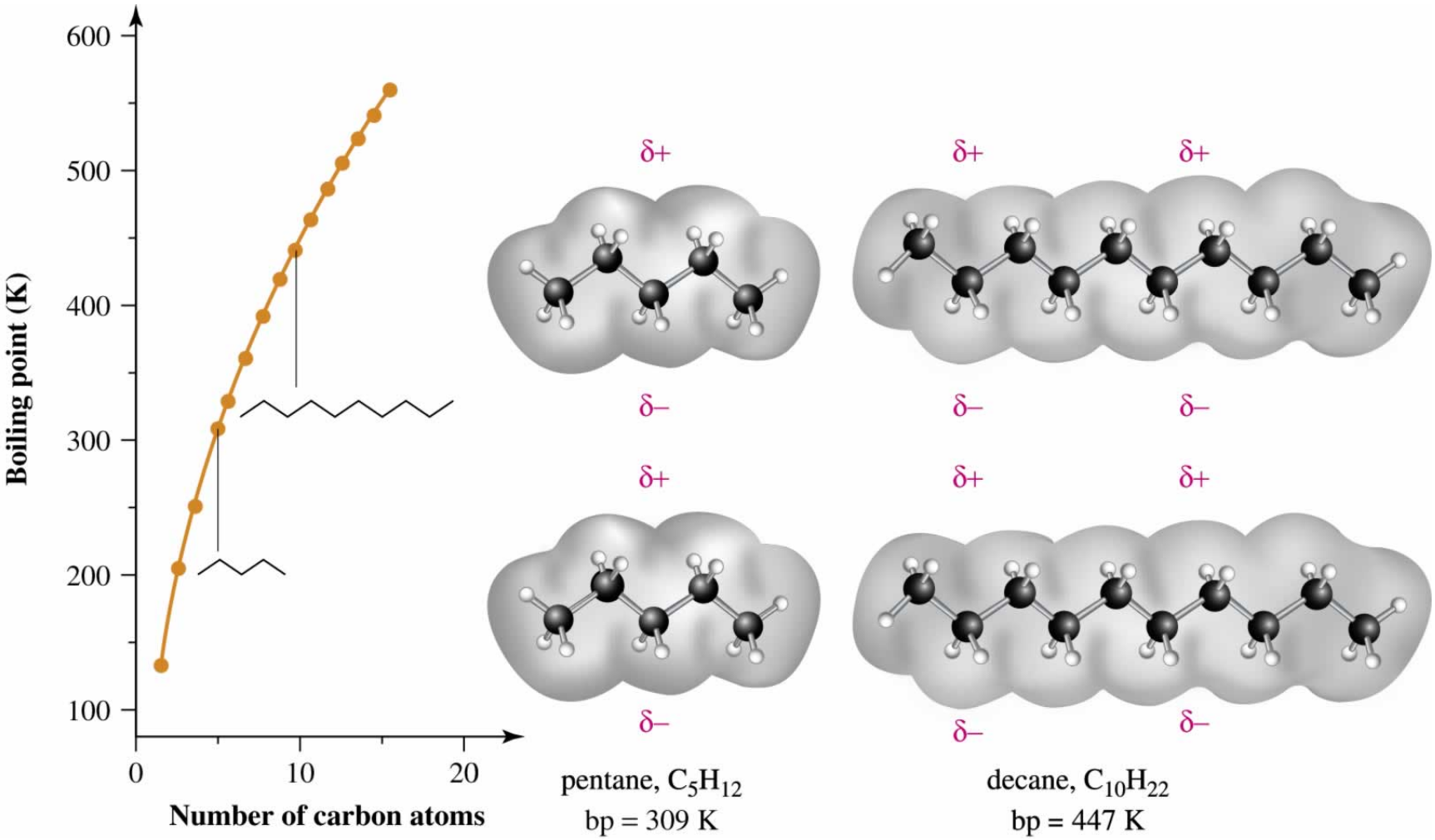






- The structure of butane can be <u>imagined</u> as consisting of CH_4 molecules linked together.
- Thus, each C centre in butane is tetrahedral (and non-polar), as each CH_4 molecule is tetrahedral.
- The lack of polar bonds in butane means there are no dipole/dipole forces between molecules.
- No parts of butane consist of N, F or O atoms with attached lone pairs or –H atoms capable of hydrogen-bonding.

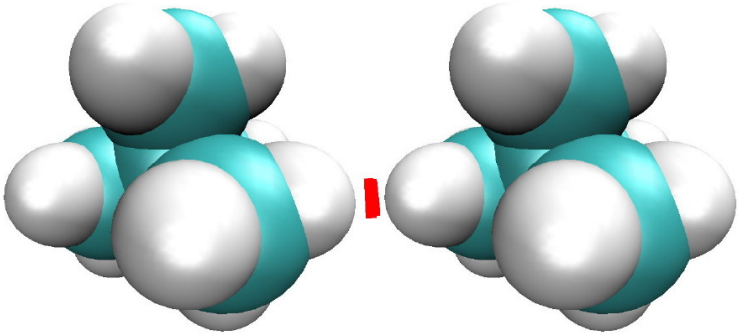
Dispersion forces in alkanes



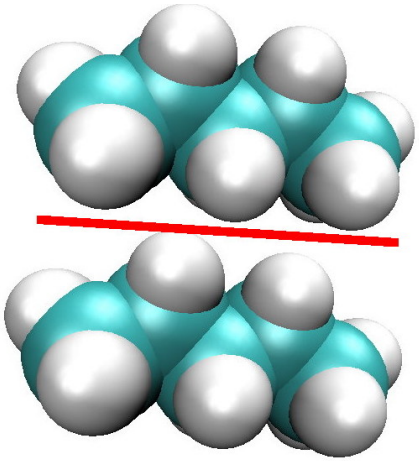
"The boiling points of alkanes increase with the length of the carbon chain because a large electron cloud is more polarisable"

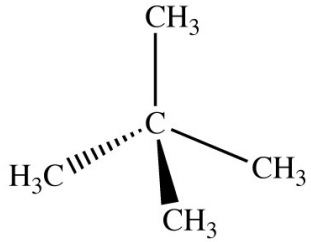
Dispersion forces in alkanes

- Surface area of contact between molecules affects the number of temporary dipole interactions — and therefore the overall attraction force.

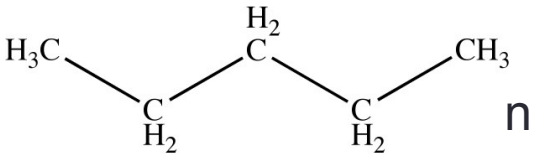


- e.g. The chain structure of n-pentane, $CH_3CH_2CH_2CH_2CH_3$ (b.p. 36°C), allows more induced dipole interactions between its molecules than neo-pentane, $(CH_3)_4C$ (b.p. 9.5°C), which is roughly spherical in shape.





neo-pentane, b.p. 9.5°C



n-pentane, b.p. 36°C

Intermolecular forces

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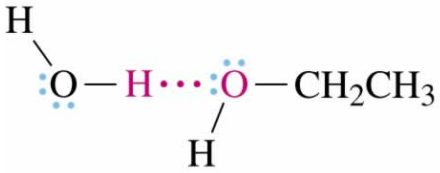
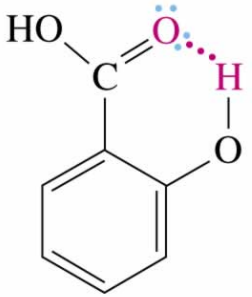
Hydrogen bonding

- This is an unusually strong type of dipole-dipole attraction of the type —Y···H—Y' (where ··· indicates the hydrogen bond, and Y & Y' = any of O, N or F).
- The strong polarisation of the H atom by these very electronegative atoms gives the H a strong attraction for the lone pair on the Y atom of the neighbouring molecule.
- 2 requirements:
  (1) need H-O, H-N, or H-F
  (2) need H-bond acceptor:
  O, N or F
- About 10 times stronger than other intermolecular forces

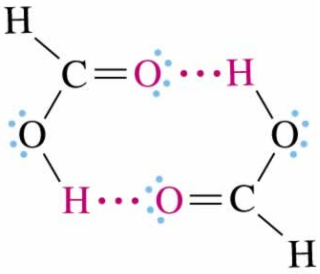
hydrogen fluoride



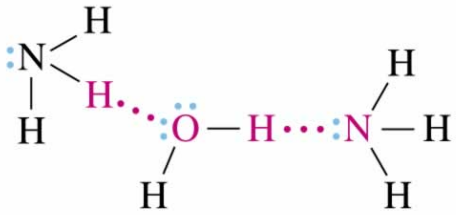
water–ethanol



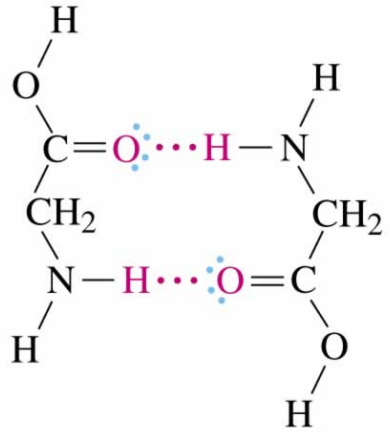
salicylic acid



formic acid



ammonia–water



glycine
(an amino acid)

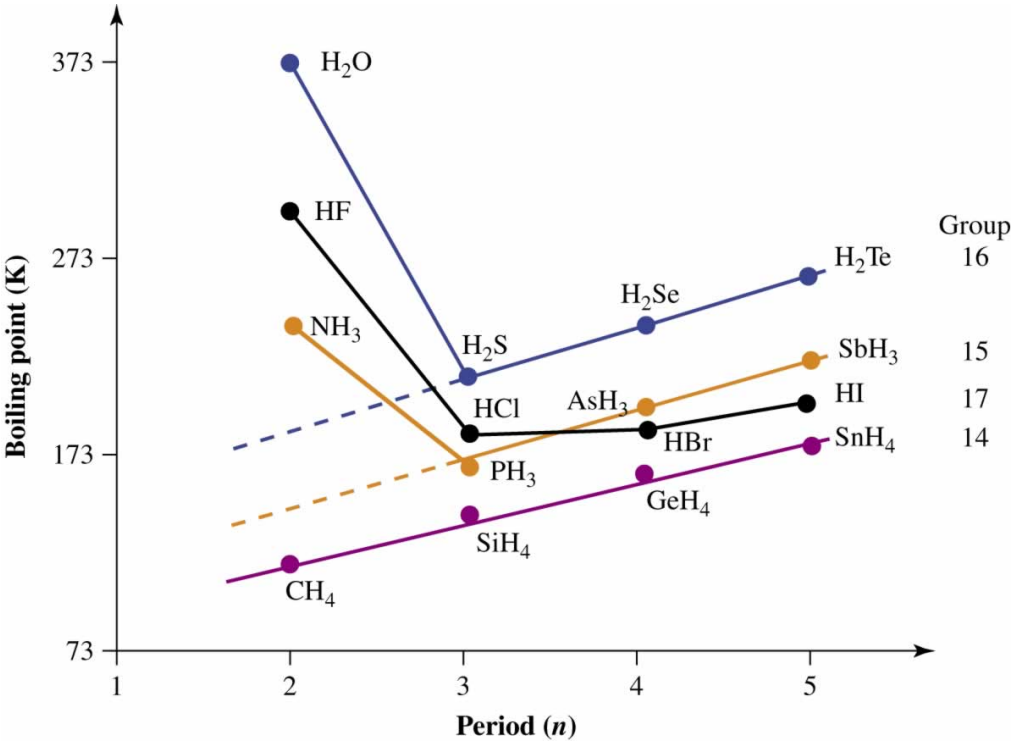
Hydrogen bonding

- If present, H-bonding dominates in determining molecular properties like m.p and b.p. :
  - e.g. Strong H-bonding is responsible for the high boiling points of NH_3, H_2O and HF versus other hydrides in their groups of the periodic table, which have only the weaker dispersion and permanent dipole attractions.

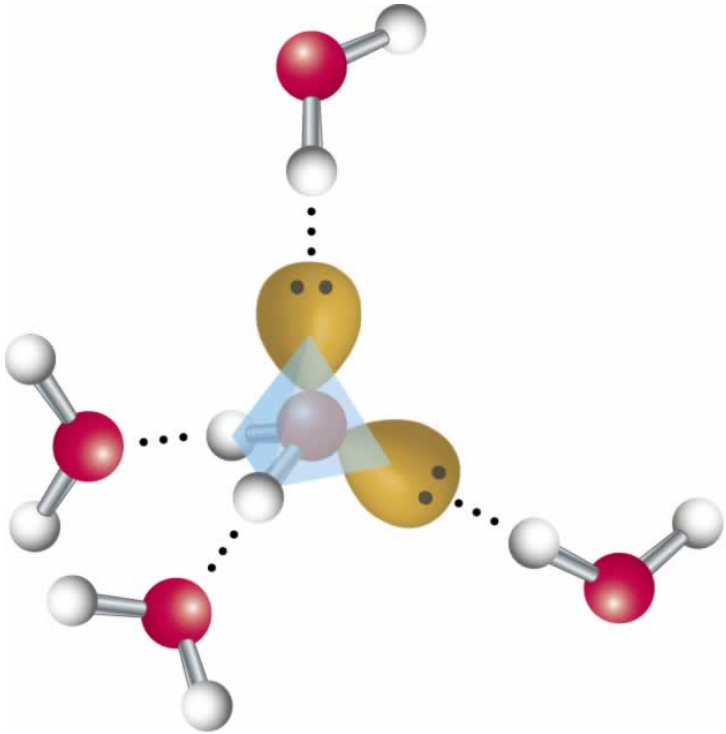
- H-bonds are often drawn as a dotted line, thus: a <u>single</u> H···F hydrogen bond is stronger than a <u>single</u> H···O one, but the b.p. of H_2O is higher (100°C) than HF (b.p. 19°C) because the average ratios of H atoms to lone pairs are 2:2 in H_2O and 1:3 in HF.

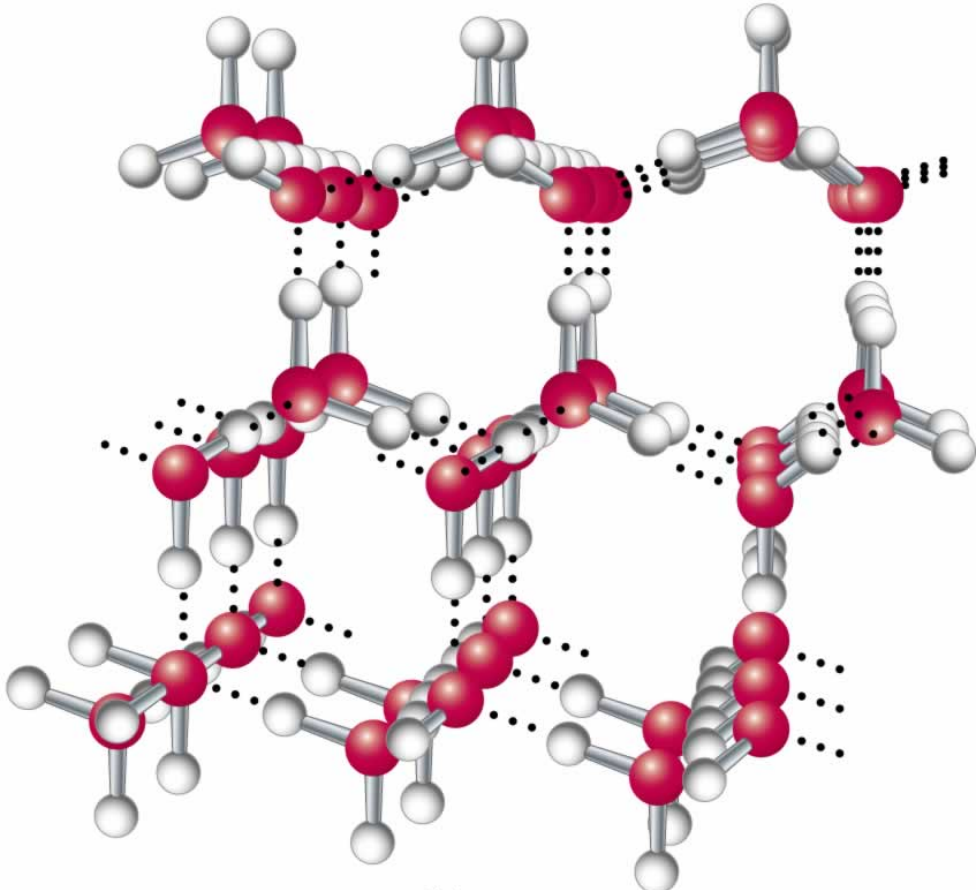
- Therefore, each H_2O molecule can form <u>more</u> hydrogen bonds <u>on average</u>, and has the greater overall intermolecular forces.

- Note that NH_3 has a mismatch of H atoms to lone pairs of 3:1 and N is less electronegative than F and O. Thus, the NH_3 b.p. is -33°C, due to the <u>weaker</u> and <u>fewer</u> (on average) H bonds.



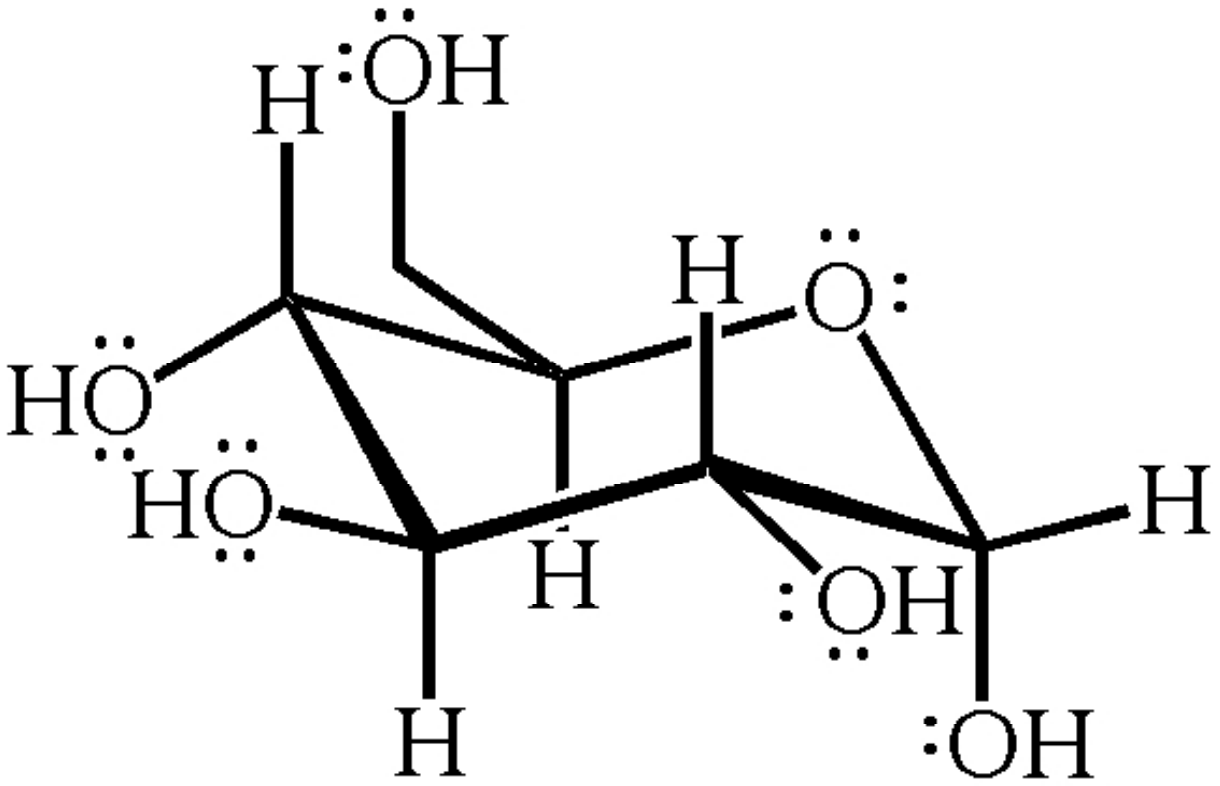
There is extensive H-bonding in ice





Molecules that bear lots of hydrogen-bonding groups are very soluble in water

- Glucose solubility ~ 770 g L^{-1}



glucose

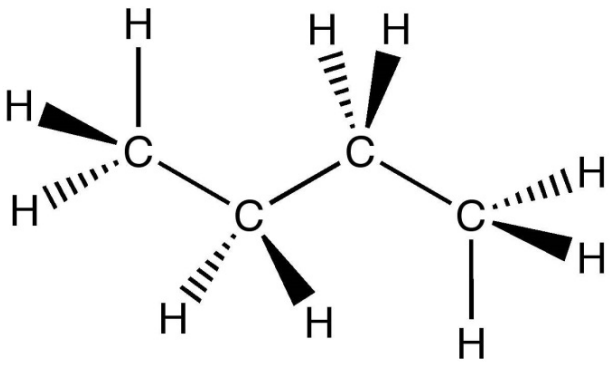
Example

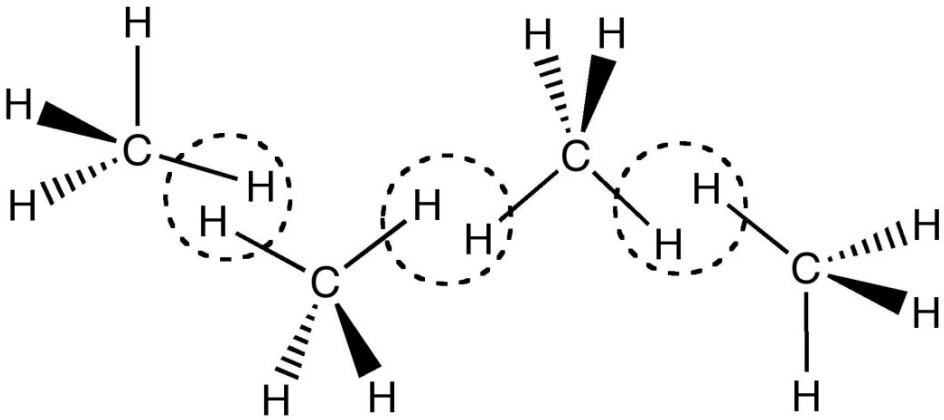
Complete the following table by ticking the appropriate boxes to indicate the types of intermolecular forces acting between molecules in each of the compounds.

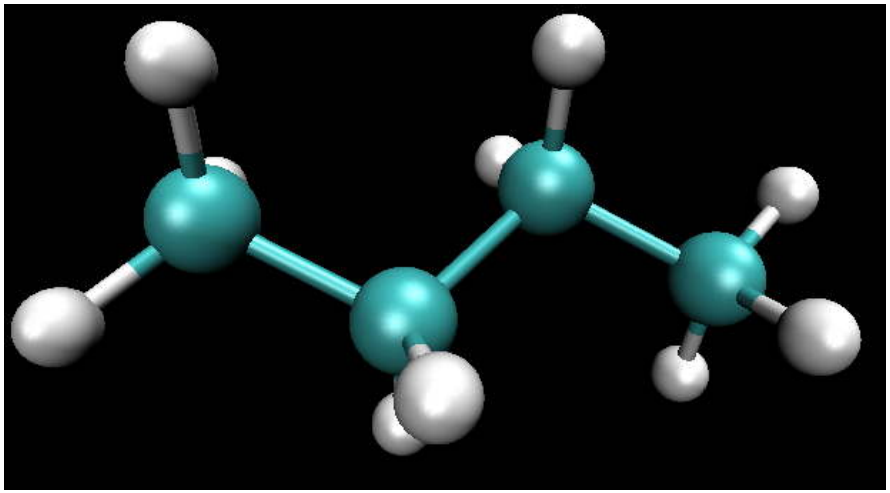
	Dispersion forces	Dipole/dipole forces	Hydrogen bonding
$CH_3CH_2CH_2CH_3$			
H_2NCH_2COOH			
$CH_3CH_2OCH_3$			
$CH_3CH_2CH_2OH$			

- All of the molecules will have dispersion forces between them.
- Dipole-dipole forces are present if the molecule has a net molecular dipole arising from polar bonds and an unsymmetrical shape (VSEPR).
- Hydrogen-bonding is present when all the requirements are met:
  —Y···H—Y' (where Y & Y' = any of O, N or F)

Butane (RECAP)

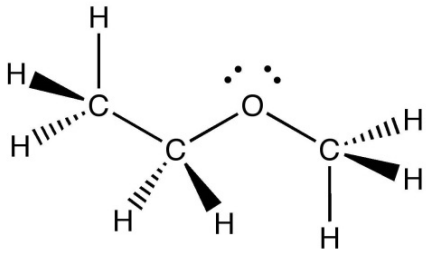


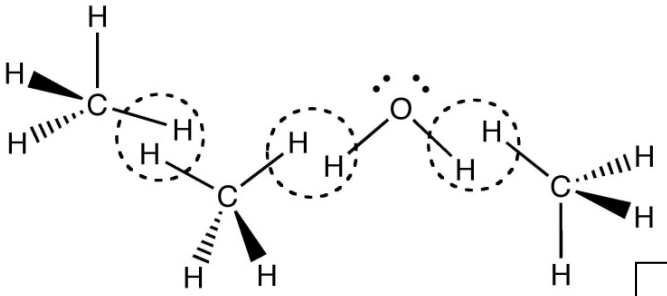


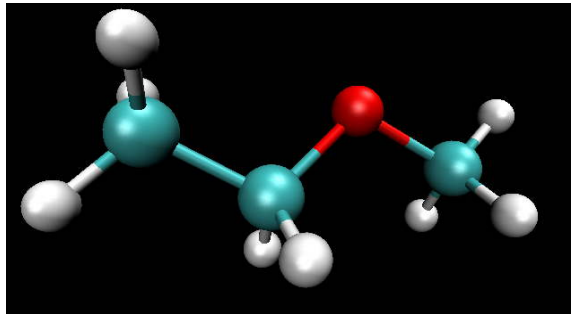


- The structure of butane can be <u>imagined</u> as consisting of CH_4 molecules linked together.
- Thus, each C centre in butane is tetrahedral (and non-polar), as each CH_4 molecule is tetrahedral.
- The lack of polar bonds in butane means there are no dipole/dipole forces between molecules.
- No parts of butane consist of N, F or O atoms with attached lone pairs or –H atoms capable of hydrogen-bonding.

Ethylmethylether $CH_3CH_2OCH_3$

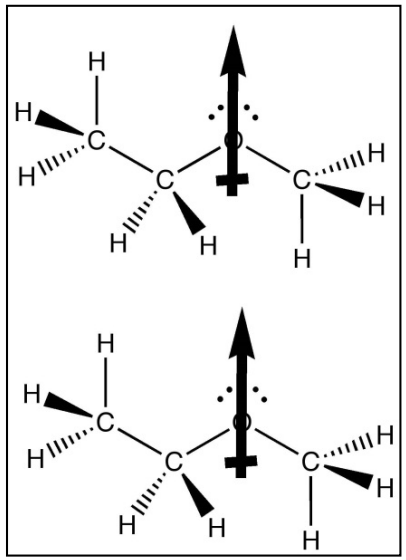






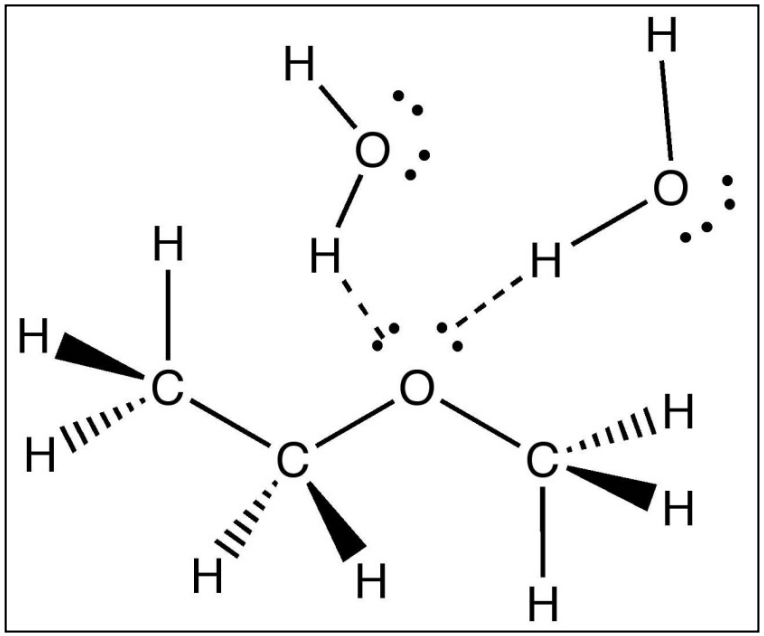
Model of $CH_3CH_2OCH_3$

dipole-dipole bonding



- The structure of ethylmethylether can be <u>imagined</u> as consisting of three CH_4 molecules linked together with one H_2O.
- The O centre is bent (and polar), as the O has two lone pairs and two bonding pairs.
- Therefore, there are dipole/dipole forces between molecules.

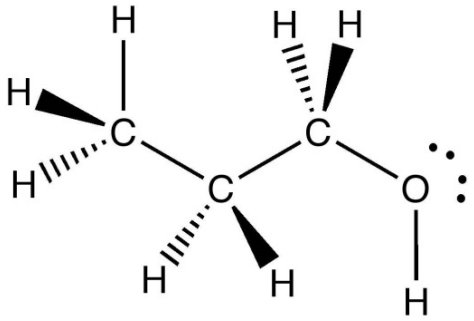
Ethylmethylether $CH_3CH_2OCH_3$

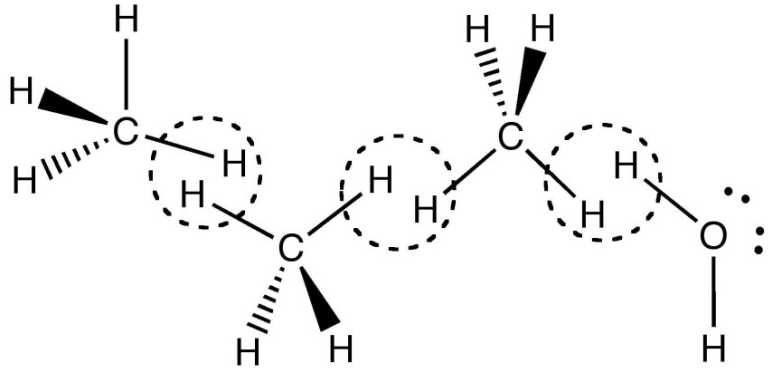


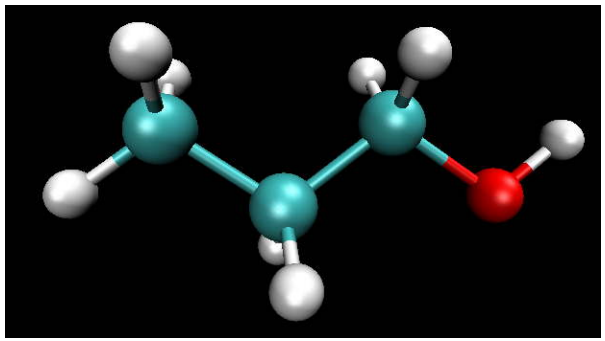
$CH_3CH_2OCH_3$ hydrogen-bonding to H_2O

- Ethylmethylether has an O atom with lone pairs that can accept an H-bond, but it does not have any H-atoms that are bound to O, N or F to fulfill the requirement for H-bonding.
- Ethylmethylether **<u>cannot</u>** hydrogen-bond between molecules of its own type.
- Ethylmethylether can hydrogen-bond to H_2O and it is soluble in water

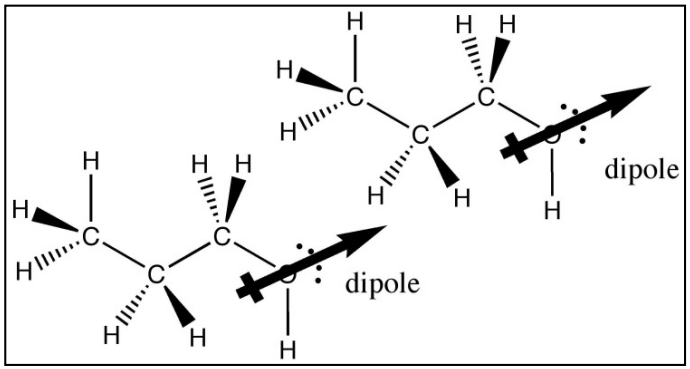
Butanol $CH_3CH_2CH_2CH_2OH$



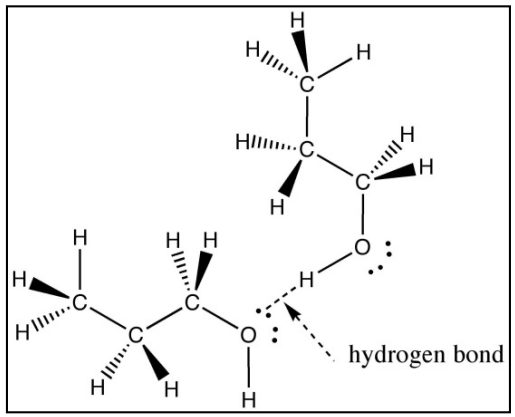




Molecular model of butanol



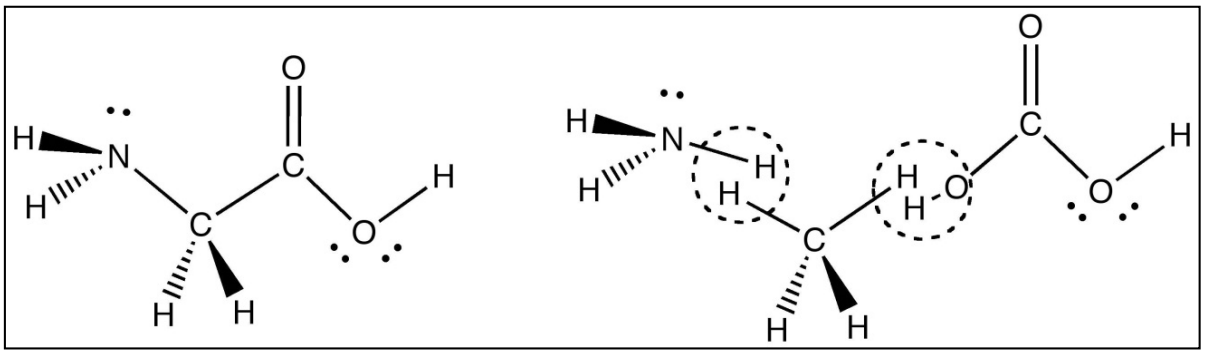
dipole-dipole bonding



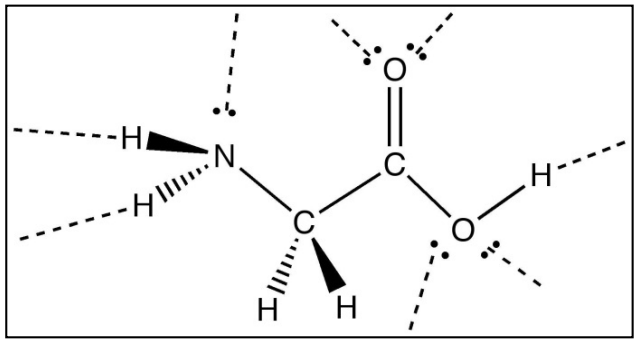
hydrogen-bonding to another molecule of itself

- There are dipole/dipole forces between molecules
- Butanol has an O atom with attached lone pairs AND an O-H linkage that can H-bond.
- Butanol can hydrogen-bond between molecules of its own type (and to other suitable molecules)
- Butanol can H-bond to H_2O and is soluble in water

Glycine $NH_2CH_2CO_2H$



Glycine $NH_2CH_2CO_2H$



hydrogen-bonding possibilities

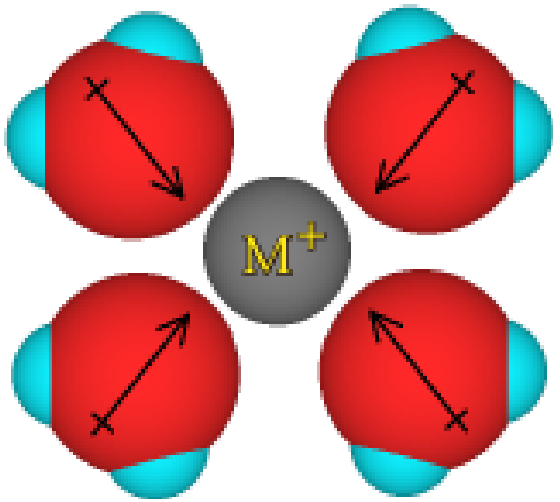
- Glycine can be <u>imagined</u> as consisting of NH_3 , CH_4 and H_2CO_3 molecules linked together.
- It has dipole-dipole bonding owing to its polar bonds.
- Its bonding is dominated by its extensive hydrogen-bonding by N and O lone pairs and N–H and O–H bonds.

Related forces

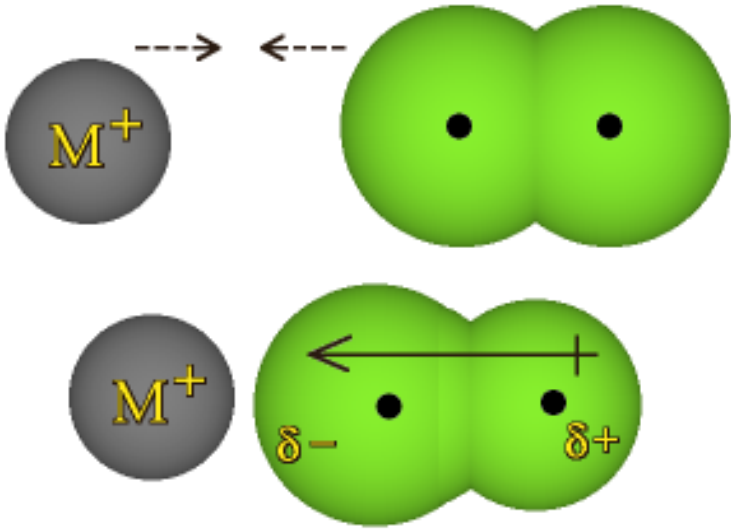
In addition, there exist ion-molecule intermolecular forces, which are related to the types discussed above.

1. **Ion-dipole:** A cation or anion has a charge that can attract the negative (δ–) or positive (δ+) end of a molecule that has a permanent dipole. This is one of the reasons why many ionic substances are quite soluble in strongly polar liquids like H_2O.

2. Ion-induced dipole: The charge of an ion can attract or repel electrons, and thereby induce a temporary dipole into a nearby molecule that is normally non-polar (this effect is discussed above, in relation to dipersion forces). The induced dipole on the molecule then enhances the charge attraction between the two species.



Ion-dipole bonding.



Ion - induced dipole.

Relative magnitude of forces

- For each of the types of forces there is considerable variation in strength, depending upon which atoms are involved.
- Points to note are:

1. Ionic, covalent and metallic forces are of similar strength — and they are generally much stronger than the van der Waals forces.
2. Of the van der Waals forces, hydrogen bonding is strongest (especially for small molecules):- If present between small molecules, it has a dominant effect in determining molecular properties (m.p., b.p.).

Type of Force	Strength (kJ/mol)	Examples
ionic	400-4000	NaCl, MgO
covalent	150-1100	Cl_2, CH_4
metallic	75-1000	Na, W, Pt, Hg
ion-dipole	40-600	$H_2O \cdots Na^+$
hydrogen bond	10-40	$H_2O \cdots HF$
ion-induced dipole	3-15	$Fe^{2+} \cdots O_2$
dipole-dipole	5-25	$CHCl_3 \cdots CHCl_3$
dipole-induced dipole	2-10	$H_2O \cdots Xe$
dispersion forces	0.05-40	Ar ⋯ Ar

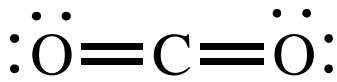
Example 1

State which species of the following pairs will have the higher boiling point, and explain why.

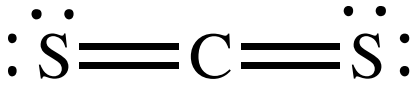
(a) Ne or Kr; (b) CO_2 or CS_2; (c) CH_4 or Cl_2; (d) F_2 or LiF; (e) NH_3 or PH_3

(a) Ne and Kr have only dispersion forces between their molecules (atoms). They have a similar shape, so the number of their electrons (which determines their polarisabilities) will determine that the b.p. Kr will be higher.

(b) Lewis/VSEPR structures of CO_2 and CS_2 show them to both be linear molecules, which will have no permanent dipole moments. They will have only dispersion forces between their molecules. CS_2 has more electrons, will be more polarisable, and will have the higher b.p.



22 electrons
b.p. –78 °C (sublimes)



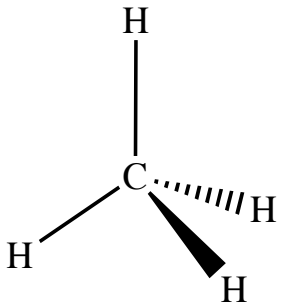
42 electrons
b.p. 46 °C

Example 1 continued…

State which species of the following pairs will have the higher boiling point, and explain why.

(a) Ne or Kr; (b) CO_2 or CS_2; (c) CH_4 or Cl_2; (d) F_2 or LiF; (e) NH_3 or PH_3

(c) Lewis/VSEPR structures of CH_4 and Cl_2 show that they have no permanent dipole moments. They will have only dispersion forces between their molecules. Cl_2 has more electrons, will be more polarisable, and will have the higher b.p.



electrons = 10

electrons = 34

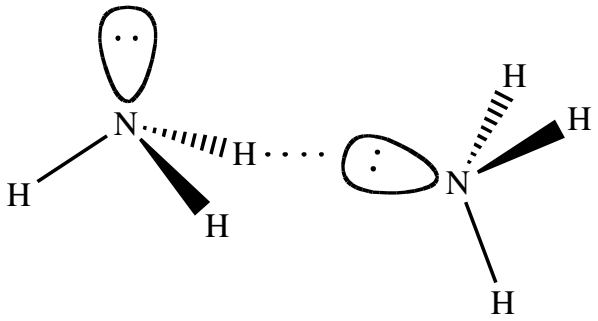
(d) LiF is ionic (ΔEN = 3) and will have strong ionic forces between the ions. Its b.p. will be much higher than that of F_2, which is a non-polar molecule having only weak dispersion forces between molecules.

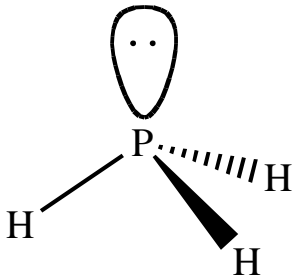
Example 1 continued…

State which species of the following pairs will have the higher boiling point, and explain why.

(a) Ne or Kr; (b) CO_2 or CS_2; (c) CH_4 or Cl_2; (d) F_2 or LiF; (e) NH_3 or PH_3

(e) Lewis/VSEPR structures of NH_3 and PH_3 show them to both be pyramidal molecules, each with a permanent dipole moment. There will also be dispersion forces between their molecules, which should be stronger for PH_3, as it has more electrons. Despite this, NH_3 will have the higher b.p. because its molecules can form hydrogen bonds: these are stronger than the other types of intermolecular forces.





Example 2

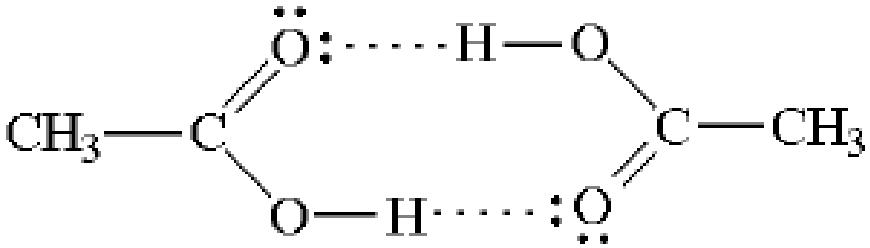
From measuring the change in the freezing point of benzene, when a certain amount of acetic acid (CH_3CO_2H) is dissolved in it, the molecular weight of the acetic acid can be calculated (covered later in course).

The calculation shows the apparent molar mass of the acetic acid to be 120 g mol^{-1}.

Account for this unexpected finding in terms of bonding.

The molar mass calculated for CH_3CO_2H is 60 g mol^{-1}.

The experimentally determined molar mass of 120 g mol^{-1} indicates that two units of CH_3CO_2H are bonded together quite strongly in the benzene solution – so that the dimer formed is essentially behaving as a stable molecule



CH_3CO_2H is molecular in nature; it can have dispersion forces, dipole-dipole forces, and hydrogen-bonding between its molecules.
The latter force is the strongest of the intermolecular forces – so it is most likely to account for the strong intermolecular bonding.

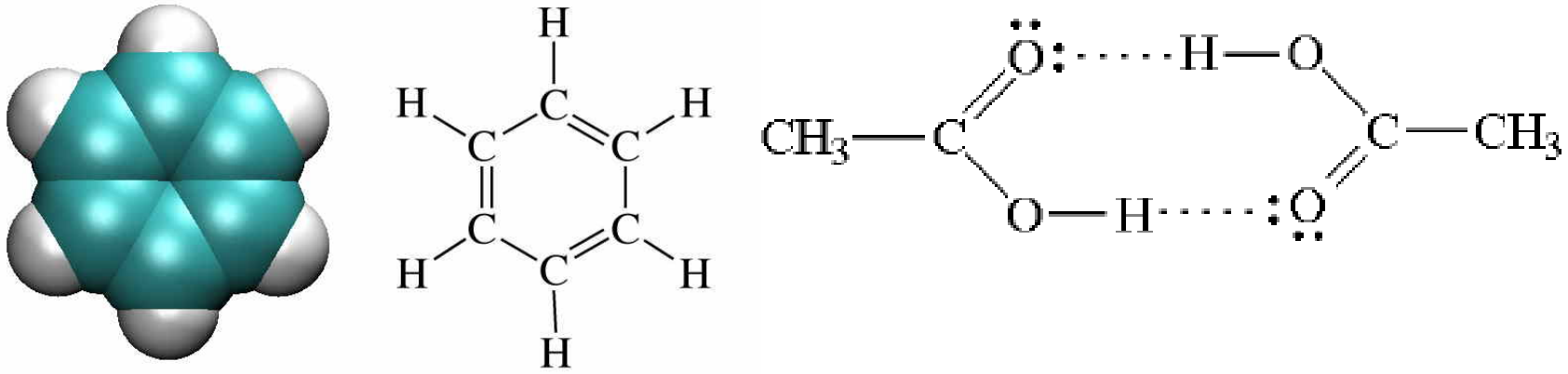
Moreover, the geometry of CH_3CO_2H permits the formation of TWO hydrogen bonds between a pair of CH_3CO_2H molecules (see diagram) – and this feature would explain the unusual stability of the dimer.

Example 2 Continued…

From measuring the change in the freezing point of benzene, when a certain amount of acetic acid (CH_3CO_2H) is dissolved in it, the molecular weight of the acetic acid can be calculated (covered later in course).

The calculation shows the apparent molar mass of the acetic acid to be 120 g mol^{-1}.

Account for this unexpected finding in terms of bonding.



Structure of benzene. Bonding between benzene and acetic acid can only be through weak dispersion forces. Benzene cannot provide hydrogen-bonding.

Question:

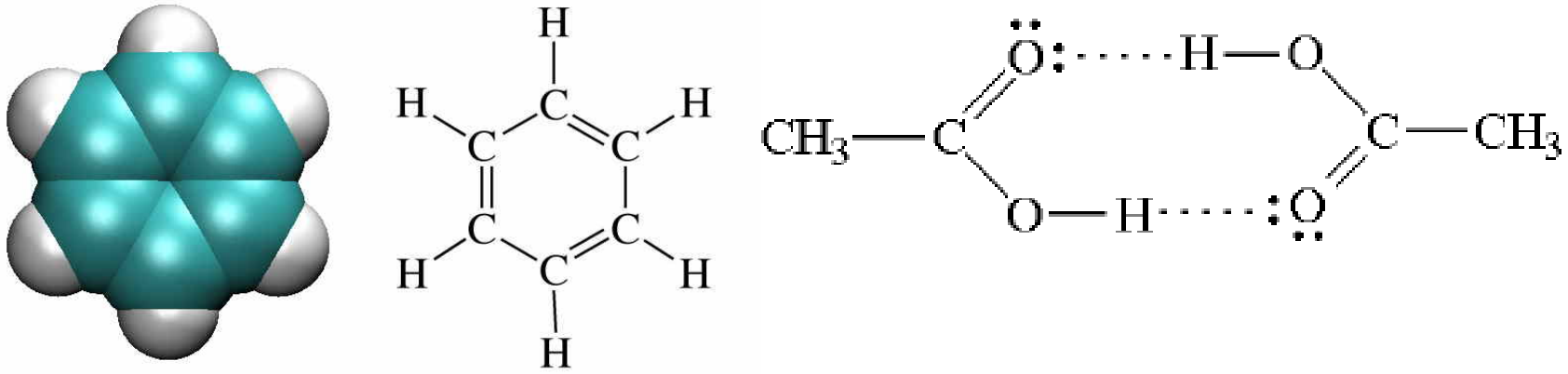
What would be the structure of acetic acid if you dissolved it in water instead of benzene?

Example 2 Continued…

From measuring the change in the freezing point of benzene, when a certain amount of acetic acid (CH_3CO_2H) is dissolved in it, the molecular weight of the acetic acid can be calculated (covered later in course).

The calculation shows the apparent molar mass of the acetic acid to be 120 g mol^{-1}.

Account for this unexpected finding in terms of bonding.



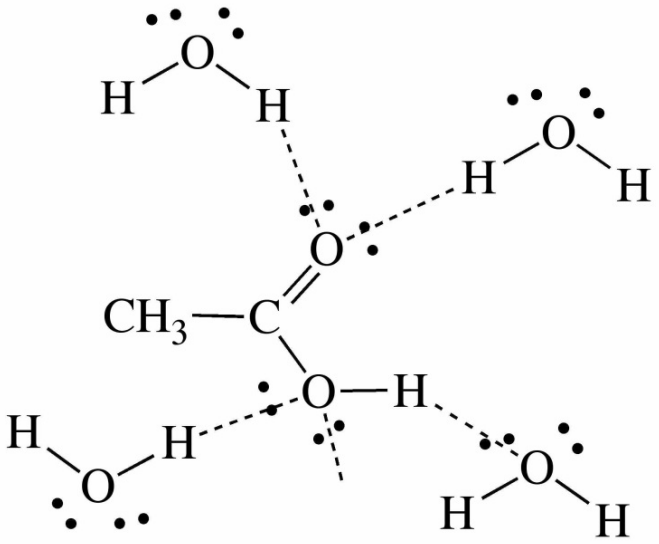
Structure of benzene. Bonding between benzene and acetic acid can only be through weak dispersion forces. Benzene cannot provide hydrogen-bonding.

Question:

What would be the structure of acetic acid if you dissolved it in water instead of benzene?

Example 2 Continued…

Water molecules can hydrogen-bond with acetic acid – so it would exist as single molecules in water solution.



CHEM1011 INTERMOLECULAR FORCES LECTURE 2

Dr Alex Donald (w.donald@unsw.edu.au;
Dalton 221)

IM Forces: Weeks 6-7

Content	Blackman Book	Learning Objectives
Intermolecular forces Dipole-dipole, dispersion forces, hydrogen bonds	6.7, 6.8	Identify the types of intermolecular forces present between particular species Relate the strength of intermolecular forces to properties such as dipole moment and polarizability
Deviations from ideal gas laws; van der Waals equation; a and b constants		Use the van der Waals equation to calculate the pressure of a non-ideal gas Explain the origin and size of *a* and *b* constants
States of matter. Comparison of properties of solids, liquids, and gases; Solids – types (atomic, molecular, ionic, metallic, network, crystalline vs amorphous) Liquids – general description; viscosity and surface tension	7.1-7.3	Classify solids as ionic, molecular, or metallic based on their properties Relate viscosity and surface tension to intermolecular forces
Properties of solutions; energy changes on dissolution, solubility, 'like dissolves like', Raoult's law, ideal and non ideal solutions; positive and negative deviations from Raoult's law. Distillation.	10.1, 10.3 10.5	Understand the process of dissolution at the molecular level Predict the relative solubility of a substance in a range of solvents

Gases

In liquids and solids the forces between molecules are reasonably strong, and the molecules are close together – so these phases are poorly compressible.

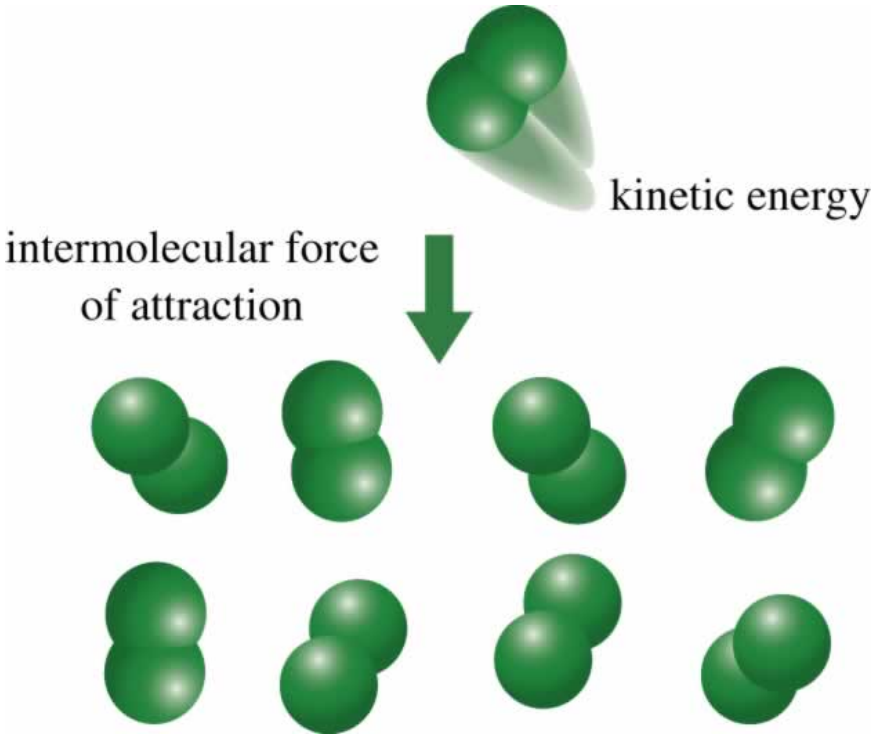
In gases the intermolecular forces are almost all broken (such forces only act momentarily upon the collision of gas molecules), and the large distances between gas molecules make gases quite compressible.

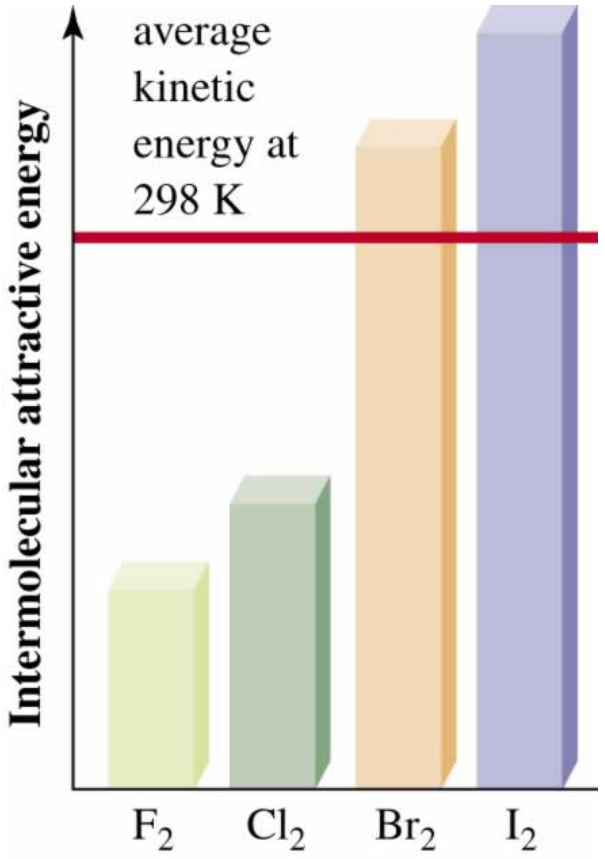
Properties of gases are:

- gases expand to fill their container
- gases have low densities
- gases are very compressible: the density of a gas depends very much on the applied pressure
- gas density depends very strongly on temperature: gases expand and contract markedly in response to temperature changes
- gases have low viscosities: gases offer little resistance to flow
- gases are always miscible: any gas will mix completely with another gas
- gases have low thermal conductivity

Intermolecular forces (RECAP)

"A substance exists in a condensed phase (solid or liquid) when its molecules have too little average kinetic energy to overcome intermolecular forces of attraction"





Remember the ideal gas law?

Studies of gases performed in the 1600's to 1700's showed that all gases closely followed two laws:

Boyle's law: $V \propto 1/P$ (constant T, n)

Charles' law: $V \propto T$ (constant p, n)

where V is the volume of a gas sample, T is its (absolute) temperature, p is its pressure.

In the 1800's, during the development of the atomic theory of matter, a third proportionality was added:

Avogadro's principle: $V \propto n$ (constant T, p)

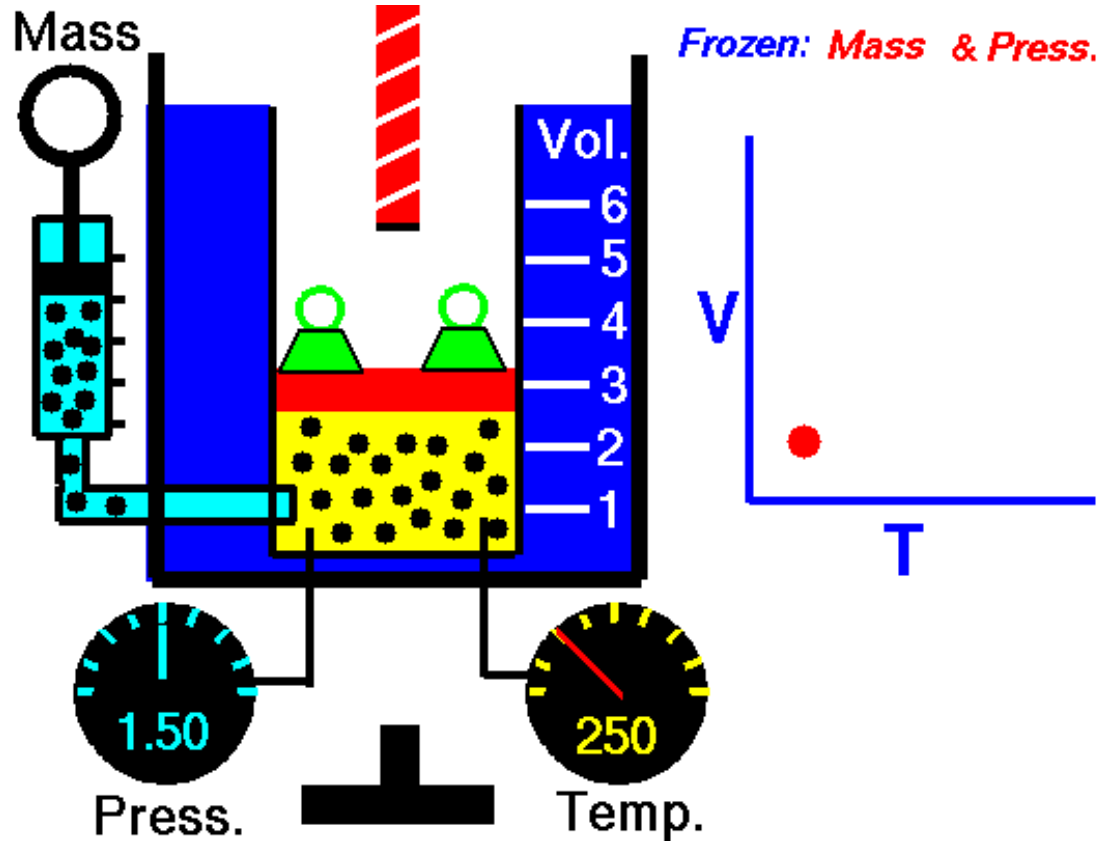
where n is the amount of gas (in moles).

Combining these expressions gives $V \propto n \times T / p$ which is commonly expressed as:

$$pV = nRT$$

which is the ideal gas equation. The numerical value of the ideal gas constant, R, depends on the units chosen to express it: $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1}$. Choose the value of the gas constant appropriate to the units in the problem at hand.

Charle's Law: $V \propto T$ (constant p, n)



http://en.wikipedia.org/wiki/File:Charles_and_Gay-Lussac%27s_Law_animated.gif

Theory of gas properties

The ideal gas equation can be derived theoretically from the kinetic molecular theory of gases. This theory is built on three assumptions about the molecular nature of gases.

1. A gas consists of particles in constant motion, and the collisions of these particles with the walls of the vessel produces the observed gas pressure.

2. The particles have negligible volume – the distance between them is so large compared to the size of the particles they can be treated as point objects.

3. Collisions between the particles are elastic, no energy is lost in such collisions and there are no forces between the particles.

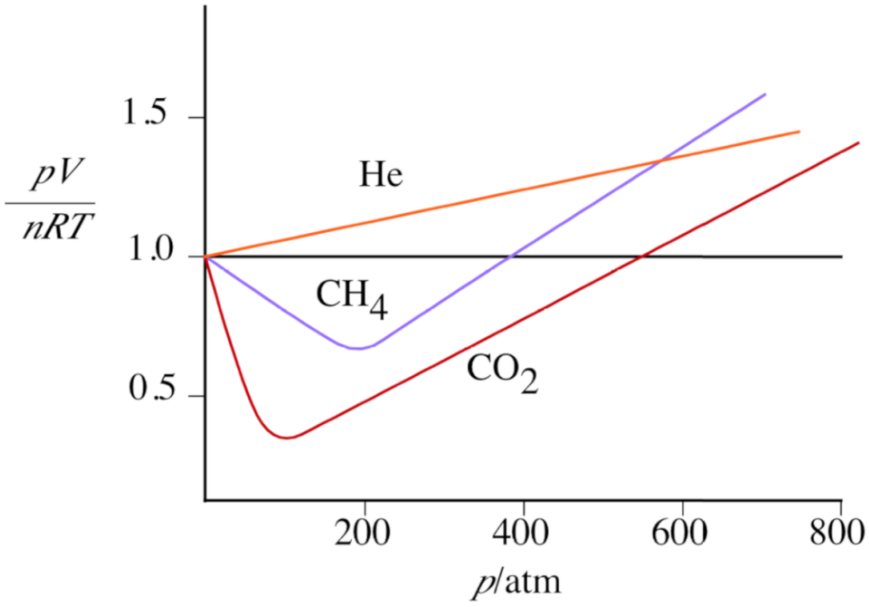
Although most gases closely obey the ideal gas equation at pressures around 1 atm and temperatures around 273 K, at high pressures and/or low temperatures their behaviour may deviate significantly. Extreme conditions of temperature and pressure are often found in industrial chemical plants and it is important to be able to predict the behaviour of gases under these conditions.

Deviations from ideality

According to the ideal gas equation, the ratio pV/nRT should equal 1. However a graph of pV/nRT (below, calculated from measured values of pressure and volume at 273 K) versus pressure shows significant deviations at pressures above 10 atm.

At low pressures (around 1 atm) the distances between the molecules are so large that the assumptions in the ideal gas equation apply accurately. At higher pressures (200 to 400 atm) the average distance between molecules is smaller and **intermolecular forces attract** the molecules to each other and reduce the pressure exerted by the molecules on the walls of the vessel. From some gases (*e.g.* helium) the attractive intermolecular forces are so weak that pV/nRT is never < 1.

At very high pressures the attractive forces are replaced by repulsive forces as the average distance between the molecules is decreased. This effect is usually referred to as being due to **molecular volume** and it causes the observed volume of the gas to be larger than that predicted by the ideal gas equation.



Deviations from ideality

Two modifications to the ideal gas equation allow it to incorporate these effects. The pressure term is increased by a factor and the volume is decreased. The resulting equation is called the **van der Waals equation**:

$(p + a(n/V)^2)(V - nb) = nRT$

The values of *a* and *b* are different for different gases and have been determined experimentally and tabulated.

For the non–polar molecules in the table note the correlation between *a*, *b* and molecular volume. For an ideal gas $a = 0$ and $b = 0$.

Gas	a / atm L^2 mol^{-2}	b / L mol^{-1}
Ne	0.211	0.0171
Ar	1.35	0.0322
Xe	4.19	0.0511
H_2	0.244	0.0266
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CH_4	2.25	0.0428
H_2O	5.536	0.0305

Deviations from ideality

One way of interpreting the van der Waals equation is to treat the two terms on the left as being an 'ideal' pressure and an 'ideal' volume.

$$\left(p_{\text{real}} + a\left(\frac{n}{V_{\text{real}}}\right)^2\right) \times \left(V_{\text{real}} - nb\right) = nRT$$

$$p_{\text{ideal}} \times V_{\text{ideal}} = nRT$$

The term $a(n/V_{\text{real}})^2$ is always positive, so for conditions where intermolecular attraction is significant, p_{real} will always be less that p_{ideal}. In other words, the 'real' pressure needs to be corrected upwards to the value it would have if the intermolecular attractions were not present. If the molecules attract each other, as a molecule moves away from its neighbours to collide with the wall, its velocity is decreased by the attraction to the other molecules. This reduces the pressure compared to not having attractive forces between the molecules.

The *–nb* term is always negative, so for gases at high densities and temperatures where the repulsion between molecules is significant the 'real' volume of the gas will be larger than the 'ideal' volume and a negative correction is needed. In a real gas the molecules themselves occupy some space and *b* specifies how much space is occupied by a mole of molecules.

Deviations from ideality

Example: A pressure cylinder of volume 1 L contains 1 mole of xenon gas at 25°C. Calculate the pressure (P_{ideal}) assuming xenon is an ideal gas. Re-calculate the pressure (P_{vdW}) using the van der Waals equation. Compare the results.

$$PV = nRT, \therefore P_{ideal} = (1)(0.0821)(298)/1 = 24.5 \text{ atm.}$$

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{1^2(4.19)}{1^2}\right)(1 - 1(0.0511)) = 1(0.0821)(298)$$

$$(P + 4.19)(0.949) = 24.5$$

$$P_{vdW} = 25.82 - 4.19 = 21.63 \text{ atm.}$$

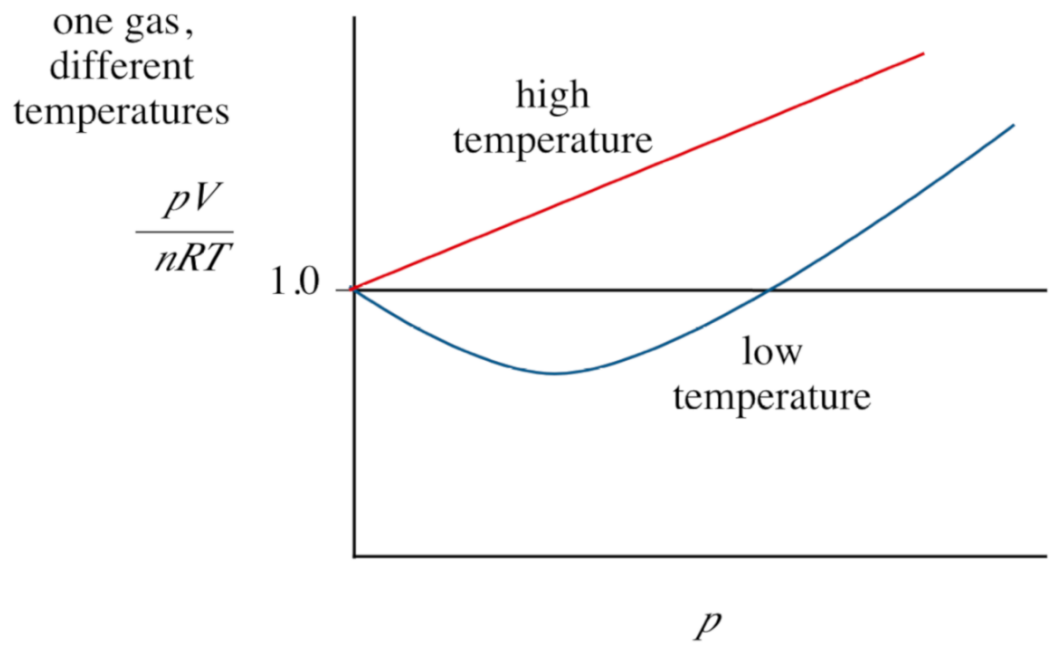
(P_{ideal} and P_{vdW} differ by about 12%).

Under these conditions the ideal gas equation predicts a pressure about 12% higher than the van der Waals equation. The average distance between molecules is large enough that the intermolecular forces attract them to each other (at very short distances they would repel), lowering the velocity with which they collide with the walls of the vessel and thus lowering the pressure. At much higher pressures, the pressure calculated from the ideal gas equation is lower than from the van der Waals equation.

Deviations from ideality

The two factors which cause deviations from ideality work against each other and, for a single gas, the factor which dominates depends on the temperature and density of the gas. At lower temperatures the average kinetic energy of the molecules is smaller than at higher temperatures. If the average kinetic energy is small compared to the intermolecular forces then it is possible for pV/nRT to be less than 1.

At higher temperatures the average molecular kinetic energy can be large compared to the intermolecular forces and the effect of molecular volume becomes dominant so that pV/nRT becomes greater than 1.



Deviations from ideality

Example for moderate temperature: compare the pressures calculated for 100 moles of Ar gas in a 12 L vessel at 300 K, using the ideal Gas Equation and the van der Waals equation.

The Ideal Gas Equation gives: $PV = nRT$,

$$P = \frac{nRT}{V} = \frac{(100)(0.0821)(300)}{12} = 205 \text{ atm}$$

The van der Waals equation:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{100^2 1.35}{12^2}\right)(12 - 100(0.0322)) = (100)(0.0821)(300)$$

$$P = 187 \text{ atm}$$

At the moderate temperature of 300 K, there is considerable intermolecular bonding during collisions of gas molecules. Thus, at any instant, the number of moles of particles (monatomics and momentary diatomics) is effectively less than 100 moles.

- Because *P* is proportional to *n*, the pressure of the real gas tends to be lower than ideal.
- On the other hand, the *P* is reasonably high, so intrinsic molecular volume is a significant fraction of the container volume – which would tend to raise the pressure.
- Overall, however, the bonding factor prevails at low temperature, and P_{real} is lower than P_{ideal}.

Deviations from ideality

Example at high temperature: Compare the pressures calculated for 100 moles of Ar gas in a 12 L vessel at 500 K, using the Ideal Gas Equation and the van der Waals equation.

The Ideal Gas Equation gives: $PV = nRT$,

$$P = \frac{nRT}{V} = \frac{(100)(0.0821)(500)}{12} = 342 \text{ atm}$$

The van der Waals equation:

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$\left(P + \frac{100^2 1.35}{12^2}\right)(12 - 100(0.0322)) = (100)(0.0821)(500)$$

$$P = 374 \text{ atm}$$

At the higher temperature of 500 K, the molecules have too much kinetic energy to form effective intermolecular bonds during collisions of gas molecules.

The pressure is quite high, and intrinsic molecular volume is a significant fraction of the total volume of the container. Thus, the actual volume of free space available for molecules to move in is somewhat less than the container volume, which tends to make the pressure higher (*n* moles in a smaller *V* gives higher *P*).

This second factor dominates at high *T*, so P_{real} is higher than P_{ideal}

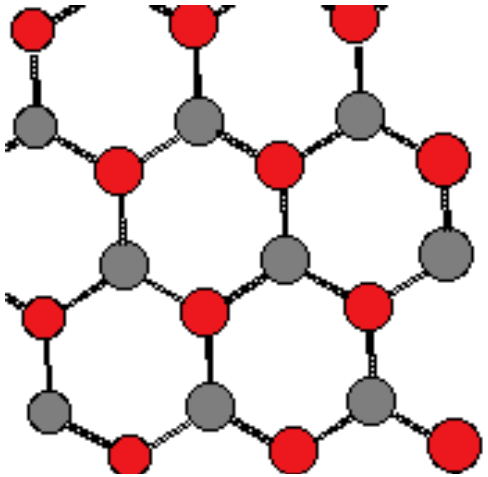
IM Forces: Weeks 6-7

Content	Blackman Book	Learning Objectives
Intermolecular forces Dipole-dipole, dispersion forces, hydrogen bonds	6.7, 6.8	Identify the types of intermolecular forces present between particular species Relate the strength of intermolecular forces to properties such as dipole moment and polarizability
Deviations from ideal gas laws; van der Waals equation; a and b constants		Use the van der Waals equation to calculate the pressure of a non-ideal gas Explain the origin and size of *a* and *b* constants
States of matter. Comparison of properties of solids, liquids, and gases; Solids – types (atomic, molecular, ionic, metallic, network, crystalline vs amorphous) Liquids – general description; viscosity and surface tension	7.1-7.3	Classify solids as ionic, molecular, or metallic based on their properties Relate viscosity and surface tension to intermolecular forces
Properties of solutions; energy changes on dissolution, solubility, 'like dissolves like', Raoult's law, ideal and non ideal solutions; positive and negative deviations from Raoult's law. Distillation.	10.1, 10.3 10.5	Understand the process of dissolution at the molecular level Predict the relative solubility of a substance in a range of solvents

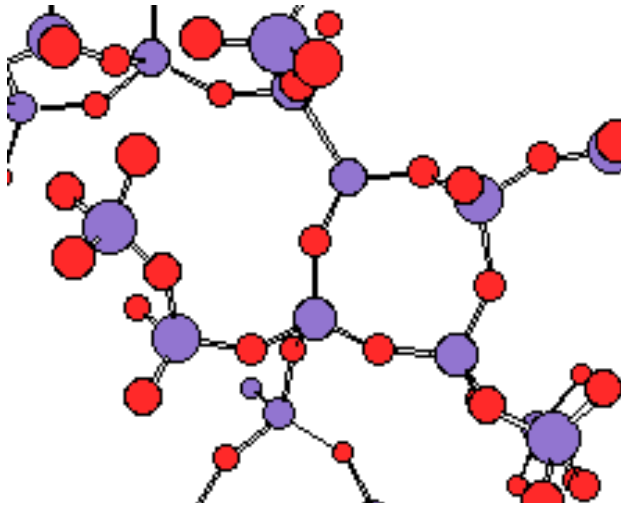
Solids

In general terms solids are substances with a fixed shape, with high density, low compressibility.

These macroscopic properties arise due to strong bonding on the microscopic scale. The bonded atoms can have a regular arrangement within molecules, and the molecules may then pack in a regular array to form a crystalline solid. A crystalline solid can also result from a long range strong bonding (covalent or ionic) of atoms. Non-crystalline amorphous solids result from a disordered network of strongly bonded atoms.



Crystalline solid.



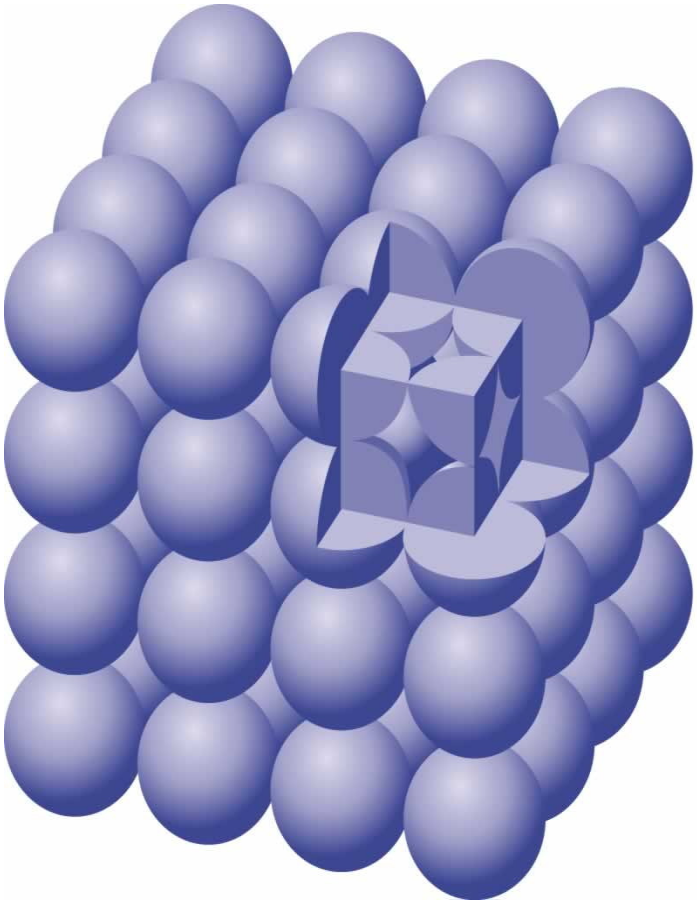
Amorphous solid.

The different chemical and physical behaviours of solids can be understood from the properties of the atoms and the bonding in the solid.

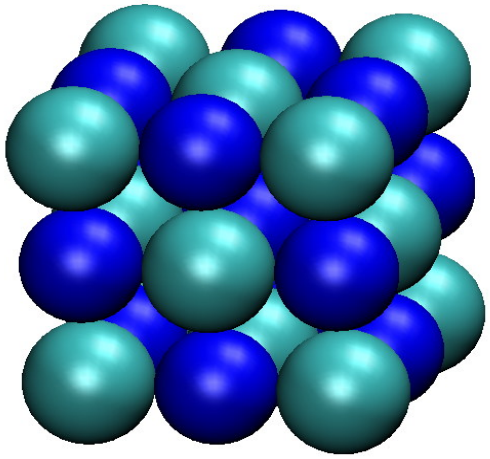
Types of solids

Atomic solids: Consist of individual atoms packed in a regular crystalline array with relatively weak dispersion forces between the atoms. Only the noble gases like Kr, Ar, Xe form crystalline atomic solids at low temperatures

Metallic solids: Atoms with a low 1st ionisation energy (i.e. metals) pack in arrays similar to atomic solids — but their valence electrons are free to move (delocalise) throughout the metal mass. Metallic bonding is very strong. Metallic solids are generally found in the s-block, transition metals, and the lower members of the p-block.

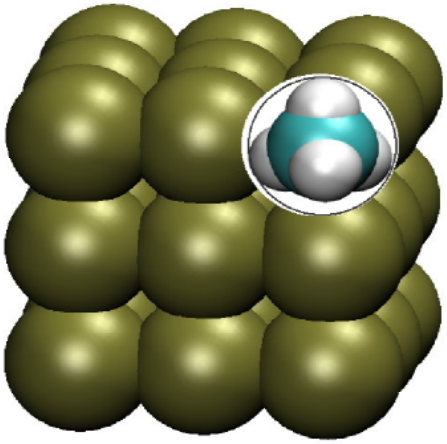


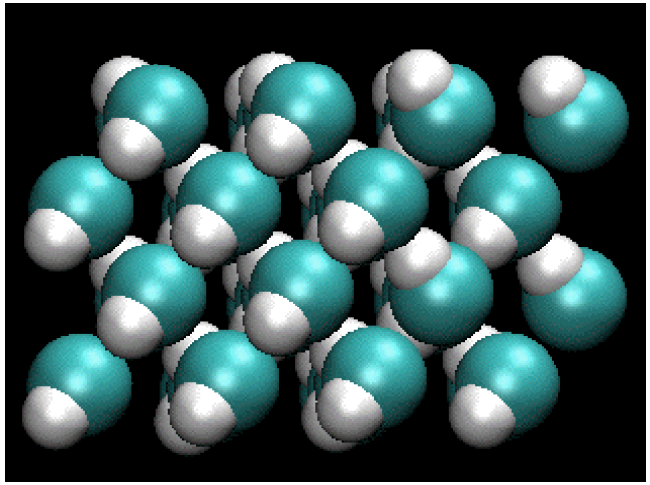
Types of solids

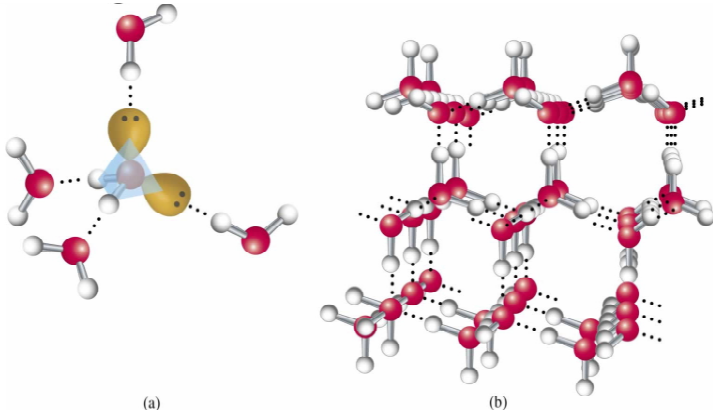


Ionic solids: Generally formed by ions, which result from atoms that have very different electronegativities — typically a metal and a non-metal. e.g. NaCl, $MgSO_4$, $BaCl_2$.

Molecular solids: Molecules containing atoms joined together by strong covalent bonds may be held together in regular arrays by intermolecular forces: dispersion, dipole-dipole and/or hydrogen bonding.

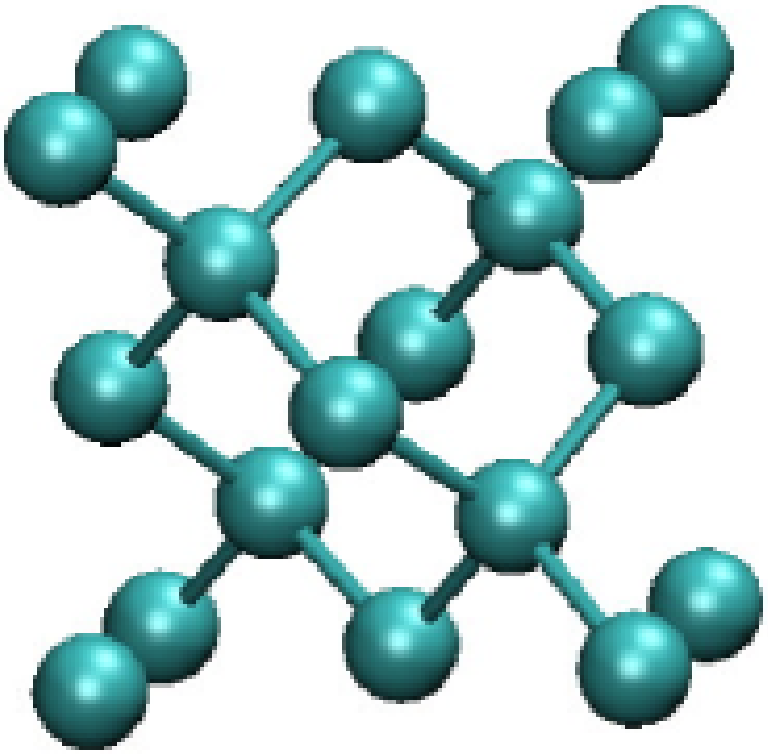


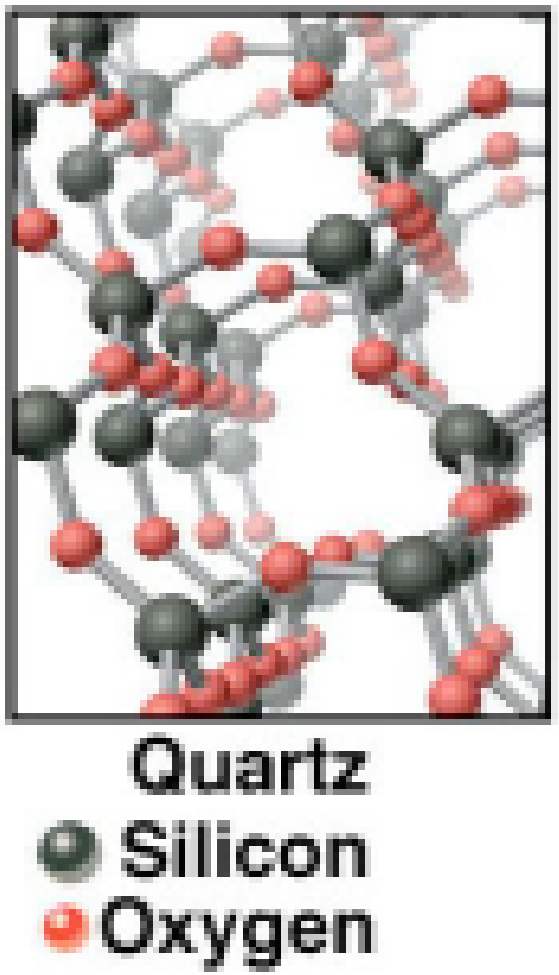




Types of solids

Network covalent solids: Atoms are linked by strong covalent bonds in an extensive three-dimensional network, through the whole solid. e.g. quartz (SiO_2) diamond (C).





Bonding in different solids

The different physical properties of solids can be understood from their different types of bonding

Solid Type	Hardness	Melting point	Thermal conductivity	Electrical conductivity
Atomic	soft	low	low	low
Metallic	variable. malleable, ductile	variable	high	high
Ionic	hard, brittle	high	low	low
Molecular	soft	variable with M.W., bonding type.	low	low
Network covalent	very hard	very high	usually low	usually low

The strong covalent bonds in network covalent solids need to be broken to melt or break the solid. Thus they are hard and have high melting points.

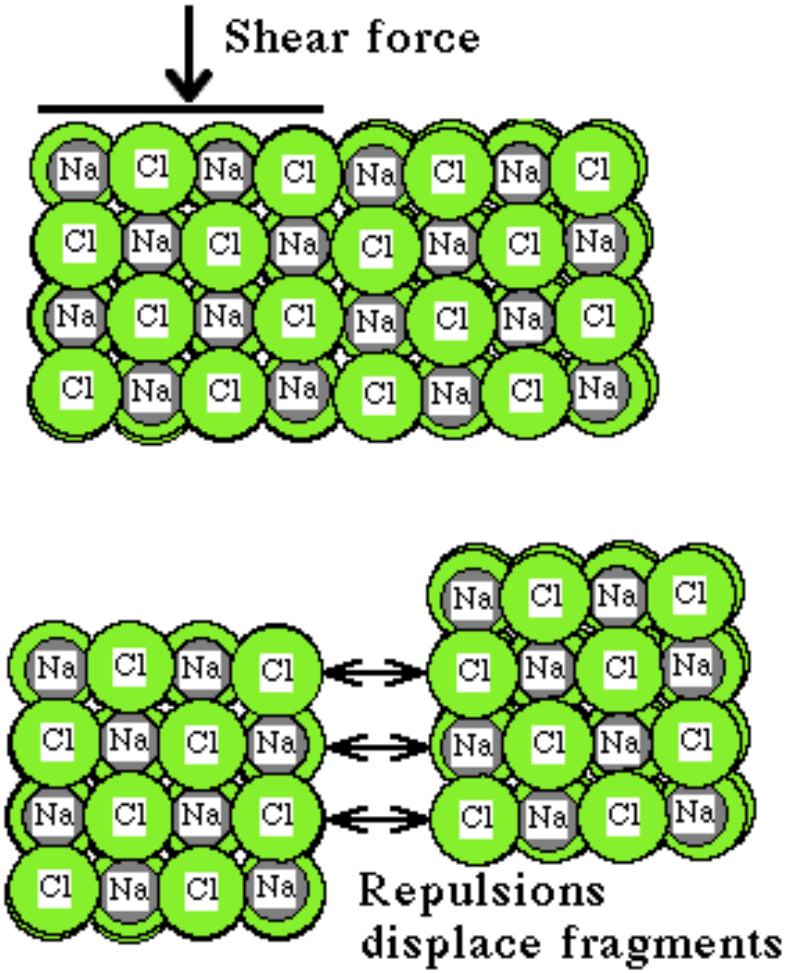
To melt or break a molecular solid requires intermolecular forces to be broken. The size of the molecule, surface area of contact, and type of intermolecular force (H-bonds strongest) affect the melting point – but it is generally low for small molecules.

Bonding in different solids

The breaking of ionic solid by shear forces momentarily brings together ions of like charge – making ionic solids brittle

The only solid with mobile charge carriers is the metal, with its mobile sea of electrons, so it is the only good electrical conductor. The mobile electrons also give good thermal conductivity.

Crystalline solids have long-range order, owing to the regular, extended, packing of its atoms or molecules. This long-range order is manifest on the large scale in the shapes of crystals formed by different ion packing modes.



Liquids

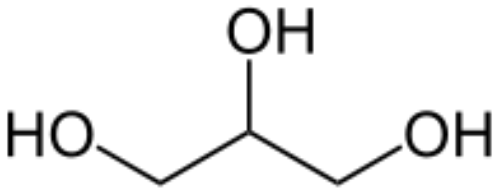
In a **liquid** the kinetic energy of the particles is comparable to the strength of the intermolecular forces. This means the particles are not bound to a particular location – they are mobile, and this is what makes a liquid able to flow. This also makes understanding and modeling liquids more difficult than solids (where intermolecular forces completely restrict particle motion) and gases (where intermolecular forces can almost be neglected).

Macroscopic (large scale) properties:
- no fixed shape, can flow, relatively high density, difficult to compress
- have a surface and surface tension

Microscopic (small scale) properties:
- particles are mobile because the thermal energy of the particles is comparable to the strength of the intermolecular forces
- average distance between particles is larger than in solid
- short range order (there is a most probable number of nearest neighbors around any one particle), but no long range order

Properties of liquids

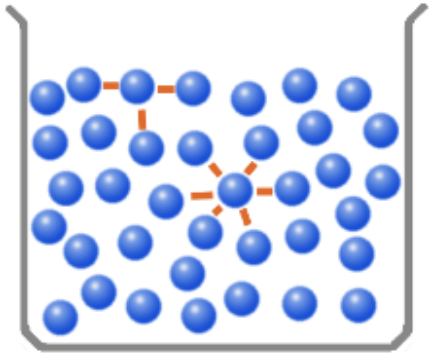
Viscosity is a measure of how poorly a liquid flows. A liquid has a high viscosity because its intermolecular bonds are strong and/or many. In order for a liquid to flow, the particles in the liquid have to move and to do so they must escape the attraction to neighbouring particles. Glycerol can form many hydrogen bonds to nearby molecules, and it has a high viscosity. H-bonding is the strongest of the intermolecular forces – so a molecule like glycerol (pictured) is very viscous because it can form a number of H-bonds between its molecules.



For example, honey has a higher viscosity than water (http://www.zeitnews.org/node/3350)

Properties of liquids

Surface tension is the resistance of a liquid to increase its surface area. Particles at the surface of a liquid are not surrounded on all sides by neighbouring particles. If a particle in the liquid is to be forced to the surface then some of the bonds to its neighbours must be broken. Thus it takes energy to expand the surface of a liquid (for example, by changing its shape).



Some insects can walk on water because if they broke the surface, the area of the surface would increase and the weight force of the insect is not large enough to do this.

CHEM1011 INTERMOLECULAR FORCES LECTURE 3

Dr Alex Donald (w.donald@unsw.edu.au;
Dalton 221)

IM Forces: Weeks 6-7

Content	Blackman Book	Learning Objectives
Intermolecular forces Dipole-dipole, dispersion forces, hydrogen bonds	6.7, 6.8	Identify the types of intermolecular forces present between particular species Relate the strength of intermolecular forces to properties such as dipole moment and polarizability
Deviations from ideal gas laws; van der Waals equation; a and b constants		Use the van der Waals equation to calculate the pressure of a non-ideal gas Explain the origin and size of *a* and *b* constants
States of matter. Comparison of properties of solids, liquids, and gases; Solids – types (atomic, molecular, ionic, metallic, network, crystalline vs amorphous) Liquids – general description; viscosity and surface tension	7.1-7.3	Classify solids as ionic, molecular, or metallic based on their properties Relate viscosity and surface tension to intermolecular forces
Properties of solutions; energy changes on dissolution, solubility, 'like dissolves like', Raoult's law, ideal and non ideal solutions; positive and negative deviations from Raoult's law. Distillation.	10.1, 10.3 10.5	Understand the process of dissolution at the molecular level Predict the relative solubility of a substance in a range of solvents

Solutions

A solution consists of a **solute** (often a solid, present in lower concentration) in a **homogeneous mixture** with a **solvent** (usually a liquid, present in higher concentration). There are several ways to specify the relative amounts of solute and solvent.

Molarity	Moles of solute per litre of solution.
Molality	Moles of solute per kilogram of solvent.
Mole fraction	Moles of solute per total moles of solute and solvent.
Mass percent (% w/w or % wt)	Mass of solute (g) per 100g solution.
Volume percent (% v/v)	Volume of solute (mL) per 100 mL of solution.
Mass per volume (% w/v)	Mass of solute (g) per 100 mL of solution.
Parts per million (ppm), parts per billion (ppb)	Mass of solute (g) per million grams of solution (ppm) or per 10^9g of solution (ppb).

Liquid–liquid solutions are better described as having two components, rather than referring to the solute and solvent. Liquids which dissolve in each other are called **miscible**. Liquids which dissolve in each other regardless of the concentrations of each liquid are called **completely miscible** (*e.g.* ethanol and water).

Solutions

In more concentrated solutions the density of the solution may be quite different to that of pure water (~1 g/mL) and thus the volume and mass of solution are not numerically equal.

Example: A solution was prepared by dissolving 50.0 g of caesium chloride in 50.0 g of water, resulting in a solution of volume 63.3 mL. Calculate the mass percent, molarity, molality and mole fraction of the CsCl.

Total mass of solution = 50.0 + 50.0 g = 100.0 g

Mass percent = mass of CsCl / total mass of solution × 100 = 50.0 / 100.0 × 100 = 50.0 % w/w CsCl

Moles of CsCl = 50.0 g / 168.35 g mol^{-1} = 0.297 mol.

Volume of solution = 63.3 mL × 1L/1000mL = 0.0633 L

Molarity = moles of CsCl / volume of solution in L = 0.297 mol / 0.0633 L = 4.69 mol L^{-1}

Mass of solvent = 50.0 g × 1kg/1000g = 0.0500 kg

Molality = moles of CsCl / mass of solvent in kg = 0.297 mol / 0.0500 kg = 5.94 mol kg^{-1}

Moles water = 50.0 g / 18.0 g mol^{-1} = 2.78 mol

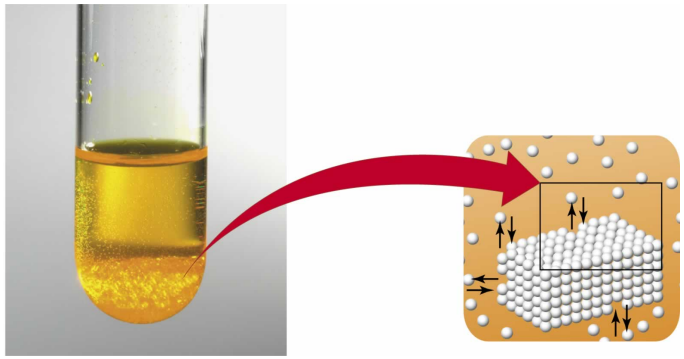
Mole fraction = moles CsCl / (moles CsCl + moles water)

= 0.297 / (0.297 + 2.78) = 0.0965

Solubility

A solute usually has a limited solubility in a solvent. *E.g.* the maximum solubility of sodium chloride in water is 365 g per litre at 20°C – whereas the maximum solubility of silver chloride is 0.00089 g L^{-1} at 10°C.

A solution that contains the maximum amount of solute that can be dissolved is called a **saturated solution**. The concentration of the solute in a saturated solution is called the **solubility** of the solute.



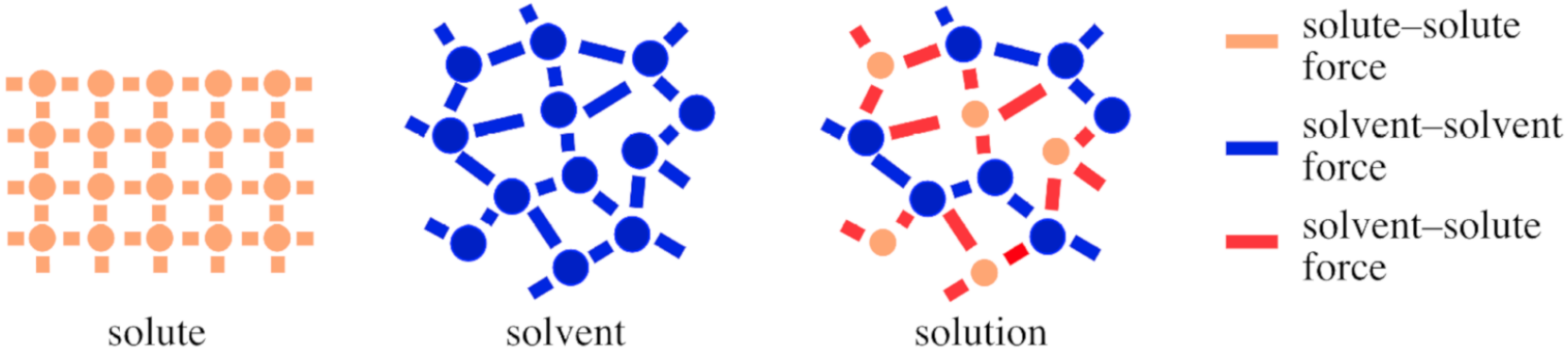
The solubility depends upon the nature of the solute, the solvent's properties, and the temperature.

Criteria can be defined and used to describe the solubility of a substance in a solvent:

- **soluble** (solubility > 0.1 mol L^{-1})
- **slightly soluble** (0.1 ≥ solubility ≥ 0.01 mol L^{-1})
- **insoluble** (solubility < 0.01 mol L^{-1})

The structure of solutions

The laws of thermodynamics determine whether a particular solute will dissolve in a solvent. Thermodynamics involves two major factors, one of which is the energy change associated with the process of dissolving the solute in the solvent.



To form a solution from the separated solute and solvent:

1. requires energy to overcome the solute – solute bonds
2. requires energy to overcome the solvent – solvent attractions
3. produces energy from the formation of solute – solvent attractions.

If the total energy required in steps 1 and 2 is much larger than the energy released in step 3 then it is not likely that the solute will dissolve in the solvent. Predicting these energy changes requires a knowledge of the strengths of chemical bonds and intermolecular forces.

The structure of solutions

In forming **aqueous solutions** the energy required to separate the hydrogen bonded water molecules is large and a solute will dissolve only if water molecules will be strongly attracted to it.

Substances which dissolve in water are usually either:

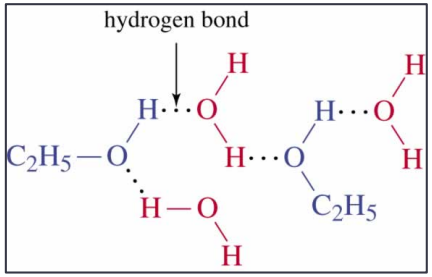
- **ionic** – they dissociate to form ions and the resulting ion – dipole (ion–water) forces are strong, or
- **molecular substances which dissociate to form ions**, or
- **molecules which can form hydrogen bonds** – and thus form H-bonds to the water molecules, or
- **very polar molecules** – and thus are attracted to water molecules by dipole – dipole forces.

Substances composed of **non–polar or slightly polar** molecules are usually insoluble in **water** because they are not attracted strongly enough to water molecules to make up the energy needed to separate the water molecules when the solute dissolves.

Substances composed of **low polarity molecules** will dissolve in **non–polar solvents**. The solute–solute and solvent–solvent forces are dispersion forces and are of comparable strengths to the solute–solvent forces found in the solution.

Ionic substances are not soluble in **non–polar solvents** because the energy to be gained in solute–solvent forces is much less than that required to break the solute–solute (ionic) bonds.

General rule of thumb:
"Like dissolves like"

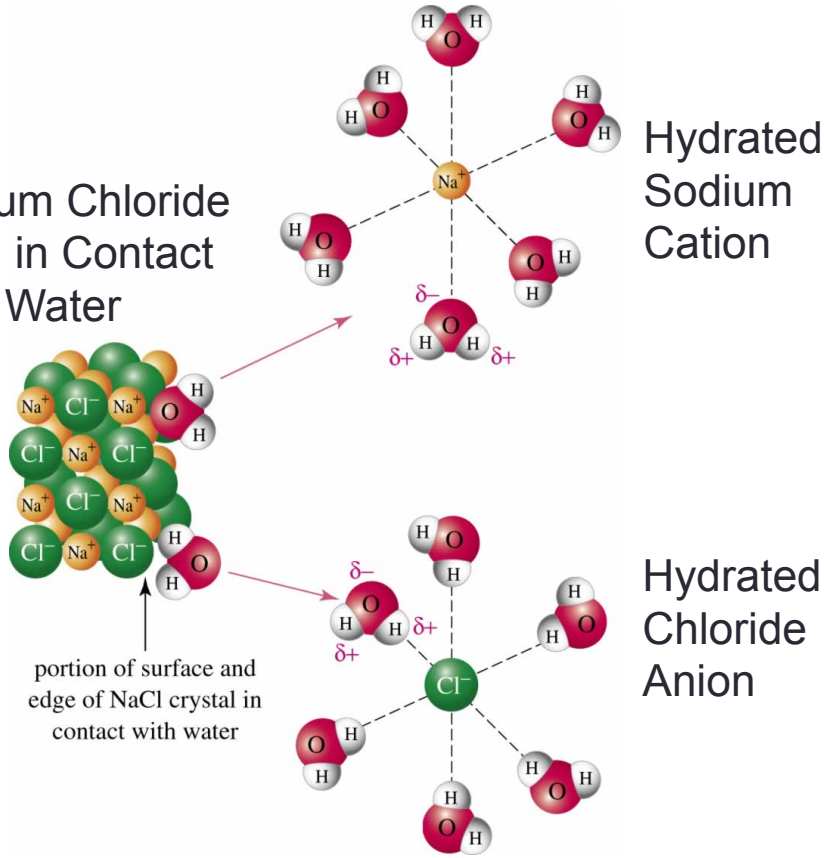


Water-ethanol

Hexane-water

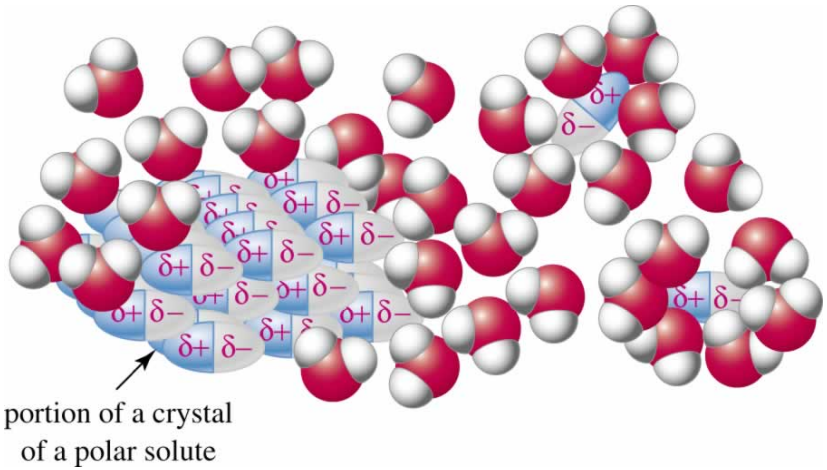
Hydration of ionic solids & polar molecular solids

Sodium Chloride Solid in Contact With Water



Although the intermolecular forces of ionic crystals are very strong, the number and strength of the interactions between polar water molecules and ions provides a strong driving force for many types of ionic substances to dissolve in water

Hydrated Polar Molecule



Crystal of a Polar Molecular Solid in Contact with Water

Polar molecules dissolve in water because the polar molecules are strongly attracted to the water molecules, resulting in hydrated polar molecules. Note the orientation of the water molecules to the partial positive vs negative charges on the polar molecule.

Examples

Questions:

(a) Will potassium nitrate be more soluble in water or benzene?
(b) Will iodine be more soluble in water or benzene?

Answers: Water is polar, benzene (C_6H_6, a ring of 6 carbon atoms with a H atom attached to each) is non–polar.
(a) Potassium nitrate is an ionic substance. It will have the greater solubility in the polar solvent, water.
(b) Iodine (I_2) is a non–polar molecule. It will have greater solubility in a non–polar solvent, benzene.

Questions:

Which substance is more soluble in water? (a) O_2 or He ? (b) CH_3OH or $CH_3CH_2CH_2CH_2CH_2CH_2OH$?

Answers:

(a) These are both non–polar and neither will be very soluble in water. Only dipole–induced dipole forces attract these molecules to H_2O and these forces will be larger for O_2 than He. O_2 will be more soluble.
(b) Both molecules have an –OH group which is polar and can form hydrogen bonds to water molecules. 1–hexanol also has a long non–polar part which is not attracted strongly to water molecules, and if this molecule were to dissolve it would disrupt many H_2O – H_2O attractions. Thus, methanol is more soluble than 1–hexanol in water.

Properties of solutions

In modeling the properties of an ideal gas it is assumed there were no forces between the gas particles. This is reasonable because the particles in a gas approach each other relatively infrequently. In a liquid the particles spend most of the time close to each other and intermolecular forces dominate the behaviour of a liquid or solution.

The properties of pure solids and liquids vary only slightly with temperature and pressure (compared to gases) and the prediction of these variations is generally more difficult than for gases. The variation in properties of *mixtures* of solids and liquids with composition are often relatively easy to predict and can give useful information about the intermolecular forces in the solute, solvent, and solution.

An **ideal solution** is one where all the intermolecular forces (solvent–solvent, solute–solvent, solute–solute) are of the same strength. The properties of a solution (*e.g.* vapour pressure) can be predicted easily if it is assumed to behave ideally, however the deviations of real solutions from ideal behaviour can be large.

Raoult's law

Dalton's law of partial pressures states: $p_{total} = p_A + p_B$.

Raoult's law allows the prediction of the vapour pressure of a solution of two miscible liquids where both components are volatile.

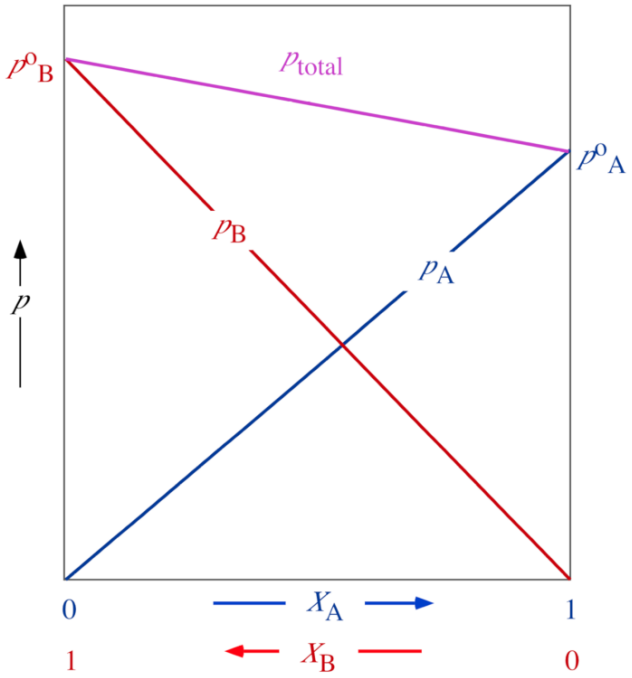
$$p_{total} = X_A \times p^o{}_A + X_B \times p^o{}_B$$

where X_A = mole fraction of component A

$p^o{}_A$ = vapour pressure of pure A

X_B = mole fraction of component B

$p^o{}_B$ = vapour pressure of pure B



The partial pressure of each gas is given by its mole fraction in the liquid times the vapour pressure of the pure liquid *e.g.* $p_A = X_A \times p^o{}_A$ and the mole fraction of each gas in the mixture is given by its partial pressure divided by the total pressure

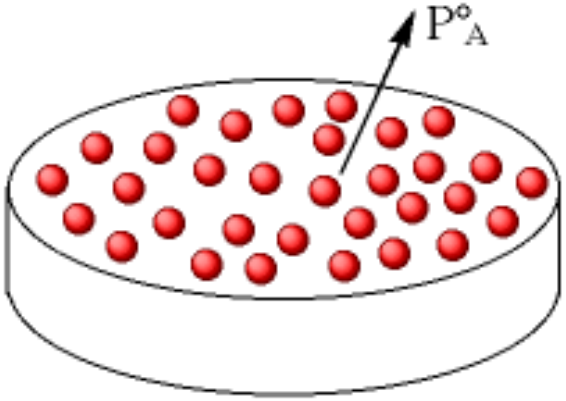
e.g. $X_{A,\,gas} = p_A / p_{total}$.

Raoult's law

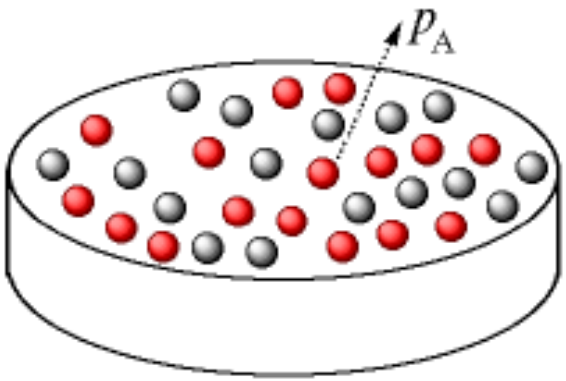
A thought experiment to help understand Raoult's law:

Imagine the surface of a pure liquid A in a beaker (red balls). 100% of all the molecules at the surface are A molecules, and the ambient temperature determines the fraction that have sufficient energy to escape (evaporate) and exert the vapour pressure of pure A, which is P°_{A} (left diagram).

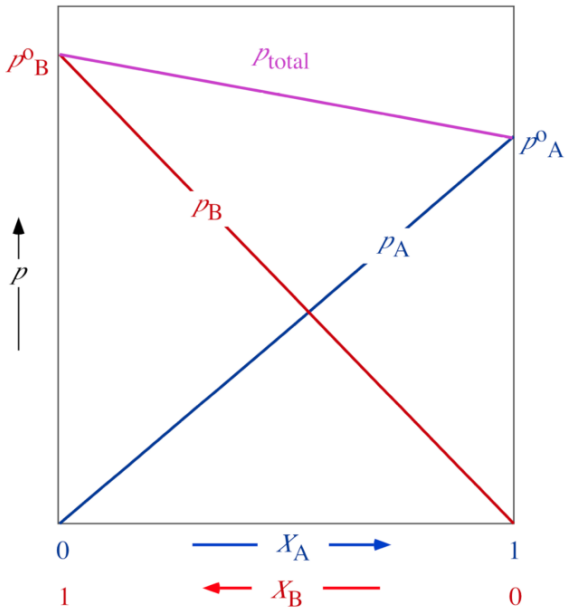
Now imaging a 1:1 mix of A and B molecules (left diagram; B molecules are grey balls). Here only 50% of the surface molecules are A on average, and (at the same T) the same fraction of these have enough energy to escape the surface to exert a vapour pressure of A from the mixture, p_A. Obviously p_A for this mixture will be 50% of $P^{\circ}A$



Pure A



50% A



Example

A solution is prepared consisting of hexane (40 mL) and pentane (25 mL) at 25°C. Assuming the solution is ideal, calculate the total vapour pressure above the solution, and calculate the mole fraction of pentane in the vapour. The pure solvents have the following vapour pressures and liquid densities at 25°C: hexane, 150 torr; 0.66 g mL^{-1}; pentane, 511 torr; 0.63 g mL^{-1}.

Vapour pressures depend upon mole fractions of components – so calculate moles:

$$n_{hex} = \frac{(40\ mL)(0.66\ g\ mL^{-1})}{(86.2\ g\ mol^{-1})} = 0.306\ mole$$

$$n_{pent} = \frac{(25\ mL)(0.63\ g\ mL^{-1})}{(72.1\ g\ mol^{-1})} = 0.218\ mole$$

Mole fractions of the liquid components are given by:

$$\chi_{hex} = \frac{(moles\ hexane)}{(moles\ hexane + moles\ pentane)} = \frac{(0.306)}{(0.306 + 0.218)} = 0.584$$

$$\chi_{pent} = \frac{(moles\ pentane)}{(moles\ hexane + moles\ pentane)} = \frac{(0.218)}{(0.306 + 0.218)} = 0.416$$

$$P_{total} = p_{hex} + p_{pent}$$

$$= \chi_{hex} \times P^{\circ}_{hex} + \chi_{pent} \times P^{\circ}_{pent}$$

$$= 0.584 \times 150\ torr + 0.416 \times 511\ torr = 87.6\ torr + 212.6\ torr$$

$$= 300\ torr$$

Example continued…

So far we showed how knowing the composition of the liquid phase allowed us to predict the partial pressures of components in the gas phase.

But what is the composition of that gas phase?

In the gas phase, the amount of a gas (mol) present is related to its partial pressure:

(PV = nRT, so P ∝ n).

For the pentane in the gas phase: $p_{pent} V_{total} = n_{pent} RT$

For all gas components in the gas phase: $P_{total} V_{total} = n_{total} RT$

Divide the first equation by the second: $= \frac{(p_{pent} V_{total})}{(P_{total} V_{total})} = \frac{(n_{pent} RT)}{(n_{total} RT)}$

Cancel V_{total}, R and T.

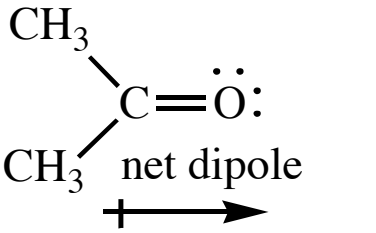
∴ The mole fraction of pentane in the gas phase is given by:

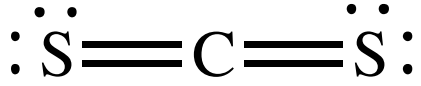
$$\chi_{pent(gas)} = \frac{(n_{pent})}{(n_{total})} = \frac{(p_{pent})}{(P_{total})} = \frac{(212.6 \text{ torr})}{(87.6 \text{ torr} + 212.6 \text{ torr})} = 0.709$$

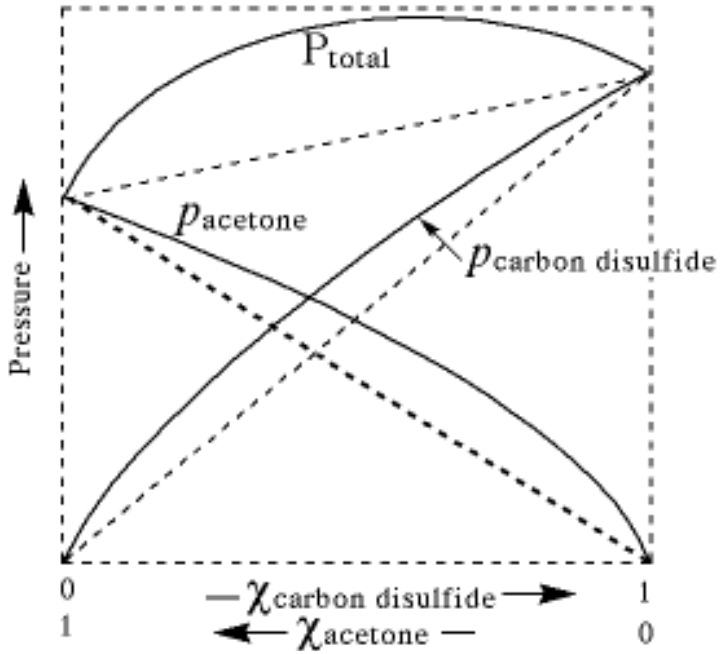
Deviations from Raoult's law

Positive deviation: When the A–B intermolecular forces are weaker than the A–A and B–B forces, a mixture of A & B will give a higher total pressure (P_{total}) than predicted by Raoult's Law for that particular proportion of A & B.

(*e.g.* acetone and carbon disulfide)



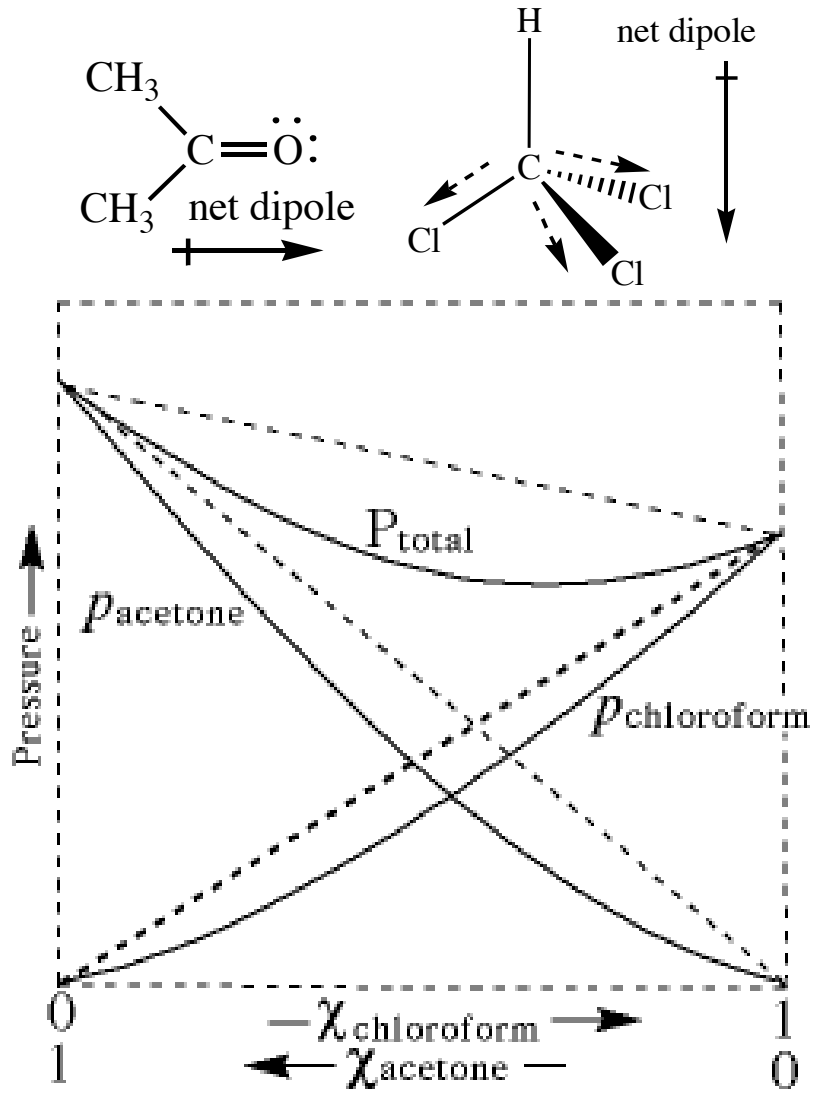




Deviations from Raoult's law

Negative deviation: When the A–B intermolecular forces are stronger than the A–A and B–B forces, a mixture of A & B will give a lower total pressure (P_{total}) than predicted by Raoult's Law for that particular proportion of A & B.

(e.g. acetone and chloroform).



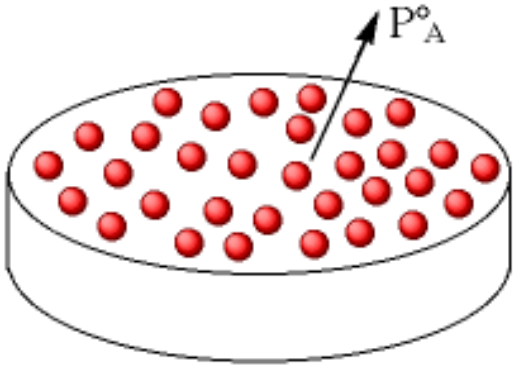
Vapour pressure of a solution

In this case the dissolved solute has no vapour pressure, so the pressure of the system is determined by the pressure of the solvent only.

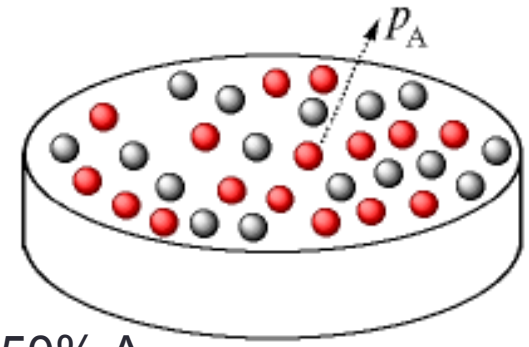
The thought experiment helps to understand the vapour pressure of a solution containing an involatile solute.

Compare the surface of pure liquid A in a beaker (A = red balls) with a 1:1 mixture of solvent A and involatile solute B in another beaker (right diagram; involatile solute = B). Here only 50% of the molecules at the surface are A on average and (at the same T) the same fraction of these have enough energy to escape the surface to exert the vapour pressure of A from the mixture, p_A. Obviously pA for this mixture will be 50% of P°_A.

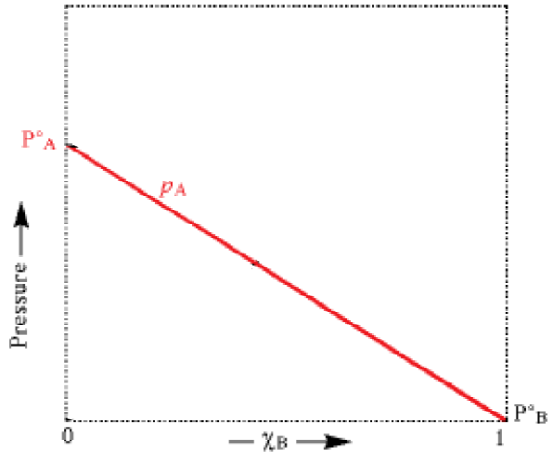
As more and more involatile solute B is dissolved in solvent A, molecules of A will be progressively less represented at the surface, and pA will drop in proportion to the drop in its mole fraction in the liquid mixture (i.e. $P_{total} = p_A = (\chi_A)(P^\circ_A)$).



Pure A



50% A



Example

What is the vapour pressure of a 1.0 M solution of glucose (molar mass = 180.2 g mol^{-1}) in water at 25 °C? The solution density is 1.00 g ml^{-1}. Pure water has a vapour pressure of 23.76 Torr at 25 °C.

Vapour pressures depends upon the mole fraction of the solvent in the solution – so calculate moles of water, then mole fraction.

1 L = 1000 mL = 1000 g of solution.

It contains 1.0 mol of glucose = 180.2 g.

Therefore the mass of water in the 1000 g of solution = 1000 – 180.2 = 819.8 g.

Moles of water = mass/molar mass = 819.8/18.02 = 45.5 mol.

Moles of glucose = 1.0 mol.

$\chi_{water} = (45.5)/(1.0 + 45.5) = 0.979$

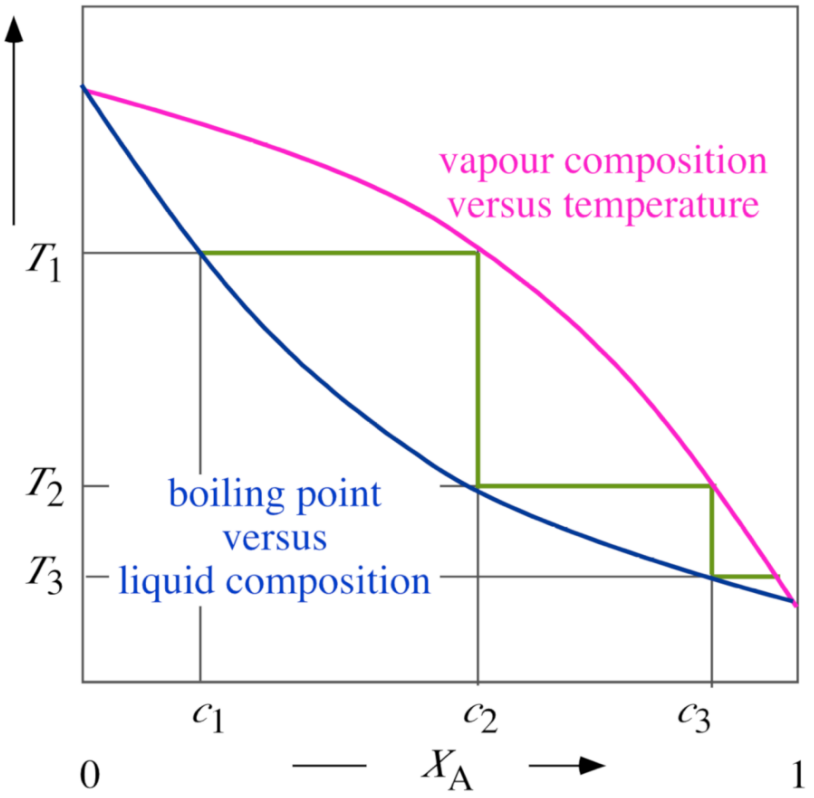
$p_{water} = (\chi_{water})(P°_{water}) = 0.979 \times 23.76 = 23.25$ Torr.

Distillation

The composition of the vapour above a mixture of two miscible liquids will likely be different to that of the solution. The vapour will be richer in the more volatile component. Condensing the vapour gives a liquid richer in the more volatile component and repeating this vapourisation/condensation cycle can separate the components of the solution. This is what happens in **fractional distillation**.

A **temperature – composition diagram** contains two graphs: one shows the variation of boiling point with composition of the liquid mixture (upper curve), the other shows the composition of the vapour in equilibrium with the mixture boiling at a given temperature (lower).

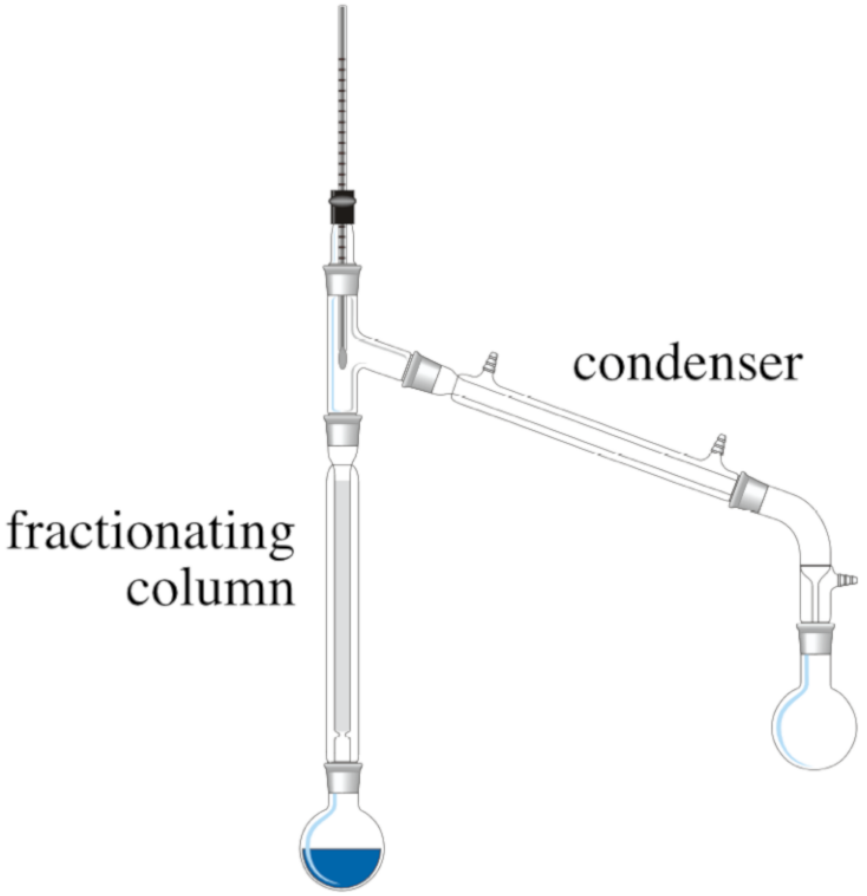
Consider a mixture of two liquids (A & B) with A being more volatile so the vapour is richer in A than the liquid. Liquid with composition *c*1 boils at temperature *T*1 and produces vapour with composition *c*2. If this vapour is condensed it produces a liquid with composition *c*2 which when evaporated gives a vapour with composition *c*3. Eventually, near–pure A can be obtained.



Distillation

It would be impractical to repeatedly vapourise a solution, condense the vapour, then vapourise the distillate etc. In practice fractional distillation is carried out by passing the hot vapours from a boiling solution through a long column (a **fractionating column**) which is packed with inert material having a large surface area. The column is thermally insulated to reduce heat loss. Vapour passing up the column comes into contact with condensed liquid coming down the column effectively allowing many evaporation–condensation cycles to take place.

Fractional distillation is used to separate the petroleum products from crude oil – the fractionating columns used in industry may be tens of metres tall.



Extra examples (concentrations)

Question: If we prepare a solution by dissolving 8.00 g of NaOH in 500 g of water, what is the molality of the solution? What is the mole fraction of NaOH?

Answer: Molality = moles of solute/kg of solvent

Moles of NaOH = 8.00 g / 39.997 g/mol = 0.200 mol

500 g x 1 kg/1000 g = 0.500 kg of water

Molality = 0.200/0.500 = 0.4 mol/kg (1 sig fig)

Moles of water = 500 g / 18.0 g/mol = 27.78 mol

Mole fraction of NaOH = 0.200 mol NaOH/(0.200 mol NaOH + 27.78 mol H_2O) = 0.007

Extra examples (Raoult's law)

Question: What is the vapour pressure of a solution containing 100 g benzene (C_6H_6) and 0.2 mol of paraffin wax (C_nH_{2n+2}; n >>20) at room temperature? The vapour pressure of ***pure*** benzene is 1.33 x 10^4 Pa at the same temperature.

Answer:

n(benzene) = m/M = 100 g/(78.11 g/mol) = 1.28 mol benzene

n(total solution) = 1.28 + 0.2 = 1.48 mol

Mole fraction of benzene = 1.28/1.48 = 0.86

Raoult's law:

p(benzene solution) = (mole fraction of benzene)x(pressure of pure benzene)

= (0.86) x (1.33 x 10^4 Pa) = 1.15 x 10^4 Pa

Extra examples (Raoult's law for two volatile solvents) [warning errors corrected]

Question: Using Raoult's law, calculate the vapour pressure of a binary mixture of acetone and water that contains 20 mol % of water. The vapour pressure of water and acetone at room temperature are 2.30×10^3 Pa and 2.13×10^4 Pa, respectively.

Answer:

Dalton's law of partial pressures: p(total) = p(water) + p(acetone)

p(acetone) = 0.8*(2.13×10^4 Pa) = 1.70×10^4 Pa

p(water) = 0.2*(2.30×10^3 Pa) = 460 Pa

p(total) = 1.70×10^4 Pa + 460 Pa = 1.8×10^4 Pa

Does this make sense? The partial pressure of the mixture should be between the vapour pressures of water and acetone, but much closer to that of acetone (because the solution is 80% acetone). This is the case as 1.8×10^4 is a little lower than the vapour pressure of pure acetone.

Extra examples (miscibility)

Rank the following compounds in order of their miscibility in water from highest to lowest?

(a) CF_4, CH_3OH, CH_3OCH_3, $CH_3CH_2OCH_2CH_3$

(b) NaCl vs Cl_2

For the compounds listed in part (a), choose the two molecules that would give you the best chance of observing a negative deviation to Raoult's law.

Thank you!