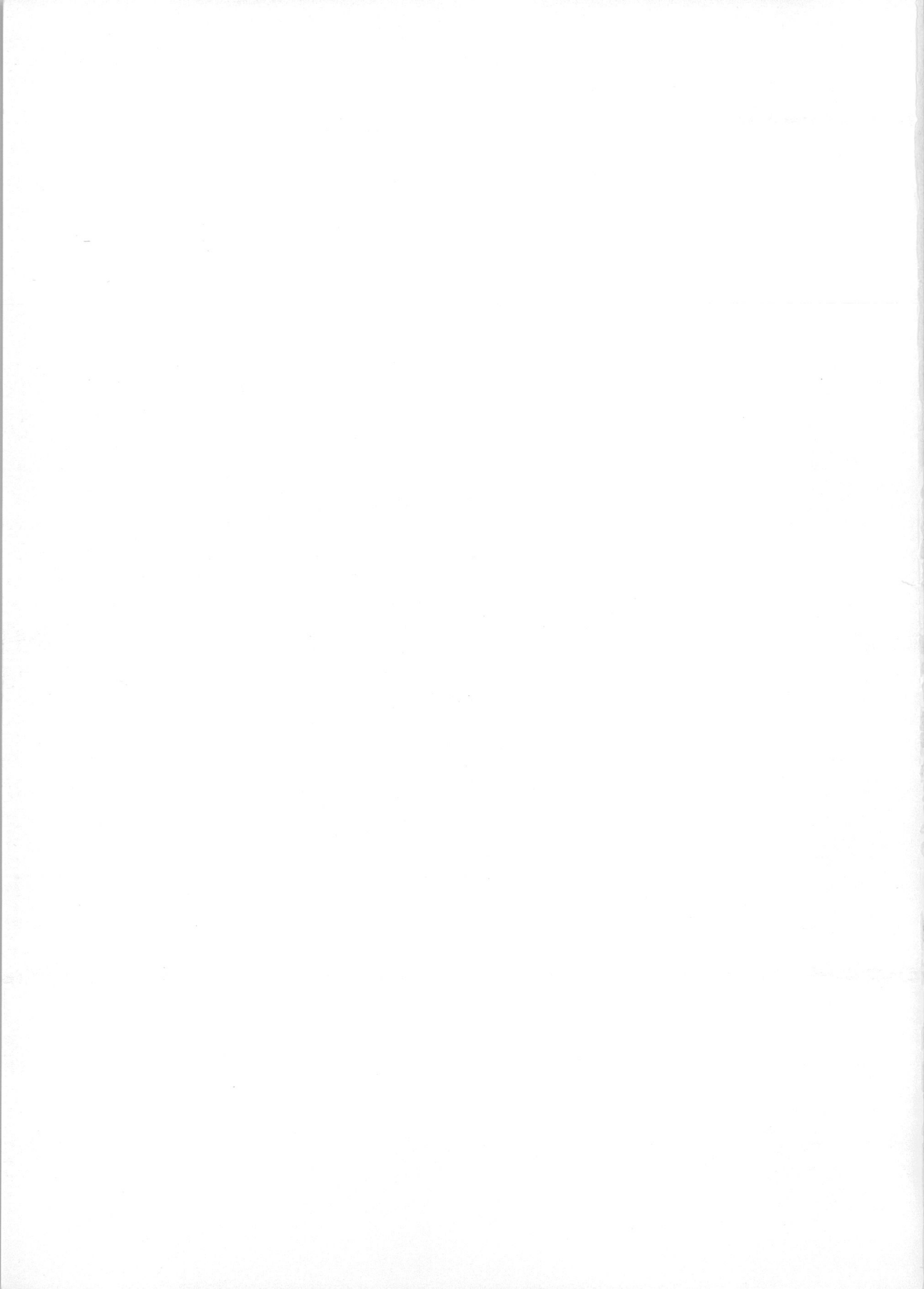




SOLUBILITY AND SOLVENTS FOR CONSERVATION PROBLEMS

Giorgio Torraca



Solubility and solvents for conservation problems

Solubility and solvents for conservation problems
by Giorgio Torraca

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Via di San Michele 13, I-00153, Rome, Italy

email: iccrom@iccrom.org

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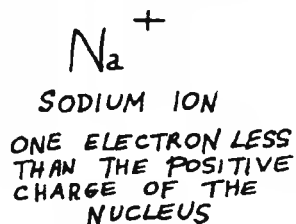
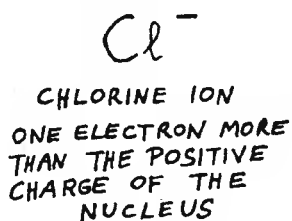
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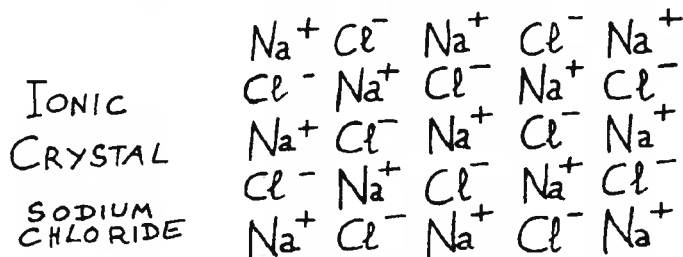
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1.2 Ionic Bond and Ionic Crystal

When an electronegative atom (say chlorine) meets a low-electronegativity one (say sodium) it can remove from it one electron; both atoms are then unbalanced from the electrical point of view.



Electrically charged atoms are called ions. Negative ions attract positive ions and form ionic bonds. Since many ions are always present even in a very small amount of material (not just one or two) they attract each other and form a regular array in the three directions of space. This is called a crystal: to be precise an ionic crystal.



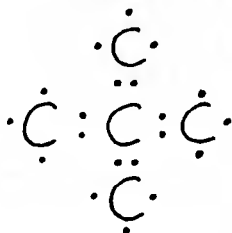
1.3 Covalent Bond and Covalent Crystal

Atoms from the centre or the right side of the electronegativity scale can share electrons when they meet and so form a bond between them: a covalent bond.

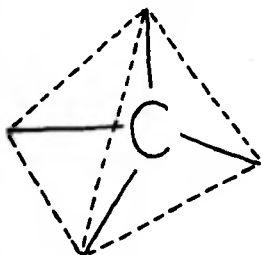


Carbon has four electrons on the outermost shell so it can form four covalent bonds with four other carbon atoms.

Each of the four can in turn bind to three more carbon atoms, and so on.



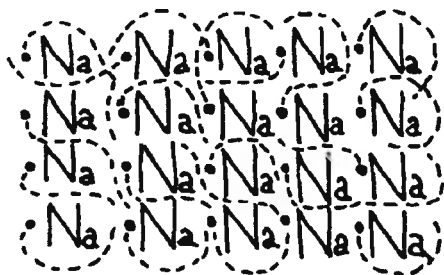
A regular, three-dimensional, array is formed; this also is a crystal, a covalent crystal to be precise. Drawing this crystal is not so easy because the bonds of every carbon atom are directed towards the apexes of a tetrahedron of which the atom is the centre.



1.4 Metallic Bond and Metallic Crystal

Atoms from the left side of the electronegativity scale can share electrons when they meet with other atoms of the same kind. The electrons so shared are not fixed between two atoms (as in the covalent bond) but are free to move around all atoms that have formed the bond.

A regular three-dimensional array is formed in this case also. This type of crystal is called a metallic crystal.



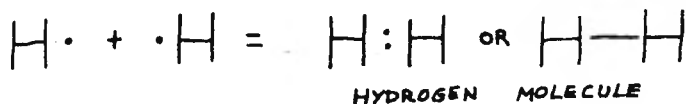
METALLIC
CRYSTAL
SODIUM

Since electrons can move around the crystal, metals conduct electrical current.

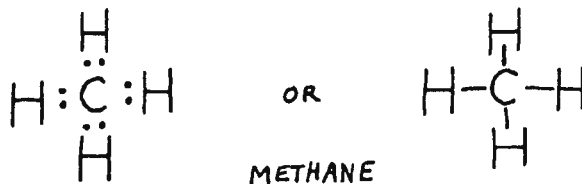
2. Molecules and Molecular Attractive Forces

2.1 Formation of Molecules

Groups composed of a small number of atoms can be formed by covalent bonds.



This is called a molecule. A molecule is formed by a definite number of atoms while a crystal contains a very large number of atoms (to be calculated only approximately).



2.2 Dipoles

If the two atoms forming one covalent bond are not exactly equal in electronegativity, the two electrons of the bond are not equally shared; instead they are closer to the electronegative atom that so acquires a small negative charge. Conversely the other atom remains slightly positive.



The bond is said to be slightly *polarized* (since it shows electrical poles).

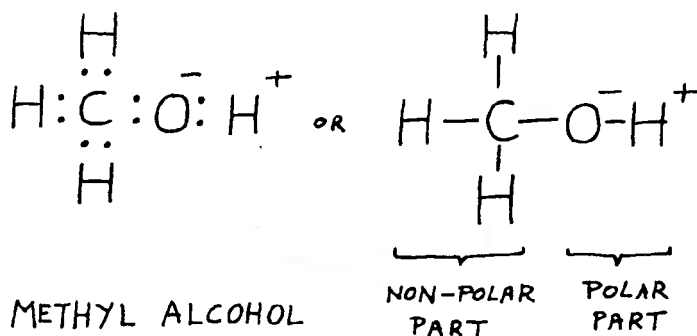
Other examples are:



These polarized bonds are called *dipoles* (i.e. pairs of poles of opposite charge).

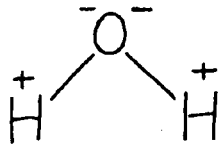
Molecules containing dipoles are called *polar*. Molecules not containing dipoles are called *non-polar*.

Some molecules have a polar part and a non polar one.

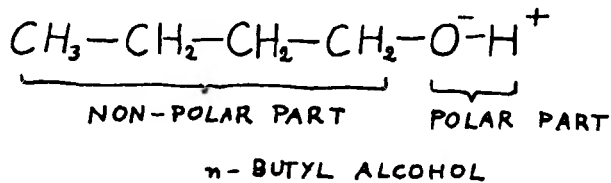


A molecule is said to be *very polar* if the polar part is more important than the non-polar one.

Water is very polar.

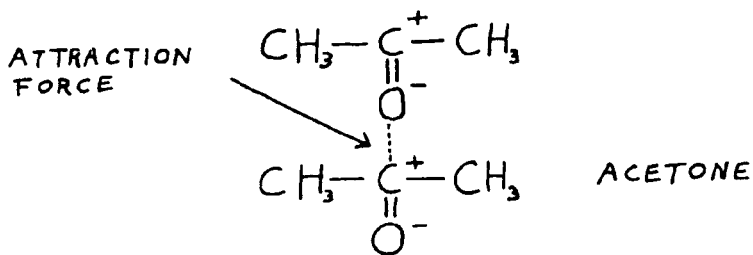


Other molecules are *weakly polar* because the polar part is lesser than the non-polar one.



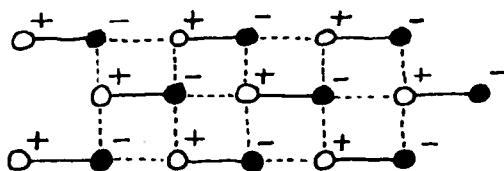
2.3 Attraction between Molecules

2.3.1 Dipole-dipole attraction



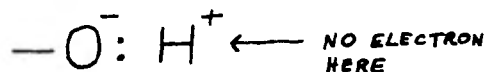
The positive part of a dipole attracts the negative part of a dipole in another molecule.

In the general case of several molecules containing an unspecified dipole $- \bullet \text{---} \circ +$ there is general attraction between molecules.

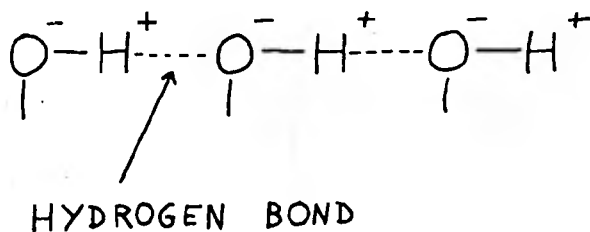


2.3.2 Hydrogen Bond

The dipole $-\text{O}^- - \text{H}^+$ is very peculiar because hydrogen has only one electron and it has been attracted by the oxygen atom.



The positive nucleus of hydrogen is completely unshielded and can develop a strong attraction towards negative atoms. This is called a *hydrogen bond*.

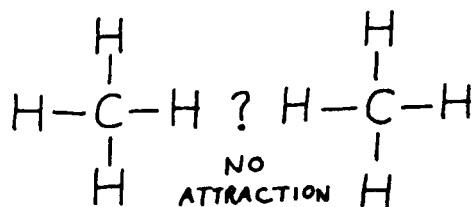


The hydrogen bond is actually a particular case of dipole-dipole attraction; it is, however, stronger than the normal dipole-dipole attraction.

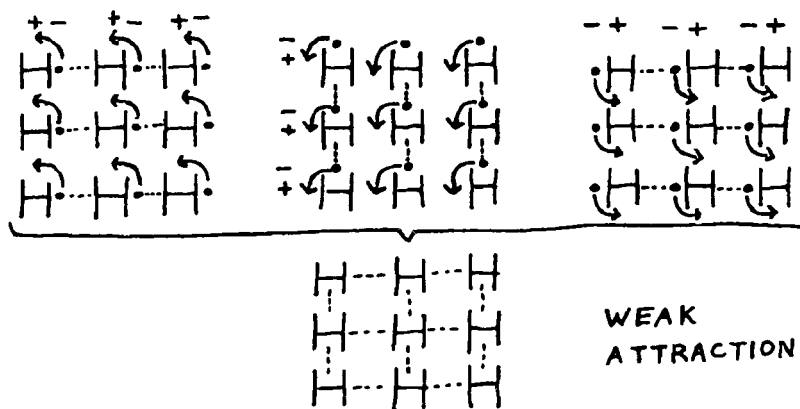
All molecules containing O–H groups can form hydrogen bonds between themselves or with other ones also containing O–H groups (like water for instance).

2.3.3 Dispersion Forces

When there is no dipole is there any attraction between molecules?



No - there are weak attraction forces due to *fluctuating dipoles* (dispersion or Van der Waals forces). Fluctuating dipoles are formed by electrons moving around the positive nucleus.



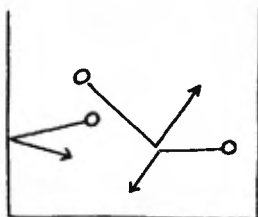
These forces are much weaker than the dipole-dipole attraction forces.

3. Gases, Liquids and Molecular Solids

3.1 Gases

If the forces of attraction between molecules are low, molecules move in space in straight lines at constant speed. The higher the temperature the greater the speed.

When the molecules hit each other or hit the walls of a container they rebound and continue their run on a new path.

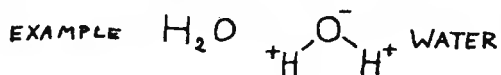
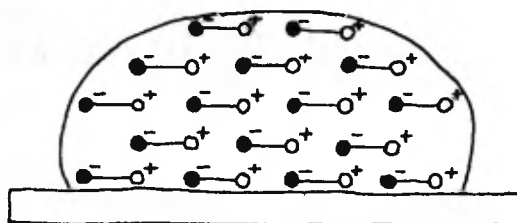


3.2 Liquids

When the molecules slow down (low temperature) or when the attraction force is great they no longer rebound when they hit each other but remain together.

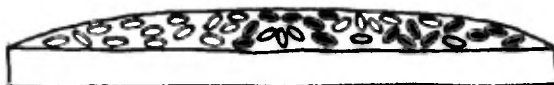
A mass of molecules attracted together but still with some freedom of movement is called a liquid.

A liquid composed of polar molecules is called a *polar liquid*. The attraction force of molecules inside the liquid is great. The liquid tends to form high drops (high surface tension).



A liquid composed of non-polar molecules is called a non-polar liquid. Internal attraction forces are low. The liquid tends to spread thinly over surfaces (low surface tension).

EXAMPLE C_6H_6

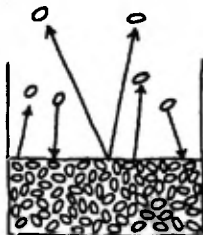


3.3 Evaporation

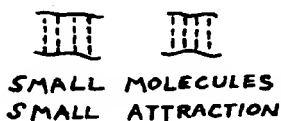
When molecules escape from the attraction forces in the liquid and go into the atmosphere we say that they evaporate.

Non-polar liquids with small molecules evaporate easily because attraction forces are low.

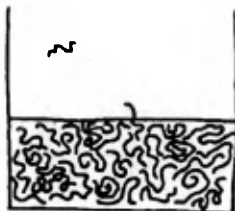
Some molecules return to the liquid (condensation).



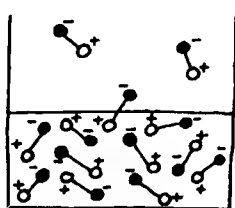
Large molecules have greater attraction forces than small molecules.



Liquids made of large molecules evaporate with difficulty.



Polar liquids are more difficult to evaporate than non-polar ones of equal molecular size.

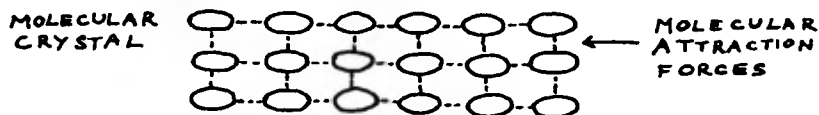


3.4 Molecular Solids

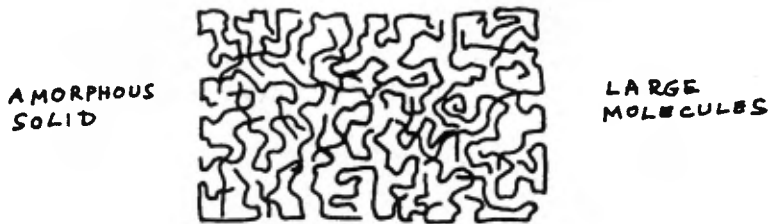
When attraction forces are very large (or temperatures very low) molecules can form solids.

Molecular solids may have an ordered structure in which molecules are stacked to form a three-dimensional array and are kept in position by attraction forces (dipole-dipole or Van der Waals).

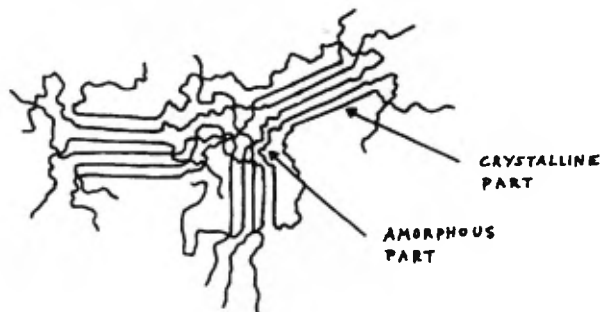
This structure is a crystal and is called molecular crystal. It occurs more frequently in the case of small molecules.



Large molecules frequently form solids that have no order whatsoever (*amorphous solids*). The molecules are blocked by strong attraction forces.



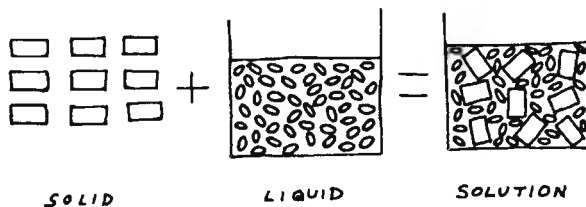
In the case of large molecules, part of the solid sometimes shows an ordered structure while the rest is amorphous.



4. Solubility

A solid is dissolved in a liquid if all atoms or molecules constituting the solid are separated by the molecules of the liquid.

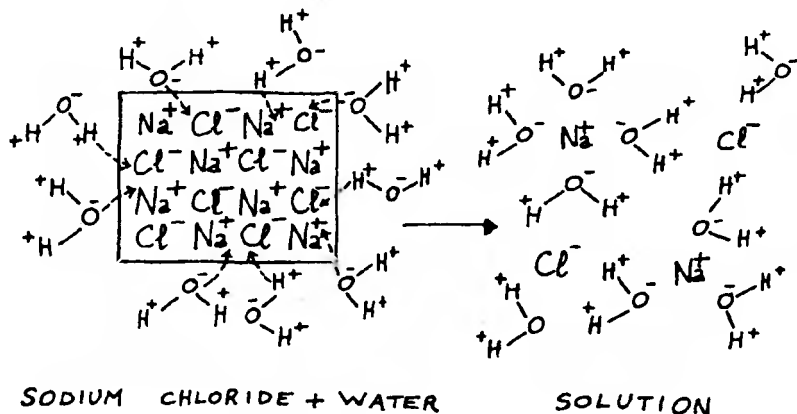
The molecules of the liquid interpose between the atoms or molecules of the solid, breaking the bonds or attractions between them.



If the liquid evaporates from the solution the solid re-forms unchanged.

It is impossible to dissolve *metallic crystals* or *covalent crystals* by means of solvents. Passage to the liquid state can be achieved only by breaking the bonds by chemical reaction but in this case it is impossible to recover the solid unchanged after evaporation of the liquid.

It is possible instead to dissolve some *ionic crystals* and some *very polar molecular solids* by means of *very polar solvents*, e.g. water, the most polar solvent.



A sodium chloride crystal is dissolved by water. Solution takes place because of the natural tendency towards:

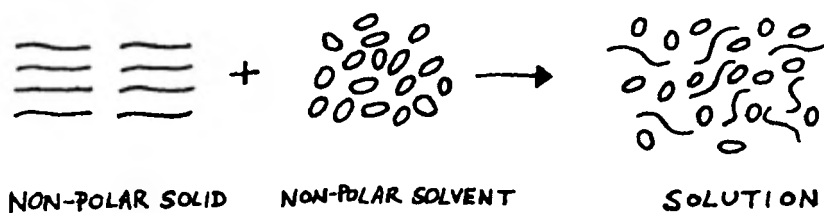
(a) Electrical attraction

The water molecules and the ions (sodium and chlorine) in the liquid exert a mutual attraction at least as great as the attraction between the ions in the solid.

(b) Disorder

Other things being equal (i.e. electrical attraction) disorder prevails. Disorder is also favoured when the temperature is increased.

It is possible to dissolve *non-polar molecular solids* in *non-polar solvents*.

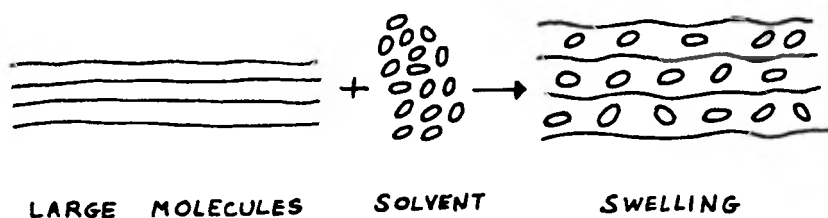


In this case there is only a weak electrical attraction (of the Van der Waals type) both in the liquid and in the solid. The same attraction can be mutually exerted by liquid and solid molecules in the solution.

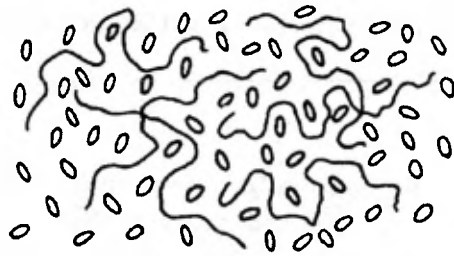
Therefore, other things being equal, disorder (= solution) prevails.

It is always difficult to dissolve large molecules even if the solvent is the most suited to the purpose. Solvent molecules require a long time to penetrate between the long molecules.

When some solvent has penetrated, the solid swells and becomes softer.

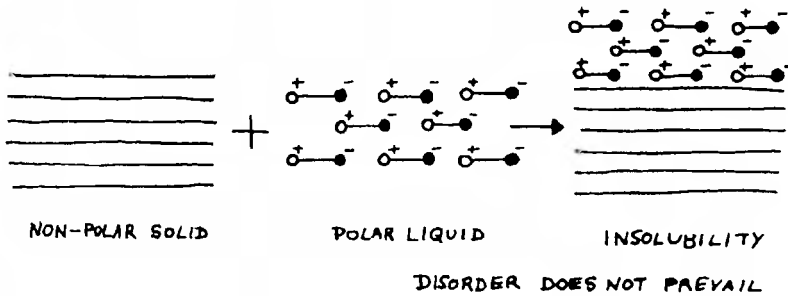


Solution takes place only when the long molecules are completely separated. It can take a very long time to reach this stage and for very large molecules it might be impossible ever to reach it.

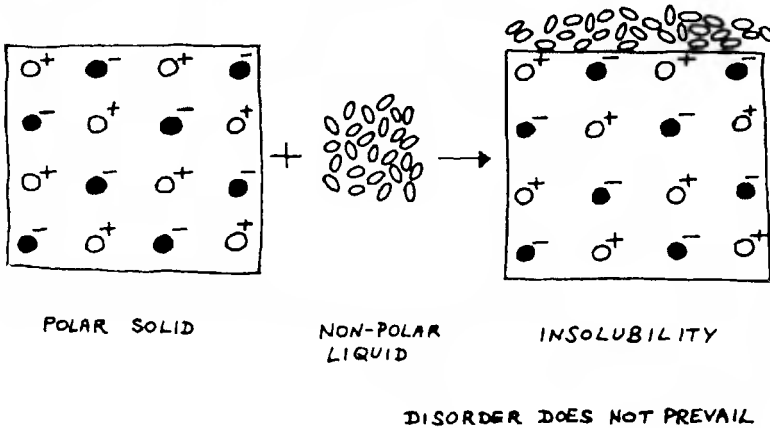


SOLUTION OF LARGE MOLECULES

5. Insolubility



In the case of disorder (= solution) the polar molecules should be separated from one another but no electrical attraction would take place with the non-polar solid. So in this case disorder does not prevail, other things being not equal.



6. Solubility in Cases of Intermediate Polarity

As a general rule a solid is dissolved by a liquid that is very similar in nature to the solid.

This means that the liquid molecules inside the liquid have between them the same forces of attraction that the solid molecules (or atoms) have between them inside the solid. It is possible in this case to exchange attraction forces between solvent and solid molecules and disorder (= solution) will prevail at the end.

To find solvents easily for all types of solids one must classify all solvents and all solids according to the attraction forces existing in them.

Most solids we are used to dealing with in conservation technology are molecular solids. They can be classified according to three types of attraction forces:

Dipole-dipole or dry polarity

Hydrogen bond or wet polarity

Dispersion or no polarity

It is important to keep dipole-dipole attraction separated from hydrogen bond because the solids that contain the latter type of attraction tend to mix well with liquids having OH groups in their molecules (water included). That is why this form of polarity has been named by us "wet polarity" (an unconventional designation used only in conservation) while the dipole-dipole attraction of molecules with no OH groups has been called "dry polarity" (another unconventional designation).

The three types of forces can be calculated (approximately) for solvent molecules. Tables are available expressing them as a percentage of the total force of attraction between molecules in the solvent.

This allows us to represent graphically all solvents and mixtures in a triangular diagram (see annex).

Calculations for solids are far more difficult and very few data are available.

It is possible, however, to evaluate the solubility behaviour of a solid by experiment, testing it against several solvents located in different points in the triangular diagram.

Usually, the positive results (solution) are collected in a more or less restricted area in the triangle which is called the solubility area of the solid.

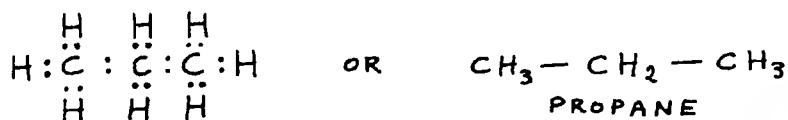
PART II

SOLVENTS

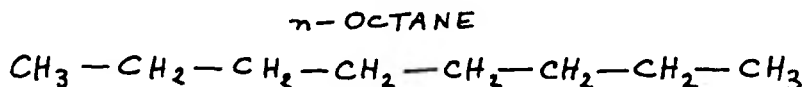
1. Hydrocarbons

1.1 Aliphatic Hydrocarbons

Molecules containing only hydrogen and carbon are called *hydrogen carbons*.



Larger molecules can be built adding other carbon atoms to form chains of atoms. Hydrocarbons composed of chain molecules are called *aliphatic*.



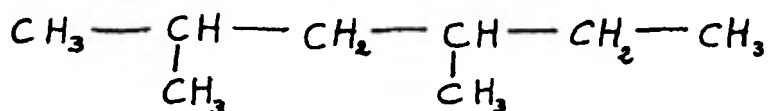
The end groups of the chain are always $-\text{CH}_3$ groups and are called *methyl* groups. The central groups $-\text{CH}_2-$ are called *methylene* groups.

Small hydrocarbons are gases (like methane and propane), middle size ones are liquids (like octane) and long chains form solids (like paraffin wax) because the force of attraction between chains increases with their length.

Hydrocarbon solvents are formed by molecules of 6 to 12 carbon atoms. Shorter molecules are too volatile while longer ones evaporate too slowly.

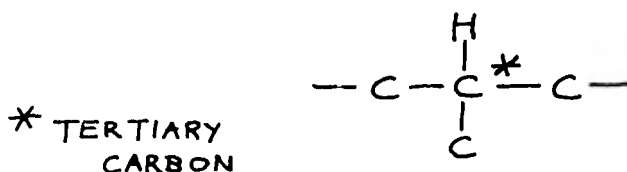
Straight chain hydrocarbons (like n-octane) are called *paraffinic*.

Branched chains are also possible:



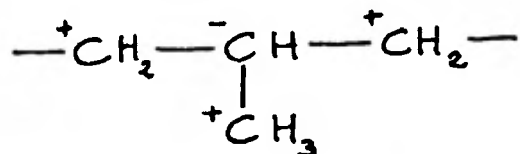
iso - OCTANE

Branched hydrocarbons are called *iso-paraffinic*. The branching point has special properties; the carbon atom from which the branching originates is called *tertiary carbon*,



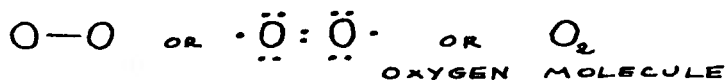
that is, a carbon bound to three other carbon atoms and to one hydrogen atom only.

Tertiary carbons are slightly negative with respect to the rest of the chain,



and react more easily with electron-hungry molecules.

Oxygen is an example of an electron-hungry molecule,



as it contains two single electrons (molecules are stable when all electrons are paired and there are 8 electrons around each atom).

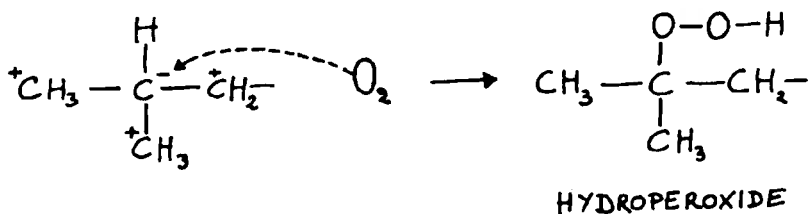
As air is composed mainly of nitrogen (about 75%) and oxygen (about 25%) molecules, all substances in our atmosphere are exposed to reaction with oxygen.

Nitrogen instead is very stable and not reactive.



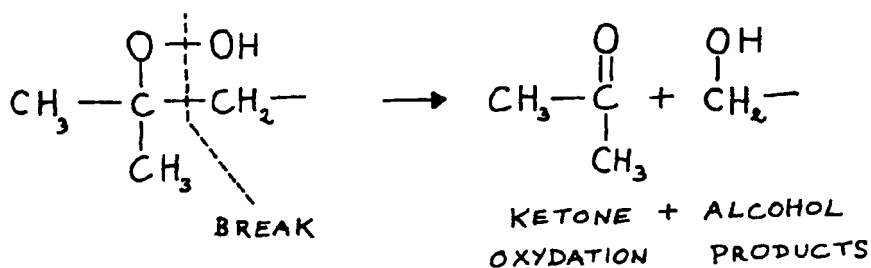
Reaction with oxygen is called *oxidation*.

A tertiary carbon is more easily oxidized than other parts of the chain.

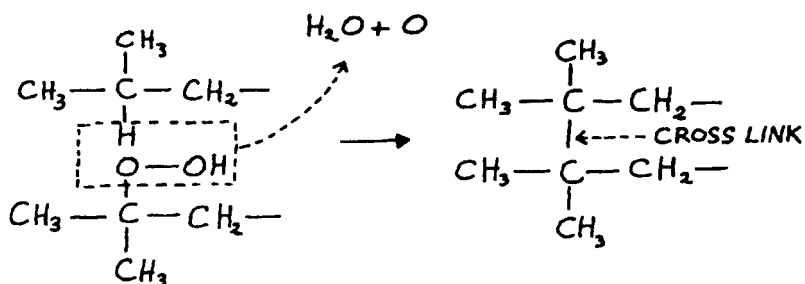


The intermediate product of oxidation (hydroperoxide) is not stable and is decomposed in two different ways.

(a) The hydroperoxide breaks.

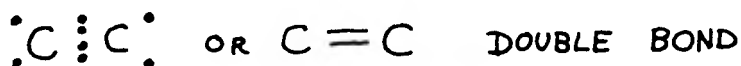
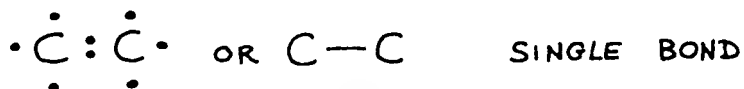


(b) A cross-link is formed between two molecules and a larger molecule is formed.

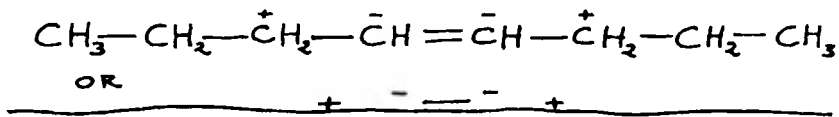


1.2 Double Bonds. Olefinic Hydrocarbons

Two adjacent carbon atoms can form two covalent bonds between them.



A double bond is a stronger link between two carbons but also a region where there are more electrons than elsewhere in the molecule.

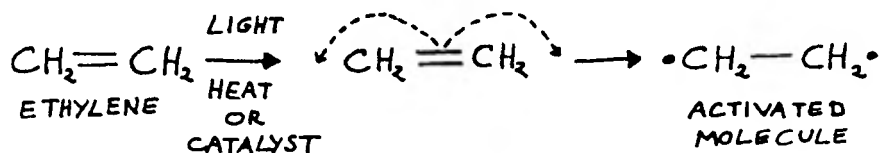


Therefore the double bond is a reactive point in the molecule, even more than a tertiary carbon.

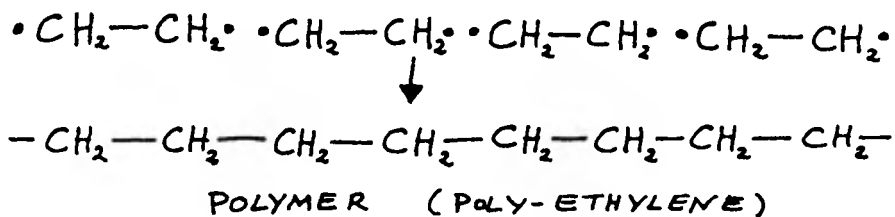
Hydrocarbons that contain double bonds are called *olefinic*. They undergo several reactions:

(a) Polymerization

The first step in this reaction is called activation. It can be caused by light (particularly ultra-violet radiation), heat or some substance capable of accelerating the reaction (catalyst).

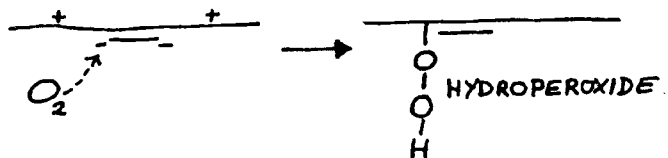


In the second step, several activated molecules join together to form long chains called *polymers*.



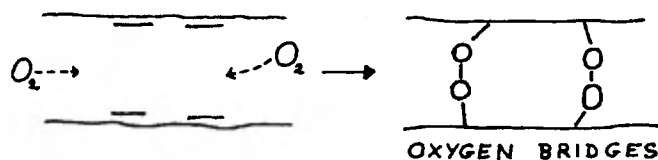
(b) Oxidation

Oxidation of double bonds is even easier than oxidation of tertiary carbon. The first step is always the formation of a hydroperoxide in the most negative point of the molecule.



Hydroperoxides are unstable and can break or cross-link as already shown.

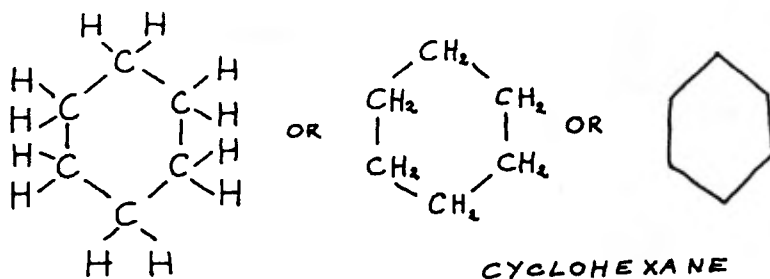
A special reaction of double bonds with oxygen is the formation of oxygen bridges.



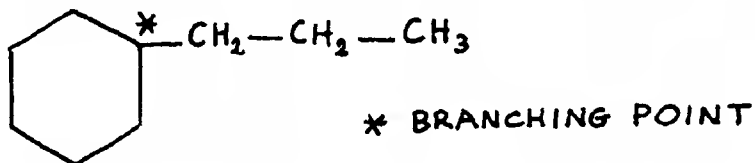
Oxygen bridges are easily formed by molecules that possess two or more double bonds.

1.3 Rings. Naphthenic Hydrocarbons

Six carbon atoms can easily join to form a ring. Also 5-atom rings can be formed but it is difficult to form other rings.

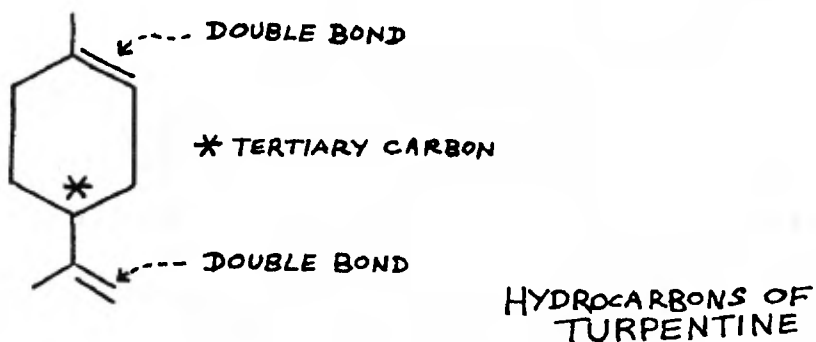


Ring hydrocarbons are called *naphthenic*. Side chains can be attached to the rings.



At the branching point in the ring there is a tertiary carbon.

Turpentine contains ring hydrocarbons with side chains and double bonds.

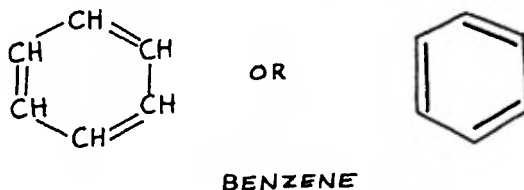


Turpentine is therefore slightly polar (branching points and double bonds are slightly negative) and rather reactive (it can polymerize or oxidize).

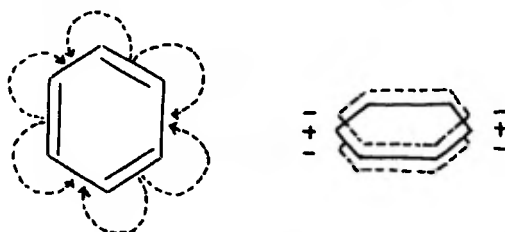
Turpentine is a good solvent of fresh natural resins. Today it can be replaced by appropriate mixtures of paraffinic and aromatic hydrocarbons that are more stable (see par. 1.6).

1.4 The Benzene Ring. Aromatic Hydrocarbons

A 6-carbon ring with three double bonds has special properties. It is called the benzene ring and all hydrocarbons containing such a ring in their molecule are called *aromatic* hydrocarbons.

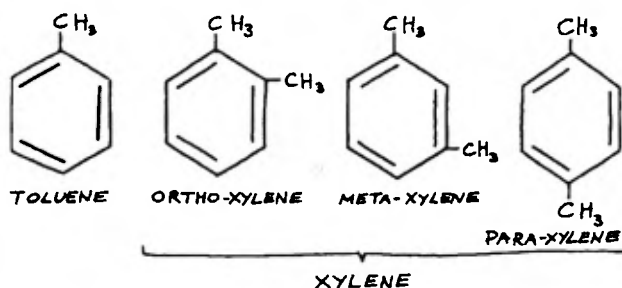


The alternated ("conjugated") double bonds allow some electrons to run around the ring, not exactly where the carbon atoms are but slightly above or below.

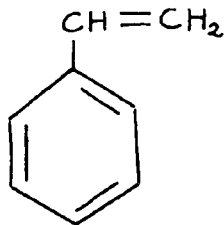


This peculiar distribution of the electrons causes a slight polarity and some other properties of the aromatic hydrocarbons (odour, toxicity).

Benzene itself is a useful solvent and other solvents are formed by adding side chains to the ring.



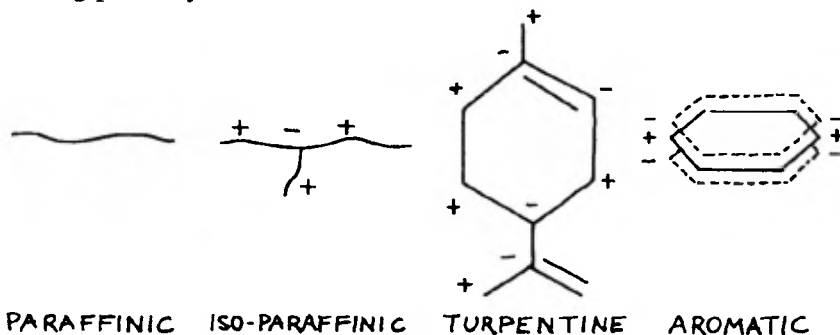
Styrene also has a double bond in the side chain.



1.5 Polarity of Hydrocarbon Solvents

Olefinic hydrocarbons are not used normally as solvents because they are unstable; turpentine is an exception.

Hydrocarbon solvents can be arranged as follows, in order of increasing polarity.



1.6 Industrial Hydrocarbon Solvents

Apart from turpentine (the liquid component of the exudate of resinous trees) and from the aromatic solvents (obtained by distillation of coal tar), all hydrocarbon solvents are obtained from mineral oil.

Several mixtures are commercially available and cover all degrees of polarity from paraffinic to aromatic hydrocarbons.

A list of some industrial solvents and their composition is given on the following page.

INDUSTRIAL SOLVENTS AND THEIR COMPOSITION

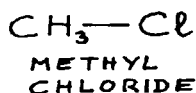
Trade Name	Paraffinic	Iso-paraffinic	Naphthenic	Aromatic	Boiling Range
	%	%	%	%	°C
Shellsol T (Shell)	100	—	—	—	180 - 190
Isopar G (Esso)	—	93	7	—	160 - 175
Shellsol B (Shell)	89	—	11	—	140 - 160
Shellsol B.8 (Shell)	82	—	10	8	150 - 190
V.M. & P.N. (Shell)	45	—	42	13	120 - 135
V.M. & P.N. (Esso)	49	—	40	11	120 - 135
White Spirit (Esso)	81	—	3	16	180 - 200
Shellsol E (Shell)	15	—	3	82	160 - 185
Shellsol A (Shell)	1	—	—	99	160 - 180
Solvesso 100 (Esso)	1	—	—	99	155 - 170

2. Chlorinated Hydrocarbons

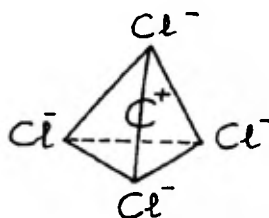
The introduction of chlorine in hydrocarbon molecules creates some polarity of the dry type.



As attraction between molecules is increased, smaller molecules are used as solvents to obtain proper evaporation rates.



Carbon tetrachloride is the least polar of this series because the molecule is symmetrical and dipoles cancel off somewhat. Chlorinated hydrocarbons are not miscible with water because they have little tendency to form hydrogen bonds.



Other chlorinated solvents derive from the ethylene and ethane molecules.



Chloroethene is less poisonous than trielene and other chlorinated solvents and is more suitable for conservation work.

Chlorinated hydrocarbons are not flammable.

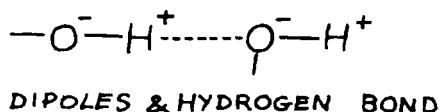
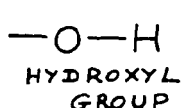
3. Functional Groups

Several solvents are made by adding a group of atoms containing oxygen and/or nitrogen to a hydrocarbon molecule.

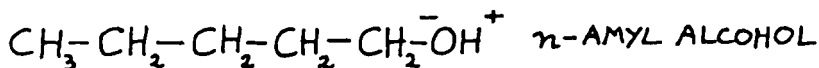
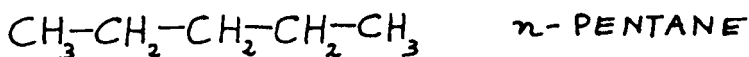
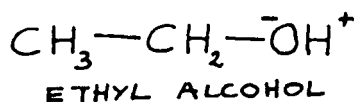
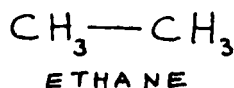
Such groups are called *functional groups*; they modify the polarity of the molecule.

3.1 Alcohols

Alcohols contain the hydroxyl group which is polarized and can form hydrogen bonds.



The hydroxyl group causes an increase of wet polarity.

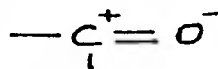
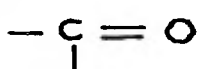


When the hydrocarbon chain is longer, wet polarity is reduced and miscibility with water is decreased.

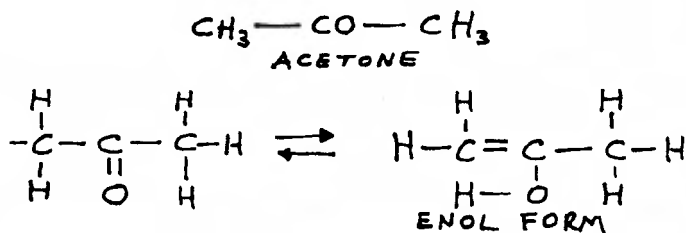
Ethyl alcohol is completely miscible with water (i.e. in any ratio) while n-amyl alcohol can mix only with a limited amount of water (or vice versa).

3.2 Ketones

Ketones are characterized by the carbonyl group which is polarized and causes an increase of dry polarity.

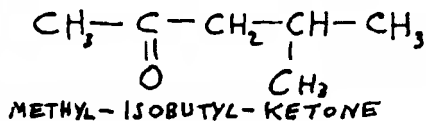
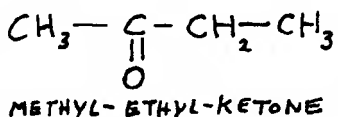


However, if a methyl or methylene group is located next to the carbonyl group, some wet polarity arises because through a shift of some bonds a hydroxyl group can be formed.



Some molecules of the ketone transform into a structure containing a hydroxyl group; the latter is called the enol form of the ketone. The arrows indicate that the reaction goes both ways (i.e. the normal ketone can be re-formed from the enol).

Other interesting ketones are:



They evaporate more slowly than acetone and are often more suitable for conservation use.

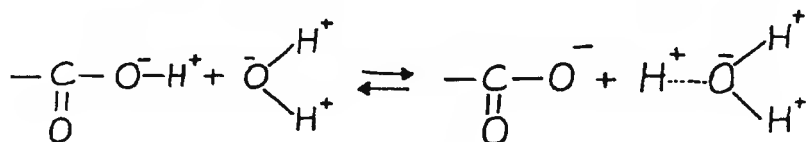
They show some wet polarity too because there are methyl and methylene groups near the carbonyl group.

3.3 Acids

Some functional groups, besides modifying polarity, also give special chemical properties to the molecule.

The group $-\text{COOH}$ is called the *acid* group.

It can react with water:



The acid group is ionized by water and yields some H^+ ions, called *hydrogen ions*.

As the arrows indicate, the reaction can go both ways, that is the ions can re-combine to form the undissociated acid.

Only a limited number of hydrogen ions are therefore present in the water solution of an acid of this type (about one hydrogen ion per 1,000 molecules).

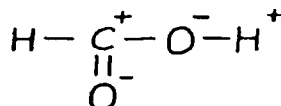
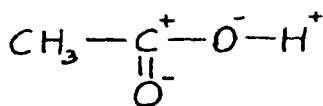
By definition, all substances that produce hydrogen ions when in contact with water are called *acids*.

The hydrogen ion tastes like lemon (the typical acid taste) and is very active from the chemical point of view, as it can corrode metals, dissolve calcium carbonate and other salts, and break down the molecules of proteins.

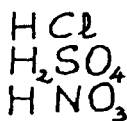
Acids of the **COOH** type are called *organic acids* and are *weak acids* because they yield a small number of hydrogen ions when in contact with water.



In the absence of water these acids behave as very polar solvents since the non-polar section of the molecules is small and polarity of wet and dry type is present.



There are other acids that are not formed from a hydrocarbon molecule, nor do they contain the **COOH** group; these are called *inorganic acids*.



HYDROCHLORIC ACID
SULPHURIC ACID
NITRIC ACID

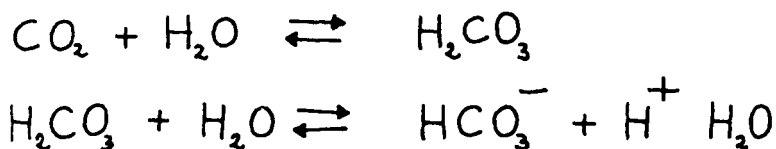
The acids listed above are *strong acids* because they produce many hydrogen ions.



The ionization reaction goes one way only, and one hydrogen ion is produced by each molecule of hydrochloric or nitric acid. (Sulfuric acid yields two hydrogen ions per molecule.)

These inorganic acids cannot be regarded as solvents even in the absence of water.

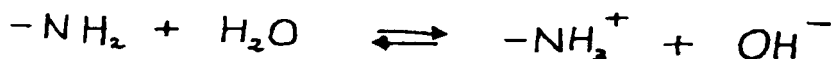
A very weak inorganic acid is formed by carbon dioxide when it dissolves in water.



As carbon dioxide is present in the atmosphere, some amount of it is always dissolved in water; this is the reason why distilled water is slightly acidic.

3.4 Amines, Bases

The group $-\text{NH}_2$ is called the *amine* group. It can react with water:



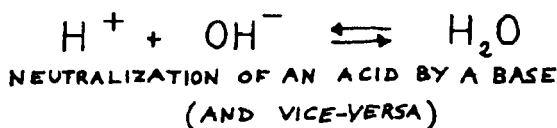
The amine is ionized by water and yields some OH^- ions, called *hydroxyl ions*.

As the arrows indicate, the reaction goes both ways, that is the ions can re-combine to form the amine again.

Only a limited number of hydroxyl ions are, therefore, present in the water solution of an amine, about one hydroxyl ion per 1,000 molecules of amine.

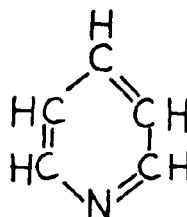
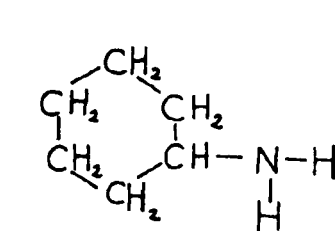
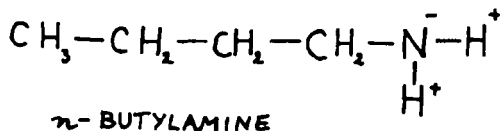
By definition, all substances that yield hydroxyl ions when in contact with water are called *bases*.

The hydroxyl ion has a bitter taste and is very active from the chemical point of view, as it can break down the molecules of fats and neutralize the acids.

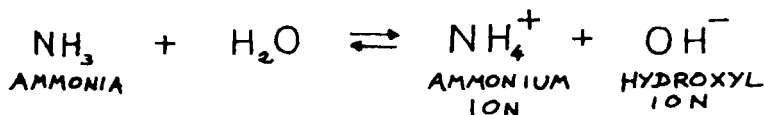


Amines are *weak bases* because they form a small number of hydroxyl ions when in contact with water.

In the absence of water, amines behave as rather polar solvents with some possibility of forming hydrogen bonds (wet polarity).

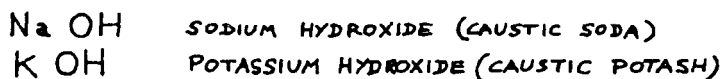


Ammonia is a base even weaker than amines. Its basicity is due to a reaction of ionization of the same type.

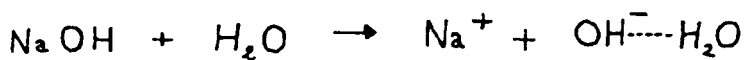


There are other bases that are neither formed from a hydrocarbon molecule nor contain the amine group.

These are the *inorganic bases*, such as:

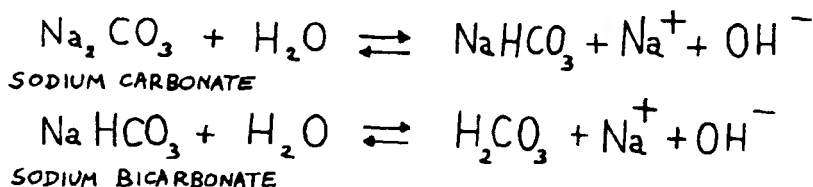


They are called strong bases (or alkalis) because they yield a large number of hydroxyl ions when in contact with water.



The reaction goes one way only and one hydroxyl ion is formed by each sodium hydroxide unit.

Some inorganic bases are weaker than the alkalis.

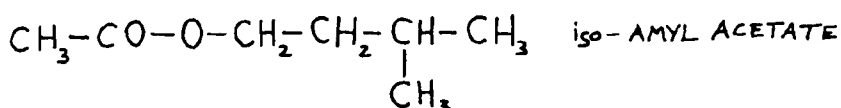
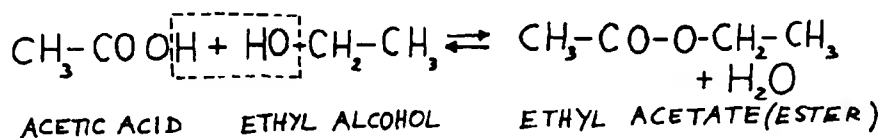


Sodium carbonate (or soda) is a weaker base than sodium hydroxide (caustic soda) because it produces far fewer hydroxyl ions. Sodium bicarbonate is much weaker still.

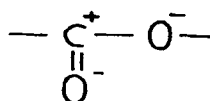
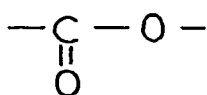
Ammonia and inorganic bases cannot be considered as solvents, although they can be used in conservation for cleaning because of their chemical activity.

3.5 Esters and Amides

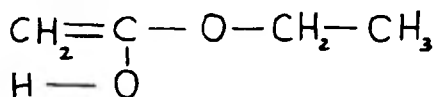
Acids can combine with alcohols to form *esters*.



All esters contain the group

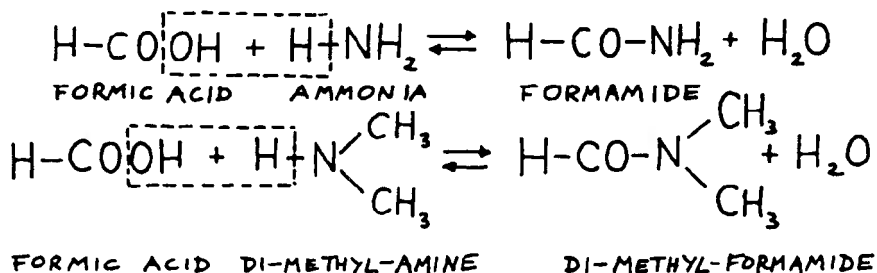


which gives some dry polarity to the molecule. However, hydrogen bonds are also possible when there is a methyl or methylene group near the carbonyl group because an *enol form* can be formed as in the case of ketones.

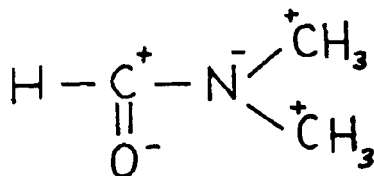


ETHYL ACETATE IN THE ENOL FORM

Acids can also combine with ammonia or amines to form *amides*.



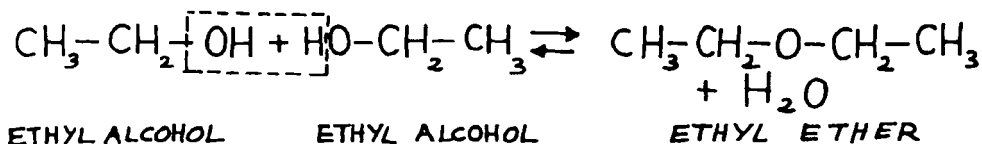
Dimethylformamide is a solvent showing high polarity, mainly of the dry type.



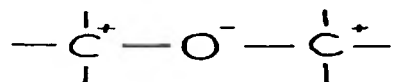
It is a good solvent for oxidized natural resins as these show polarity of the dry type too.

3.6 Ethers

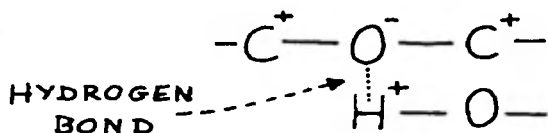
Ethers are formed by the combination of two alcohols.



The polarity of the ether group is mainly of the dry type

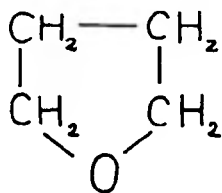


but attraction towards hydrogen-bonding molecules is possible through the oxygen atom.

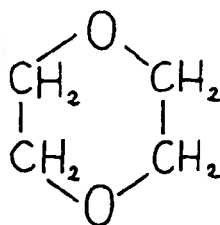


Ethyl ether is far too volatile and flammable to be currently used in conservation (the treatment of highly-decayed waterlogged wood is an exception).

Tetrahydrofuran and dioxane are interesting as solvents, although rather volatile; they have special ring structures.

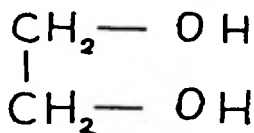


TETRAHYDROFURAN



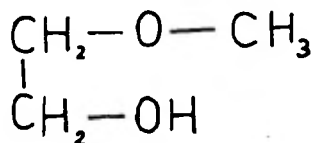
DIOXANE

Some solvents of interest are derived from an alcohol containing two alcoholic groups in the molecule.



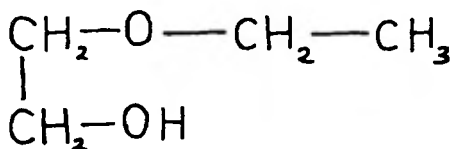
ETHYLENE GLYCOL

An ether can be formed on one alcoholic group only with methyl alcohol



ETHYLENE GLYCOL
METHYL ETHER
(METHYL CELLOSOLVE)

or with ethyl alcohol.



ETHYLENE GLYCOL
ETHYL ETHER
(CELLOSOLVE)

The cellosolves show special solvent properties because they have both dry and wet polarity groups in their molecules.

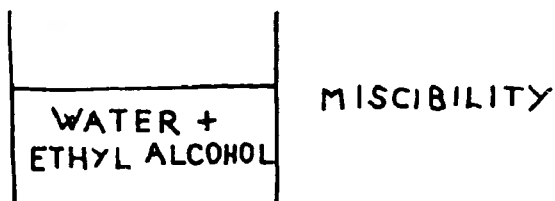
PART III

SOLUTIONS, EMULSIONS AND USE OF SOLVENTS

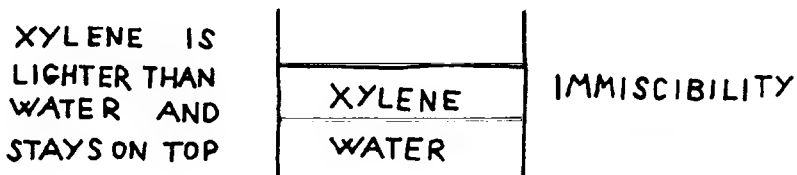
1. Miscibility of Liquids

When two liquids are mixed together they can form a single liquid phase; in this case a separation between the two liquids is no longer visible. This is the case when water and ethyl alcohol are mixed, for instance.

Such liquids are said to be *miscible*.

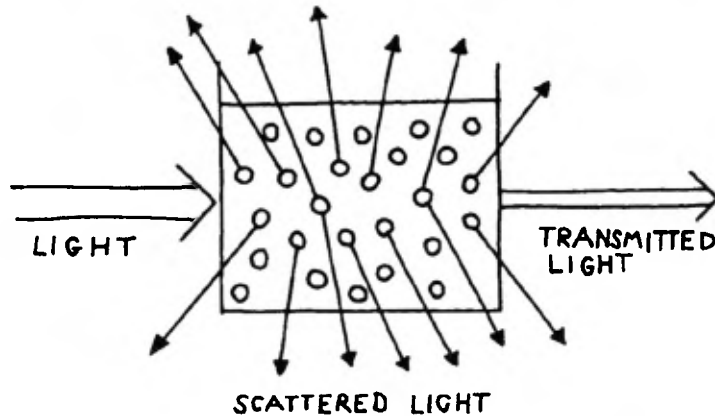


In other cases two separate liquid phases are formed and the separation between them is clearly visible. This is the case with water and xylene.



If the two layers are energetically mixed together the unity of the layer is broken but the two liquids remain separated. Depending on the

situation, we can obtain a suspension of droplets of xylene in water or vice-versa.



Even if the droplets are very small they show their presence by scattering light in all directions.

The transparency of the liquid is sharply reduced and it assumes a white, milky appearance (because the incident light is white).

The suspension is not stable unless stabilized by surface active agents. As soon as the mechanical action is stopped, two clear layers of liquids are re-formed.

The rules for miscibility are the same as the rules for solubility: liquids of similar nature mix well because they can exert mutual attraction forces and, other things being equal, disorder prevails.

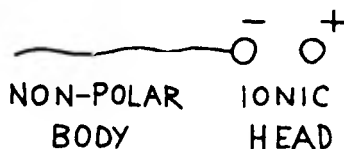
Liquids of different natures do not mix because they cannot exert mutual attraction forces between their molecules, so disorder does not prevail.

In intermediate cases the triangular diagram of solvents can help predict miscibility or immiscibility.

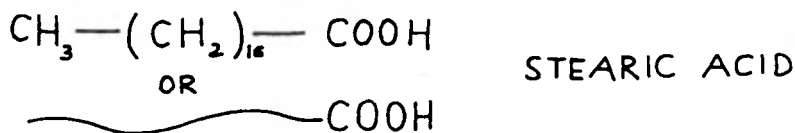
2. Surface Active Agents. Emulsions

Unsuitable suspensions of immiscible liquids can be stabilized by *surface active agents*.

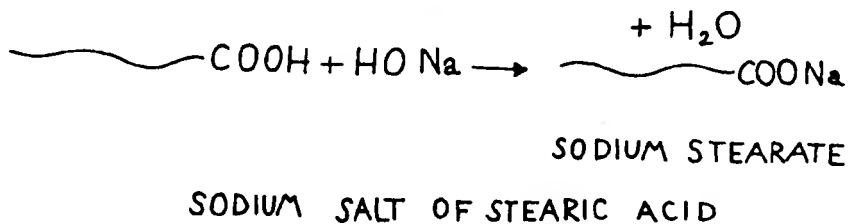
The molecules of surface active agents are composed of a long non-polar body on which a polar head is attached. In the most common type the polar part is composed of a large negative ion and a small positive ion.



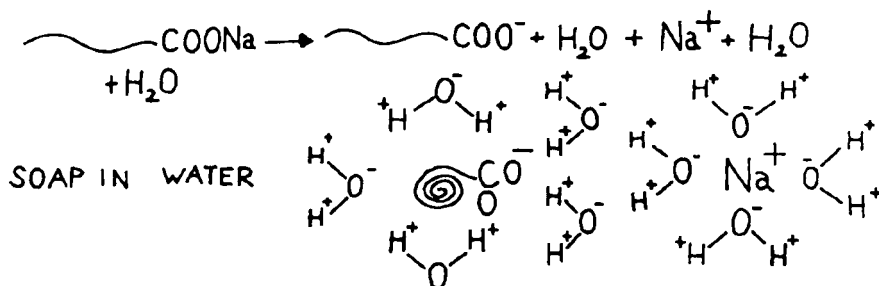
Such molecules can be prepared starting from organic acids with a very long hydrocarbon chain.



If this acid is neutralized by caustic soda the *sodium salt* of the acid is formed.

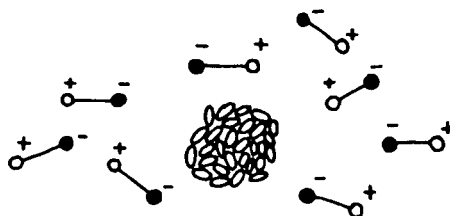


In contact with water the salt is ionized and water molecules surround the positive ion and the negative part of the acid.

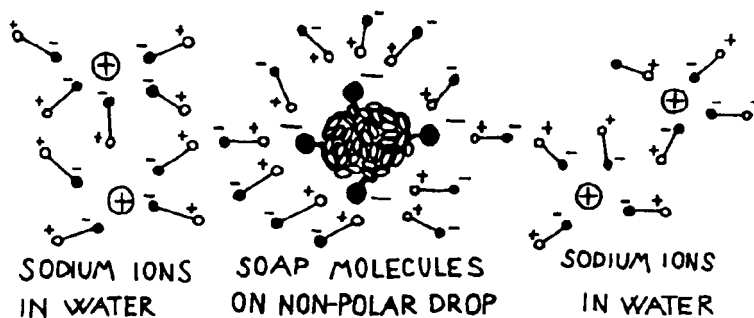


The current name of this material is *soap*. The surface activity of soap is due to the fact that the non-polar tail can adhere to non-polar materials while the polar head can establish hydrogen bonds with water molecules.

If we consider a drop of a non-polar substance that forms an unstable suspension in water,

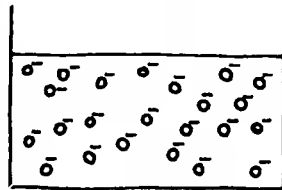


we see how the suspension can be stabilized by the addition of soap.



In this condition the droplets of the non-polar substance do not show any tendency to join because they bear electrical charges of the same sign (negative) and so repel each other.

A stabilized suspension is called an *emulsion*.

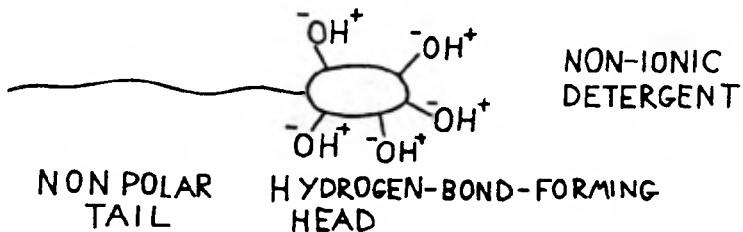


EMULSION
(STABILIZED
SUSPENSION)

Emulsions are easily distinguished from solutions because of their opaque, milky-white appearance (milk is an emulsion) due to the scattering of light. True solutions are clear.

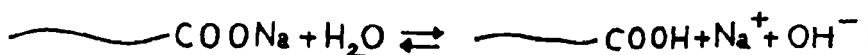
The cleaning action of soaps and other surface active agents (all included under the general name of detergents) is due to the formation of stabilized suspensions where dirt particles that are not easily dissolved are dispersed in water.

Non-ionic detergents are made of a non-polar tail joined to a polar head that contains several alcoholic groups (OH) or other groups capable of forming hydrogen bonds with water molecules.



Non-ionic detergents can perform the same functions as soap without releasing sodium ions and causing basicity of the solution.

Sodium salts of weak organic acids cause some basicity (and can so damage base-sensitive materials) according to the reaction:



This reaction is called *hydrolysis*: basic hydrolysis if hydroxyl ions are formed (as in the case above), acid hydrolysis if hydrogen ions are formed.

3. Concentration of Solutions

When a liquid is mixed with another substance (or more than one) and a solution results, the composition of the solution can be expressed by indicating the amount of substance that is dissolved in a given amount of the solution. This is called the *concentration* of that substance in the solution.

When solids are dissolved in liquids the concentration is often expressed as the weight of solid, in grams, dissolved in 100 ml of solvent; as there is in general little difference between the volume of the solution and that of the solvent, this can be considered to be approximately equivalent to the definition of concentration given above.

EXAMPLE : 10 GRAMS OF NaCl ARE DISSOLVED
IN 500 MILLILITERS OF WATER
CONCENTRATION OF NaCl IN WATER $\frac{10}{500} = 2\% (w/v)$

The w/v symbol (which means weight/volume percentage) indicates the type of units used to calculate the percentage.

Weight/weight (w/w) or volume/volume (v/v) percentages are also used, the latter type in the case of the mixing of liquids.

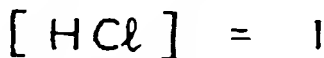
EXAMPLE: ACETONE IS DILUTED 1 TO 4 WITH WATER
 (i.e.) 3 PARTS WATER ARE MIXED WITH 1 PART ACETONE
 CONCENTRATION OF ACETONE $\frac{1}{4} = 25\% (v/v)$

When concentrations are expressed in percentages, it is important that the type of percentage intended (w/v, w/w or v/v) be indicated, as the figures can change when passing from one type of percentage to another.

In chemical work, concentrations are also expressed in moles per litre. One mole is a number of grams equal to the molecular weight of the substance dissolved.

EXAMPLE: HYDROCHLORIC ACID HCl
 MOLECULAR WEIGHT = 36
 1 MOLE = 36 g
 SOLUTION 1 mol = 1 MOLE/LITER = 36 g/LITER = 3.6 g/100 ml = 3.6% (w/v)
 SOLUTION 0.5 mol = 0.5 mole/LITER = 18 g/LITER = 1.8% (w/v)

A solution containing 1 mole per litre is called one molar (abbreviation 1 mol or 1M); a solution half as concentrated would be 0.5 molar (0.5 mol or 0.5M).



The square brackets are used to indicate molar concentrations. Put simply, the equation above means that a solution of hydrochloric acid is 1 molar.

4. Acid and Basic Solutions. pH

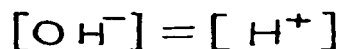
It is often interesting to know whether a solution in water is acid, neutral or basic.

According to the definitions of acids and bases it can be stated that:

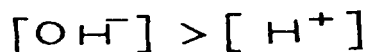
(a) A solution is acid if there are more hydrogen ions than hydroxyl ions.



(b) A solution is neutral if there are as many hydrogen ions as hydroxyl ions.



(c) A solution is basic if there are more hydroxyl ions than hydrogen ions.



So we should know the concentrations of both H^+ and OH^- to be able to tell if the solution is acid or basic.

However, because of the existence of the neutralization reaction that goes both ways (equilibrium of neutralization),



the product of the molar concentrations of H^+ and OH^- must be constant, that is equal to a number that is known. We write this statement in symbols as follows:

$$[\text{H}^+] \times [\text{OH}^-] = \text{CONSTANT}$$

$$\text{CONSTANT} = 10^{-14}$$

This number is an extremely small one, having 13 zeroes after the point and before the first figure that is 1.

According to the equation above, if we know $[\text{H}^+]$ we can calculate $[\text{OH}^-]$ and vice-versa. Normally only $[\text{H}^+]$ is measured to find out whether a solution is acid, neutral or basic.

Since $[\text{H}^+]$ is often a very small number, with several zeroes after the point, it is transformed in order to make it simpler.

If a solution is neutral

$$[\text{H}^+] = [\text{OH}^-] \quad \text{AND} \quad [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$$

so $[\text{H}^+] = 10^{-7} \quad [\text{OH}^-] = 10^{-7}$

To make the number 10^{-7} simpler, we transform it into its reciprocal 10^7 and the latter into its logarithm 7. We call this last number the pH of the solution.

$$\text{pH OF A NEUTRAL SOLUTION} = 7$$

An extremely basic solution can have a concentration of hydroxyl ions equal to one (this would be the case of caustic soda 1 molar).

According to our definitions:

$$\text{IF } [\text{OH}^-] = 1 \text{ AND } [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] \times 1 = 10^{-14} \quad [\text{H}^+] = 10^{-14}$$

$$\text{RECIPROCAL} = 10^{14} \quad \text{LOGARITHM} = 14 \quad \text{pH} = 14$$

$$\text{pH OF AN EXTREMELY BASIC SOLUTION} = 14$$

A very acid solution can have a concentration of hydrogen ions equal to 0.1 (this would be the case of hydrochloric acid 0.1 molar).

In this case:

$$\text{IF } [\text{H}^+] = 0.1 = 10^{-1} \text{ AND } [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$$

$$[\text{OH}^-] = 10^{-13} \quad [\text{H}^+] = 10^{-1}$$

$$\text{RECIPROCAL} = 10^1 \quad \text{LOGARITHM} = 1 \quad \text{pH} = 1$$

$$\text{pH OF A VERY ACID SOLUTION} = 1$$

In the case of a concentration of hydrogen ions equal to 1 (as would be the case of hydrochloric acid 1 molar) the pH would not be 1 but 0, because

$$[\text{H}^+] = 1 = 10^0 \quad \text{RECIPROCAL} = 10^0 \quad \text{LOGARITHM} = 0$$

$$\text{pH OF AN EXTREMELY ACID SOLUTION} = 0$$

pH values can be measured by means of indicators, that is dyes that change colour at a given pH (like tea when lemon is added).

pH can also be measured in an electrical way by means of pH meters.

5. Use of Solvents. Evaporation Rate

A solvent should have an evaporation rate suitable to the operation it must perform.

In the cleaning of paintings, for instance, if the solvent evaporates too soon (as is often the case when acetone is used) it is very difficult to soften properly the layers of oxidized varnishes and to remove them before the solvent disappears.

Conversely, if the evaporation is too slow the solvent can remain in contact with the original paint layer for a long time and soften it. In such a condition the paint layer can be easily damaged by a slight mechanical action.

Another unfavourable effect of solvents that evaporate slowly is the fact that moist surfaces are rapidly soiled by dust which easily adheres to them.

Examples of solvents showing excessively small evaporation rates are glycerine and triethanol amine.

When a solvent is used as the carrier of an adhesive in order to consolidate an object by impregnation, a high evaporation rate can inhibit penetration of the consolidant while a slow evaporation can leave the object sticky for a long time.

Evaporation rates are easily evaluated if the vapour pressure of the solvent at room temperature is known. This is measured in millimetres of mercury, in short mm Hg (remember that liquids boil when their vapour pressure equals 1 atmosphere and that 1 atmosphere equals 760 mm Hg).

Solvents showing vapour pressures between 2 and 5 mm Hg at room temperature are probably the best suited for conservation works of the types mentioned above. An enlarged range, from 1 to 20 mm Hg, can still be accepted as a general specification for conservation.

Unfortunately, often the vapour pressure at room temperature is not found easily for several solvents (some data are reported in the table of solvents, annexed to this text). In such cases the boiling point of the solvent can give a useful indication.

Hydrocarbon solvents that boil between 130°C and 170°C appear the best suited for conservation work.

Boiling point figures can be lower for polar solvents because the vapour pressure decreases more sharply with the temperature.

Water (boiling point 100°C) is an acceptable solvent while ethyl alcohol (boiling point 78°C) is a little “fast” but still usable.

6. Hazards of Solvents. Toxicity and Flammability

Most solvents are toxic and cause poisoning upon prolonged exposure to their vapours.

The dangerousness of a solvent is best evaluated by considering the maximum allowable concentration (in air) or threshold limit (TL) allowed by health regulations for continued exposure of industrial workers.

This concentration is expressed in parts per million (ppm). A low figure (below 25 for instance) shows a relatively high toxicity. A figure between 25 and 100 corresponds to an average toxic level (several common solvents fall into this range), while between 100 and 1,000 toxicity can be considered low. Above 1,000 no toxicity at all can be presumed.

It must be borne in mind, however, that the tables of maximum allowable concentrations in air are periodically revised and that all revisions to date have lowered the figures because new long-range toxic effects of some solvents have been discovered.

It is, therefore, advisable to consider all solvents as potentially dangerous and take proper precautions to control their concentration in air and to reduce the exposure time of the operators.

Particular care must be taken in the cleaning of paintings when prolonged exposure to concentrated solvent vapours is possible.

Precautions must also be taken when flammable solvents are used.

Flammability is evaluated by measuring the *flash point* of the solvent.

The flash point is the temperature above which a mixture of solvent vapours and air can be ignited by a flame or a spark.

If the flash point is below room temperature or only slightly above, fire precautions must be seriously considered, particularly if large amounts of solvent are used.

Transport regulations consider all liquids having a flash point inferior to 37°C as potentially dangerous.

It is seldom realized that fire starts generally in the vapour phase, not in the liquid itself. Therefore, when a volatile solvent is used and the air becomes saturated with solvent vapours, it can be ignited by a spark (a normal electric switch produces a spark when operated) or a cigarette, even if the ignition source is kept distant from the flammable liquid.

7. Mixtures of Solvents

Solvent mixtures are frequently used in conservation. Their solubility properties can be estimated if the three solubility parameters of all components are known. One multiplies the parameters of each component by its concentration in the mixture and sums up the result.

For maximum precision molar percentages (number of moles per hundred moles of mixture) should be used, but in view of the uncertainty over the values of the parameters themselves, volume concentrations (v/v) or weight concentrations (w/w) can be used instead.

As an example let us calculate the approximate parameters of a mixture of methyl isobutyl ketone (30% v/v), methyl cellosolve (30% v/v) and dimethylformamide (40% v/v).

	PARAMETERS		
	N	D	W
M. I. K.	58	22	20
METHYL-CELLOSOLVE	39	22	39
DIMETHYLFORMAMIDE	41	32	27

PARAMETERS MULTIPLIED BY CONCENTRATIONS

	N	D	W
M. I. K. (30%)	$58 \times \frac{30}{100}$	$22 \times \frac{30}{100}$	$20 \times \frac{30}{100}$
METHYL-CELLOSOLVE (30%)	$39 \times \frac{30}{100}$	$22 \times \frac{30}{100}$	$39 \times \frac{30}{100}$
DIMETHYLFORMAMIDE (40%)	$41 \times \frac{40}{100}$	$32 \times \frac{40}{100}$	$27 \times \frac{40}{100}$

PARAMETERS OF MIXTURE

	N	D	W
M. I. K.	17.4	6.6	6.0
METHYL-CELLOSOLVE	11.7	6.6	11.7
DIMETHYLFORMAMIDE	16.4	12.8	10.8
	45.5	26.0	28.5 = 100

The mixture can thus be located in the triangular diagram and its behaviour towards solids, whose solubility area is known, can be evaluated.

If acid or basic components (and water) are added to solvents, the solvent properties of the mixture cannot be evaluated from the solubility parameters alone; the possible chemical reactions of hydrogen or hydroxyl ions must be considered too.

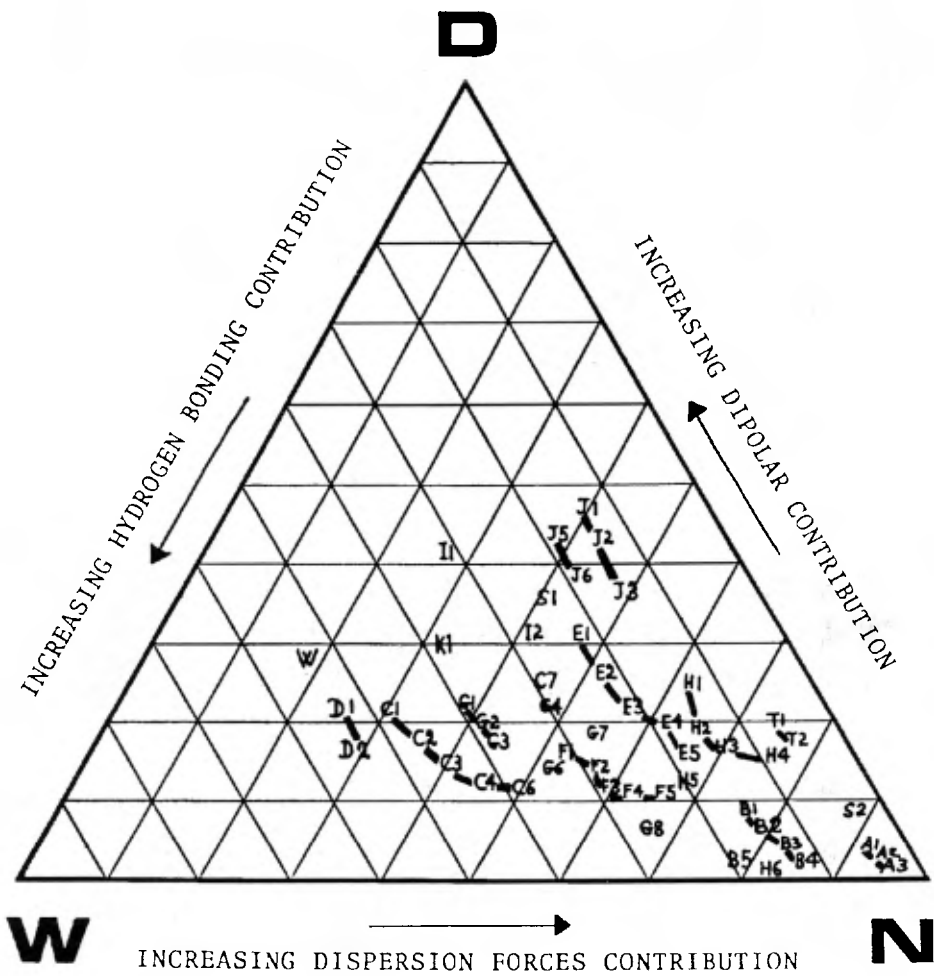


DIAGRAM OF SOLVENTS

Data from *Predicting Resin Solubilities* by J.P. Teas, printed by Ashland Chemicals Company, Columbus Ohio. See also the Table of Solvents in the following pages.

- D = dipole-dipole attraction
- W = hydrogen bond
- V = dispersion forces

TABLE OF SOLVENTS

Diag. ref.	Name of Solvent	B. P. °C	Vapour Pressure mmHg at °C	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters			Other Names	
							N	D	W		
Aliphatic Hydrocarbons											
A 1	Mineral spirits	150-196	14	50	0.77	500	38	90	4	6	white spirit
A 2	V.M. & P. naphtha	118-139	—	—	0.75	470	-7	94	3	3	
A 3	Odourless mineral spirits	181-200	—	—	0.76	—	54	98	1	1	odourless solvent
—	n-Heptane	99	40	22	0.68	400	-4	100	0	0	
Aromatic Hydrocarbons											
B 1	Benzene	80	74.6	20	0.88	10	-11	78	8	14	
B 2	Toluene	110	22	20	0.86	100	4	80	7	13	
B 3	Xylene	138-140	10	30	0.87	100	17	83	5	12	solvensolxylene
B 4	Ethyl benzene	136	10	25	0.86	100	15	87	3	10	
B 5	Styrene	146	6.5	25	0.91	50	31	78	4	18	
Cyclic Hydrocarbons											
T 1	Dipentene	175	2	20	0.84	100	41	75	20	5	
T 2	Turpentine	154-170	4	20	0.85-0.87	100	34	77	18	5	
—	Cyclohexane	81	77	20	0.78	300	-20	94	2	4	

Diag. ref.	Name of Solvent	B. P. °C	Vapour Pressure mmHg	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters			Other Names
							N	D	W	
Alcohols										
C 1	Methyl alcohol	65	95	0.79	200	10	30	22	48	methanol
C 2	Ethyl alcohol	78	40	0.79	1000	12	36	18	46	ethanol
C 3	Propyl alcohol	97	21	0.80	200	25	40	16	44	propanol
—	Isopropyl alcohol	82	33	0.79	400	12	—	—	—	isopropanol
C 4	Butyl alcohol	117	5.5	0.81	50	24	43	15	42	butanol
—	Secondary butyl alcohol	99	12	0.81	50	23	—	—	—	sec-butanol
—	Isobutyl alcohol	108	9	0.80	100	37	—	—	—	isobutanol
—	Tertiary butyl alcohol	82	42	0.78	100	11	—	—	—	tert-butanol
—	n-Amyl alcohol	138	1	0.82	100	37	46	13	41	
C 6	Cyclohexanol	161	1	0.95	50	67	50	12	38	
D 1	Glycerol	290	0.0025	1.26	—	175	25	23	52	glycerin
D 2	Ethylene glycol	198	0.06	1.11	100	115	30	18	52	glycol
—	Ethylene chlorohydrin	128	4.9	1.20	1	60	—	—	—	2-chloroethanol
C 7	Diacetone alcohol	168	1	0.93	50	65	45	24	31	
—	Methyl isobutyl carbinol	132	3	0.81	25	54	50	10	40	2-pentanol-4 methyl
W	<u>Water</u>	100	17	1.00	n.p.	n.i.	18	28	54	

Diag. ref.	Name of Solvent	B. P.		Vapour Pressure mmHg at °C	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters			Other Names	
		°C	mmHg					N	D	W		
Ketones												
E 1	Acetone	56	178	20	0.79	750	-19	47	32	21		
E 2	Methyl ethyl ketone	80	77	20	0.81	200	-6	53	26	21		
—	Methyl n-propyl ketone	102	16	20	0.81	200	7	—	—	—		
E 3	Methyl isobutyl ketone	117	7.5	25	0.80	50	17	58	22	20		
—	Mesityl oxide	129	9	20	0.86	15	32	55	24	21		
E 4	Methyl isoamyl ketone	144	—	—	0.82	100	35	62	20	18	2-hexanone-5-methyl	
E 5	Di-isobutyl ketone	168	1.7	20	0.81	50	49	67	16	17	4-heptanone-- 2,6-dimethyl	
E 6	Cyclohexanone	156	4.5	25	0.95	25	44	55	28	17		
Esters												
F 1	Ethyl acetate	77	73	20	0.90	400	-4	51	18	31		
F 2	Propyl acetate	102	35	25	0.89	200	14	57	15	28		
F 3	Butyl acetate	126	10	20	0.88	150	22	60	13	27		
F 4	Isobutyl isobutyrate	147	10	38	0.86	—	49	63	12	25		
F 5	Amyl acetate	149	5	25	0.88	100	25	60	12	28		
—	Isoamyl acetate	143	6	25	0.88	100	23	60	12	28		

Diag. ref.	Name of Solvent	B. P. °C	Vapour Pressure mmHg at °C	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters			Other Names
							N	D	W	
Ethers										
-	Ethyl ether	35	439	20	0.71	400	-45	-	-	ether
G 1	Methyl cellosolve	125	6	20	0.97	25	38	39	22	39
G 2	Ethyl cellosolve	135	4	20	0.93	100	40	42	20	38
G 3	Butyl cellosolve	171	0.6	20	0.90	50	60	46	18	36
G 4	Diethylene glycol ethyl ether	202	0.13	20	0.99	-	96	48	23	29
G 6	Cellosolve acetate	156	1	20	0.97	25	47	51	15	34
G 7	Tetrahydro furan	65	114	15	0.89	200	-17	55	19	26
G 8	Dioxane	101	37	25	1.03	25	11	67	7	26
Chlorinated Solvents										
H 1	Methylene chloride	40	440	25	1.33	100	n.i.	62	26	12
H 2	Ethylene chloride	84	78	20	1.26	50	13	67	19	14
H 3	Trichloro ethane	74	100	20	1.34	350	n.i.	70	19	11
H 4	Chlorobenzene	132	10	22	1.11	75	29	75	17	18
H 5	Trichloro ethylene	87	58	20	1.46	50	n.i.	68	12	20
-	Chloroform	61	160	20	1.49	10	n.i.	67	12	21
H 6	Carbon tetrachloride	77	91	20	1.59	5	n.i.	85	2	13

Diag. ref.	Name of Solvent	B. P. °C	Vapour Pressure mmHg at °C	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters			Other Names
							N	D	W	
Nitrogen Compounds										
I 1	Formamide	211	—	1.13	—	154	28	42	30	
I 2	Dimethyl formamide	153	4	0.94	10	67	41	32	27	
J 1	Nitromethane	101	28	1.13	100	35	40	47	13	
J 2	Nitroethane	115	16	1.05	100	28	44	43	13	
J 3	Nitropropane	132	7	1.00	15	18	50	37	13	
J 5	Acetonitrile	80	100	0.79	40*	6	39	45	16	methyl cyanide
J 6	Butyronitrile	118	—	0.80	—	—	46	38	16	propyl cyanide
Bases										
—	n-Butylamine	78	—	0.76	5	-12	59	14	27	
—	Cyclohexyl amine	134	15	0.87	10	32	65	11	24	
—	Pyridine	115	20	0.98	5	20	56	26	18	
K 1	Ethanol amine	171	6	1.02	3	85	32	29	40	monoethanol-amine
—	Triethanol amine	343	—	1.13	—	179	—	—	—	
—	Morpholine	128	—	1.00	20	38	—	—	—	

* very toxic liquid

Diag. ref.	Name of Solvent	B. P. °C	Vapour Pressure mmHg	Sp. Gr.	Toxicity TLV ppm	Flash Point °C	Fractional Solubility Parameters N D W	Other Names
	Acids							
-	Formic acid	101	40	1.23	5	69	- - -	
-	Acetic acid	118	11	1.05	10	40	- - -	
	Sulphur Compounds							
S 1	Dimethyl sulphoxide	dec 100	0.37	20	1.10	95	41 36 23	
S 2	Carbon disulphide	46	360	20	1.27	-30	88 8 4	

SOLUBILITY PARAMETERS OF SOME POLYMERS AND RESINS

	N	D	W
Poly-methyl-methacrylate	51	27	22
Poly-ethyl-acrylate (Lucite 2042)	55	32	13
Poly-vinyl-acetate (Mowilith 50)	51	27	22
Poly-vinyl-butyral (Butvar B76)	46	24	30
Poly-vinyl-chloride (Vipla KR)	54	26	20
Epoxy resin, before setting (Epikote 1001)	44	28	28
Polystyrene (Polystyrene LG)	63	22	15
Polyamide (Versamide 930)	56	5	39
Petroleum hydrocarbon resin (Piccopale 110)	72	13	15
Nitro-cellulose	38	38	24
Ethyl-cellulose	47	28	25
Urea-formaldehyde resin	48	20	32
Rosin ester (Cellolyn 102)	57	19	24

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1. The first part of the document is a list of names and addresses of the members of the committee.

2. The second part of the document is a list of the names and addresses of the members of the committee.

3. The third part of the document is a list of the names and addresses of the members of the committee.

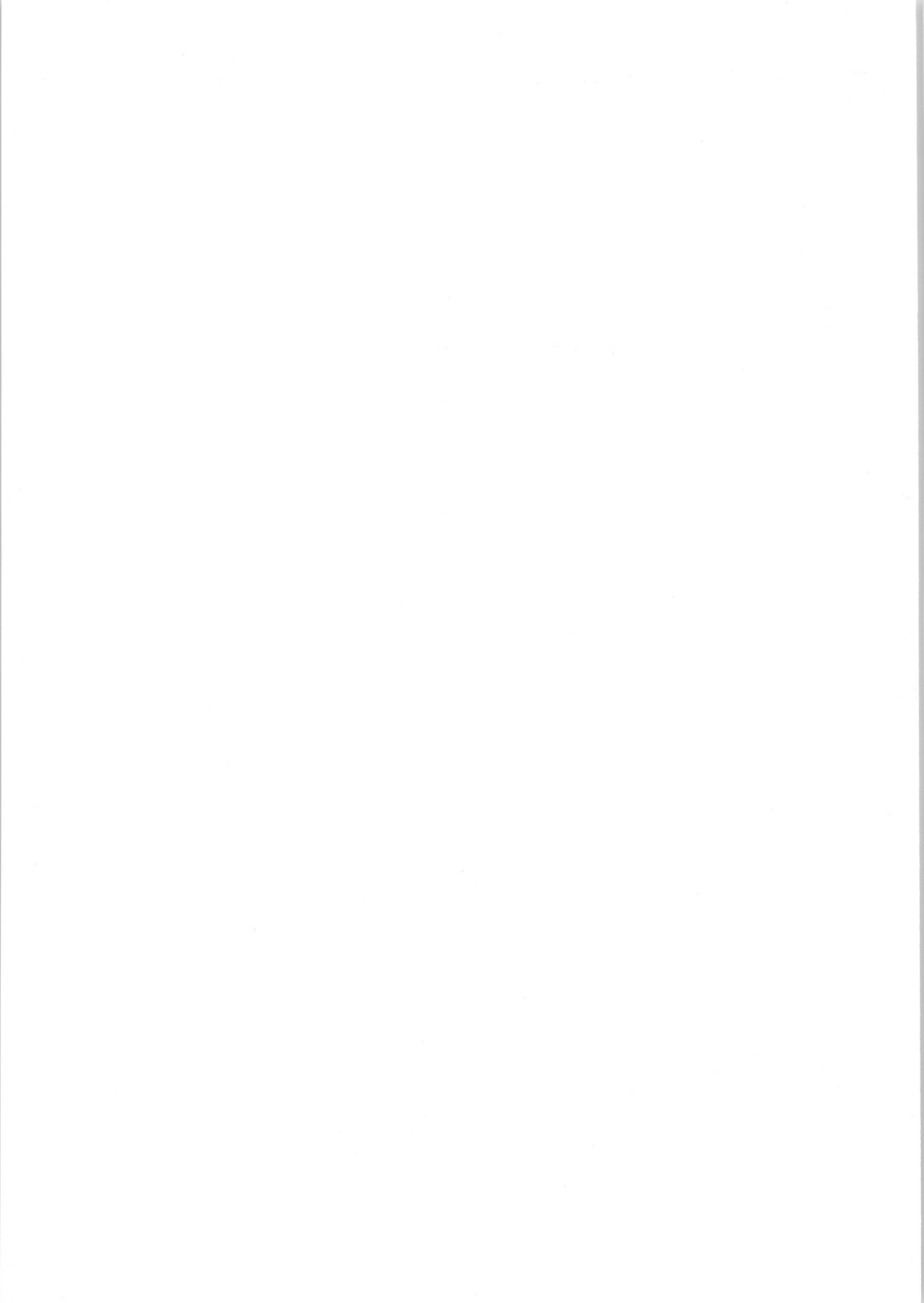
4. The fourth part of the document is a list of the names and addresses of the members of the committee.

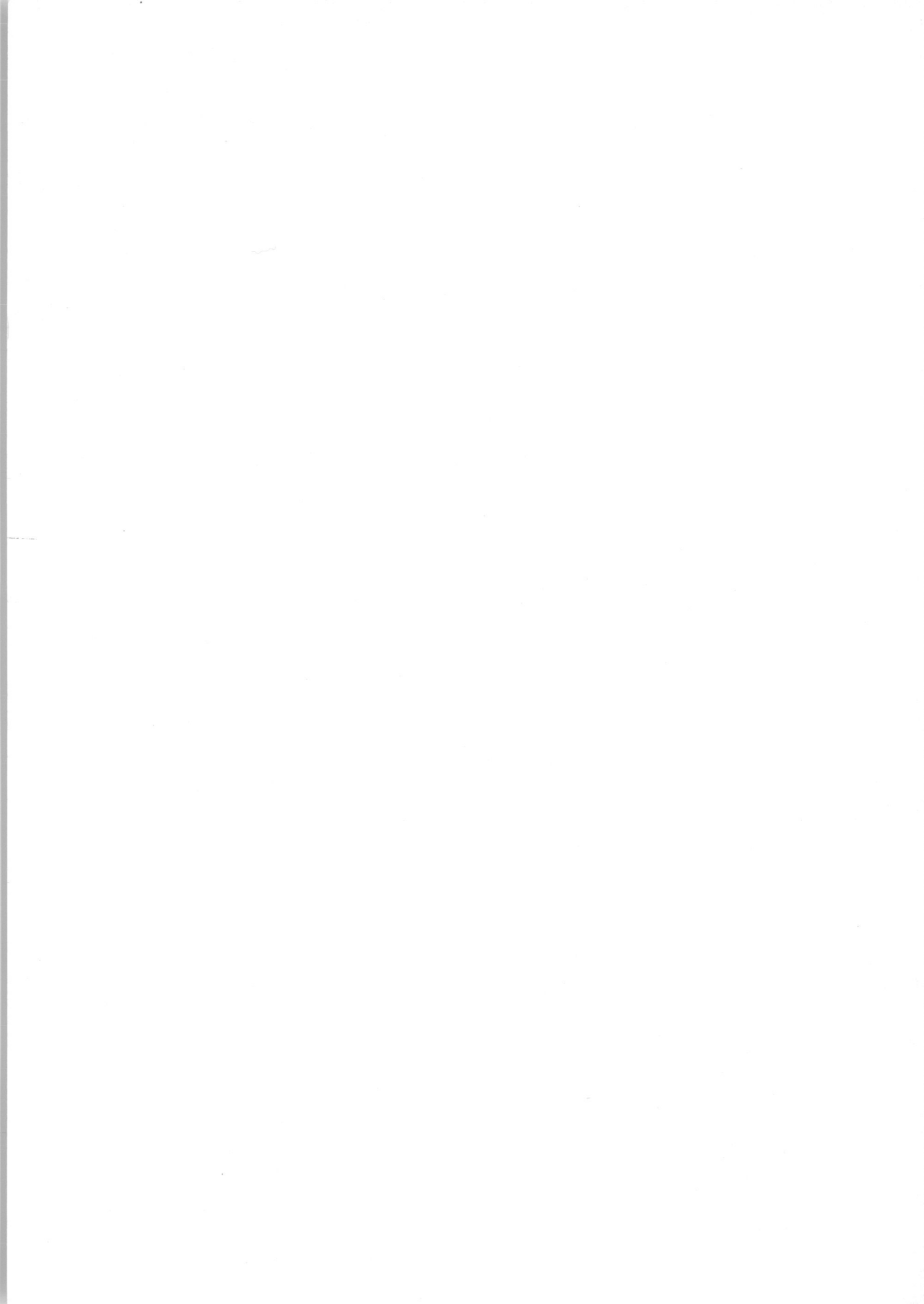
5. The fifth part of the document is a list of the names and addresses of the members of the committee.

6. The sixth part of the document is a list of the names and addresses of the members of the committee.

7. The seventh part of the document is a list of the names and addresses of the members of the committee.

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