States of matter

Matter is made of atoms. The physical state of matter depends on how the particles are arranged in space, on the forces involved and on the mobility of particles.

Solids

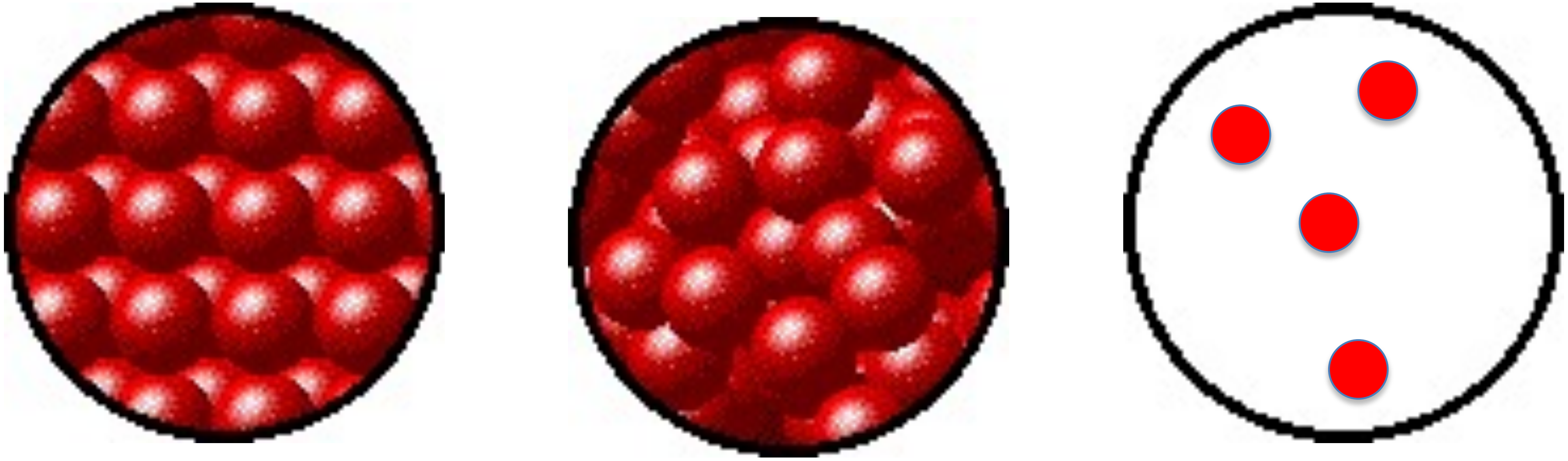
- strong cohesive forces
- tight packing
- ordered
- low mobility

Liquids

- weak cohesive forces
- tight packing
- disordered
- high mobility

Gas

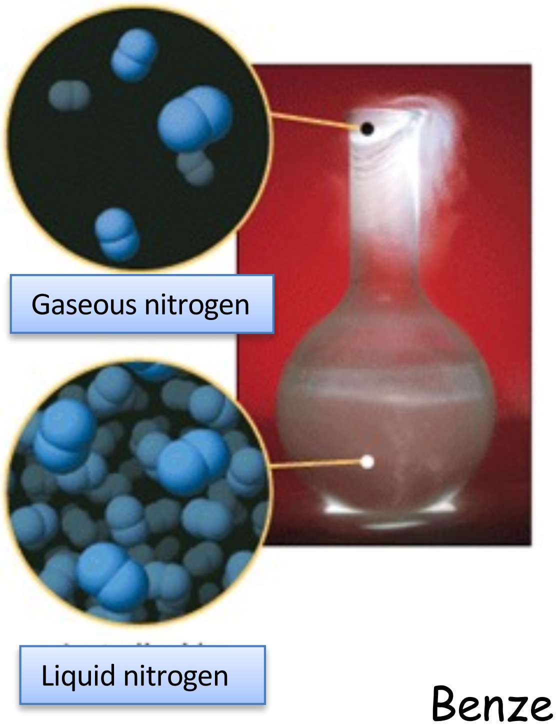
- no cohesive forces
- very low density
- disordered
- very high mobility

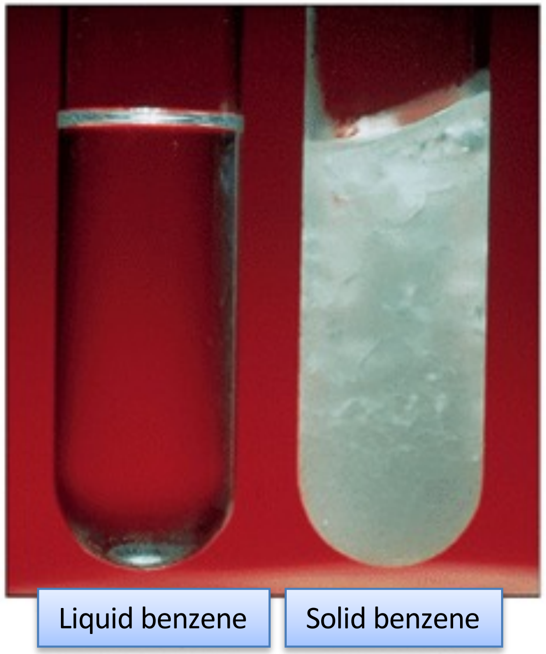


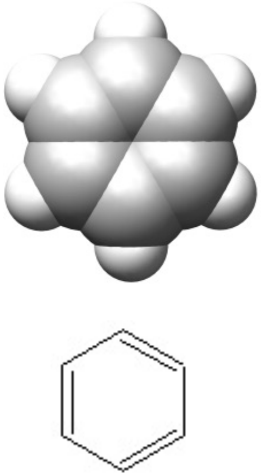
Intermolecular forces, liquids and solids

The majority of chemical elements are solid at 25 ° C and 1 atm. Only 11 elements are in gaseous form under these conditions (H_2, N_2, O_2, F_2, Cl_2 and noble gases) , 2 are liquids (Hg e Br_2).
Many compounds are gaseous (CH_4 e CO_2) or liquid (H_2O) at standard temperature and pressure, but most are solids.

When 300 ml of liquid N_2 evaporate,they produce more than 200 L of gas at 25 ° C and 1 atm







Benzene (C_6H_6) has approximately the same volume in the solid and in the liquid phase

Intermolecular forces

- attractive and repulsive forces vary in a wide range of energies and depend on the environment (solvation, packing).
- are directly related to properties such as melting point, boiling point and the energy required to transform a solid into a liquid or a liquid into a vapour.
- determine the solubility of gases, liquids and solids in various solvents.
- are crucial in determining the structures of biological molecules such as DNA and proteins.

- ion-ion
- ion-dipole
- dipole-dipole
- dipole-induced dipole
- induced dipole-induced dipole

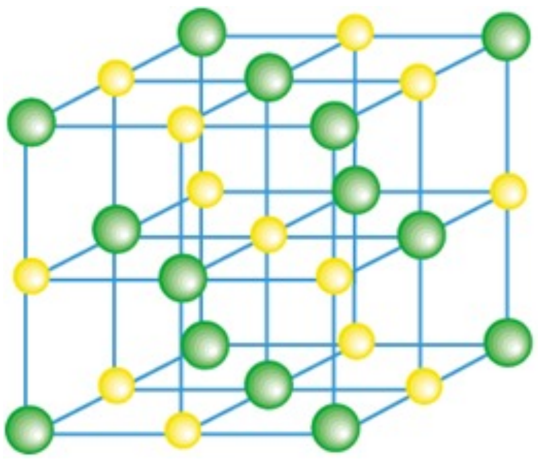
van der Waals forces

RELATIVE STRENGTH OF NON-COVALENT INTERACTIONS

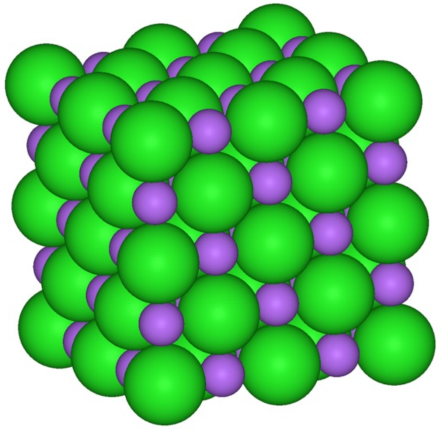
INTERACTION	E ∝ distance	Energy (kJ/mol)
ion – ion	$\propto 1 / r$	400-800
ion – dipole	$\propto 1 / r^2$	40–600
dipole –dipole	$\propto 1 / r^3$	20-30
ion – induced dipole	$\propto 1 / r^4$	5–10
dipole – induced dipole	$\propto 1 / r^6$	2–10
induced dipole– induced dipole	$\propto 1 / r^6$	0.05–40

Solid state

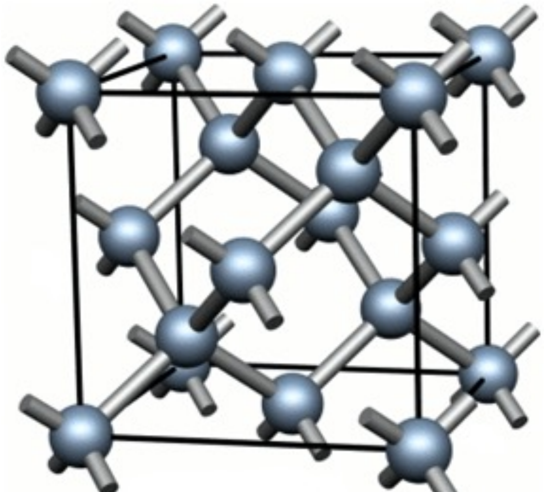
In the solid state, particles (atoms, ions or molecules) occupy fixed positions and their movement is limited to vibrational motions. Generally, particles are ordered in crystal lattices.



LiCl



NaCl



C_n diamante

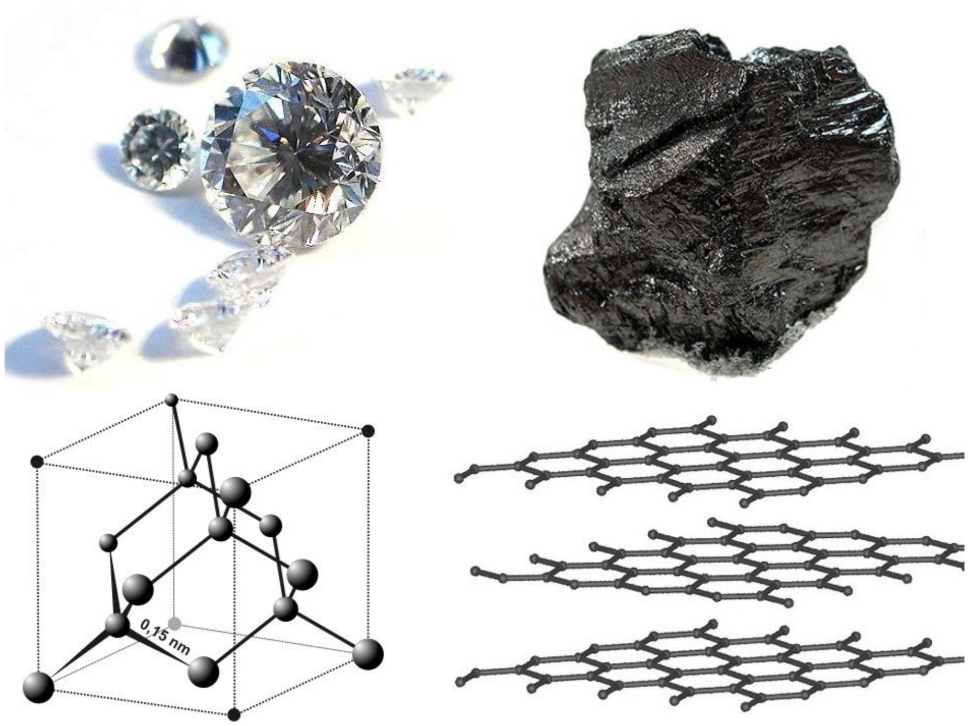
The cohesive forces that hold together particles in the solid state, can vary in intensity. In many cases we have ionic or covalent bonds, in other we have hydrogen bonds. Some molecules are held together by hydrophobic interactions (van der Waals forces).

Classes of solids

The rational criteria for classifying various types of solids, is based on the type of bond that holds together the particles. We can identify four classes, each characterized by a homogeneous chemical and physical behavior, determined by the nature of bonds

- ionic solids
- metallic solids
- molecular solids (made of molecules)
- covalent solids
- amorphous solids

Foto: Charles D. Winters



- Diamond and graphite, two allotropes of carbon, are covalent solids.

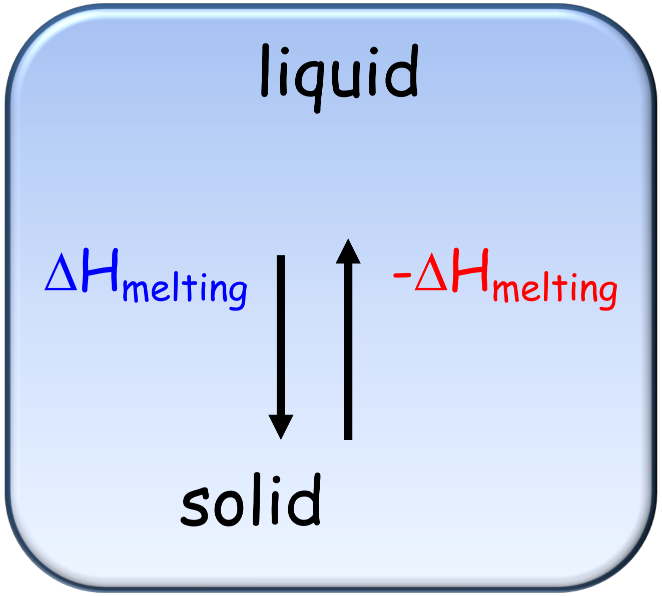
Structures and properties of various types of solids

type	examples	Structural units	Forces in action	properties
ionic	NaCl, K_2SO_4, $CaCl_2$, $(NH_4)_3PO_4$	Positive and negative ions	ionic: attarction between negative and positive charges	hardness, brilliant, high $T_{melting}$, low electrical conductivty, often soluble in H_2O
metallic	Fe, Ag, Cu, alloys	Metal ions (delocalized electrons)	Metallic: electrostatic attraction between ions and electronds	Malleability, ductility,electric and heat conductivity, wide range of $T_{melting,}$
molecular	H_2, O_2, I_2, H_2O, CO_2, CH_4, CH_3OH	molecules	Dispersion forces, dipole-dipole forces, hydrogen bonds	$T_{melting}$ and $T_{eboiling}$ form low to moderate. Low conductivity.
Covalent (reticular)	diamond, graphite, quartz, silicon	Atoms bound in a tri- or bi-dimensional lattice	covalent	High hardness and $T_{fusione}$, low electric and heat conductivity
amorphous	glass, nylon, polyethylene	Aperiodic covalent bonds	Covalent + Dispersion forces, dipole-dipole forces, hydrogen bonds	Non crystalline, wide $T_{melting}$ range, low electric conductivity

Physical propertied of solids

Melting is the conversion from solid to liquid.
The melting point of a solid is the temperature at which the crystal lattice collapses and the solid becomes liquid.

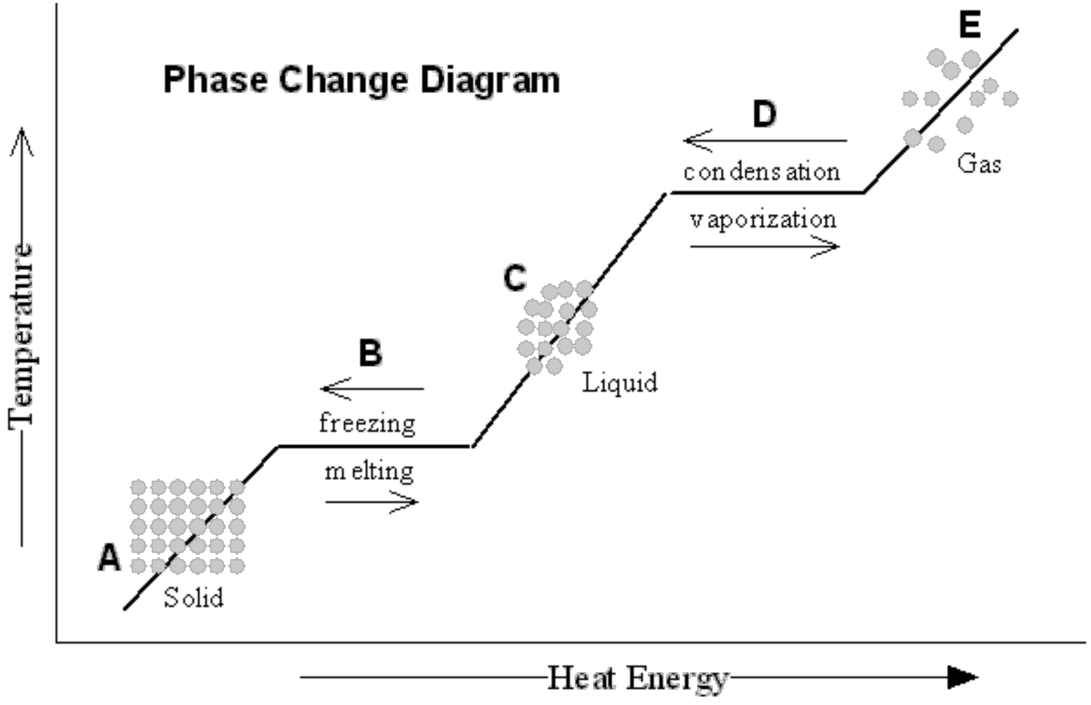
Heat absorbed during melting= melting enthalpy= $\Delta H_{melting}$
Heat lost during solidification= solidification enthalpy= $-\Delta H_{melting}$



liquid

$\Delta H_{melting}$ ↓ ↑ $-\Delta H_{melting}$

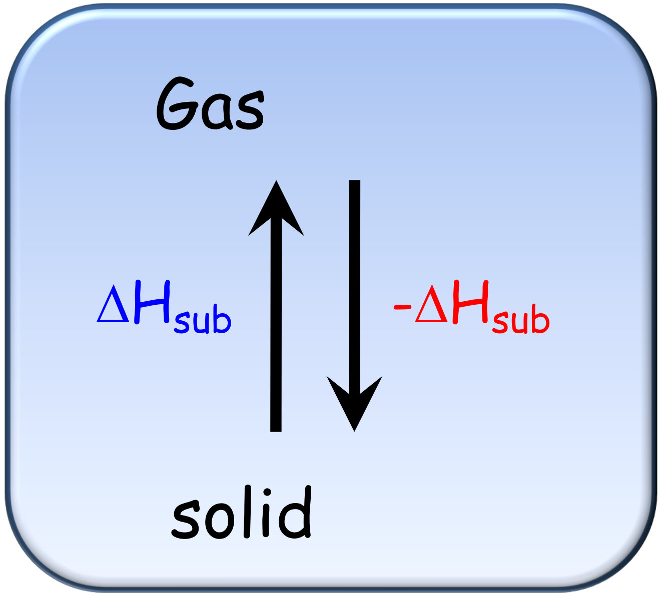
solid



Melting points of some elements and compounds

Element/ compound	$T_{melting}$ (° C)	$\Delta H_{melting}$ (kJ/mol)	Intermolecular forces
metals			
Hg	–39	2.29	metallic
Na	98	2.60	
Al	660	10.7	
Ti	1668	20.9	
W	3422	35.2	
Apolar molecular solids			
O_2	–219	0.440	Dispersion forces
F_2	–220	0.510	
Cl_2	–102	6.41	
Br_2	–7.2	10.8	
Polar molecular solids			
HCl	-114	1.99	Dispersion forces
HBr	-87	2.41	
HI	-51	2.87	
H_2O	0	6.02	Hydrogen bonds
Ionic solids			
NaF	996	33.4	Ion-ion
NaCl	801	28.2	
NaBr	747	26.1	
NaI	660	23.6	

Sublimation is a transition from solid to gas. It is an endothermic process. The energy required is called enthalpy of sublimation: $\Delta H_{sublimation}$

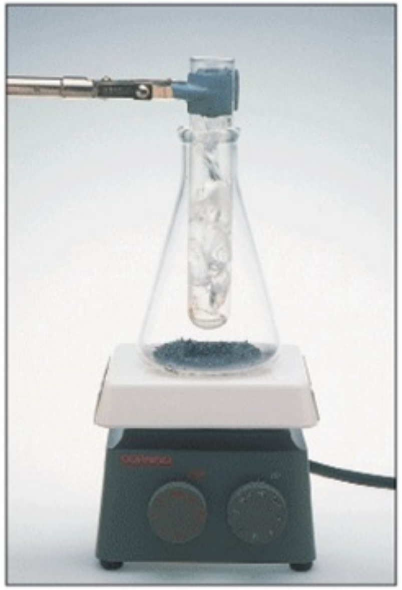


Gas

ΔH_{sub}

$-\Delta H_{sub}$

solid



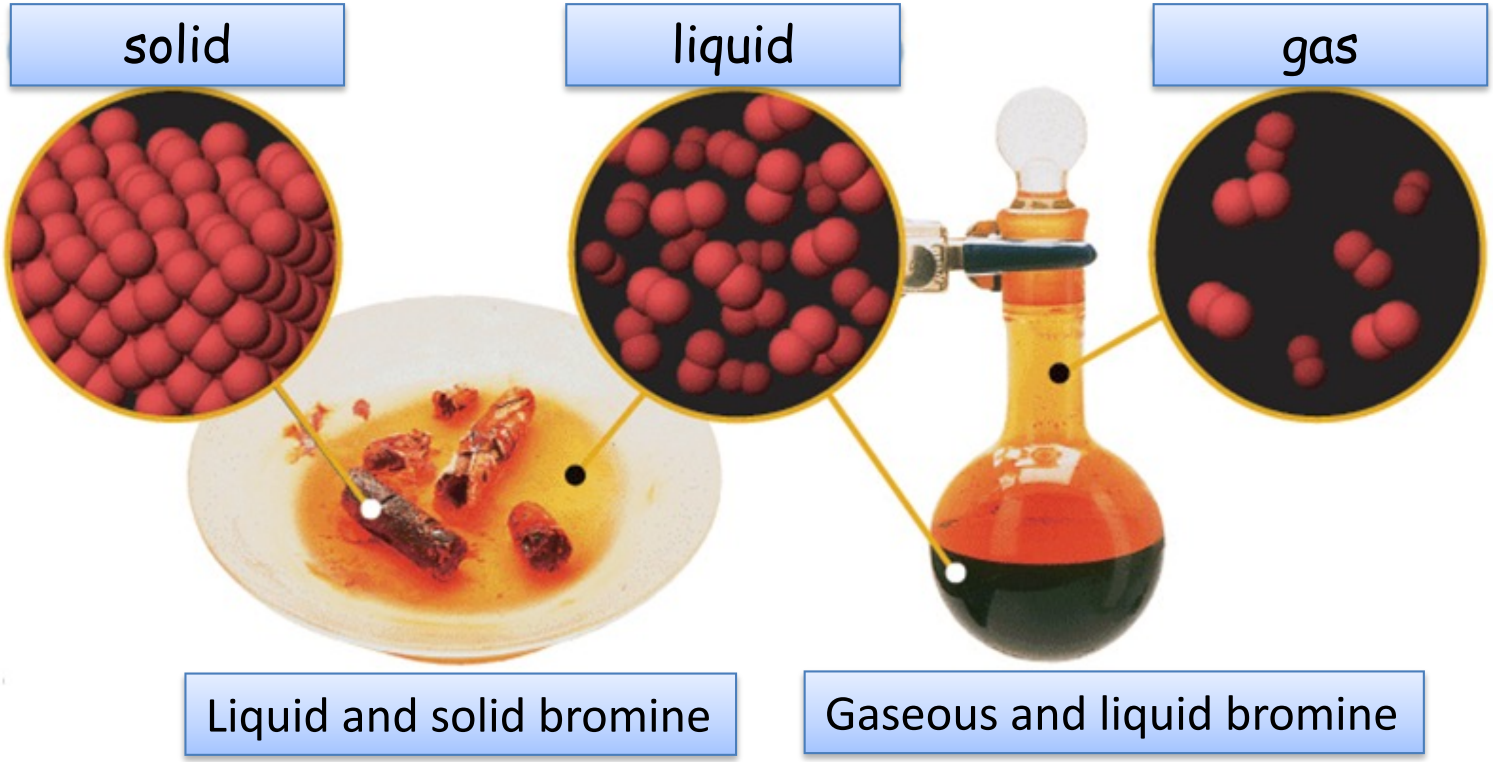
I_2 sublimates upon heating with warm water.

Ice in the tube induces I_2 condensation. (deposition)

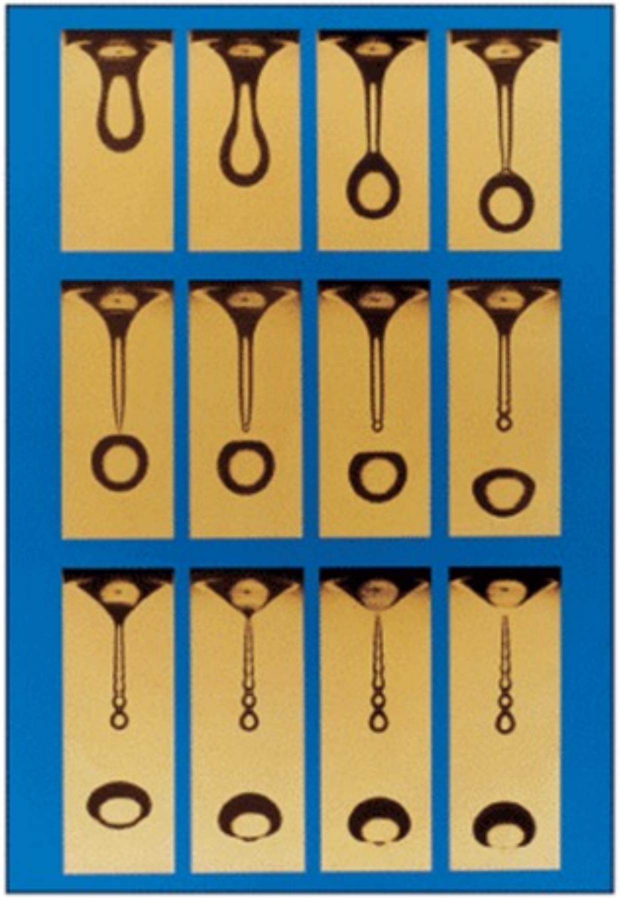
Dry ice (solid CO_2) sublimates at room temperature
(inverse process: deposition)

Liquids

The most difficult to describe. The molecules of a gas under normal conditions are far from each other and can be considered independent. The structure of solids can be described easily because the particles (atoms, ions or molecules) are close to each other but are regularly spaced. In liquids, however, the particles interact with each other as in a solid but are disordered.



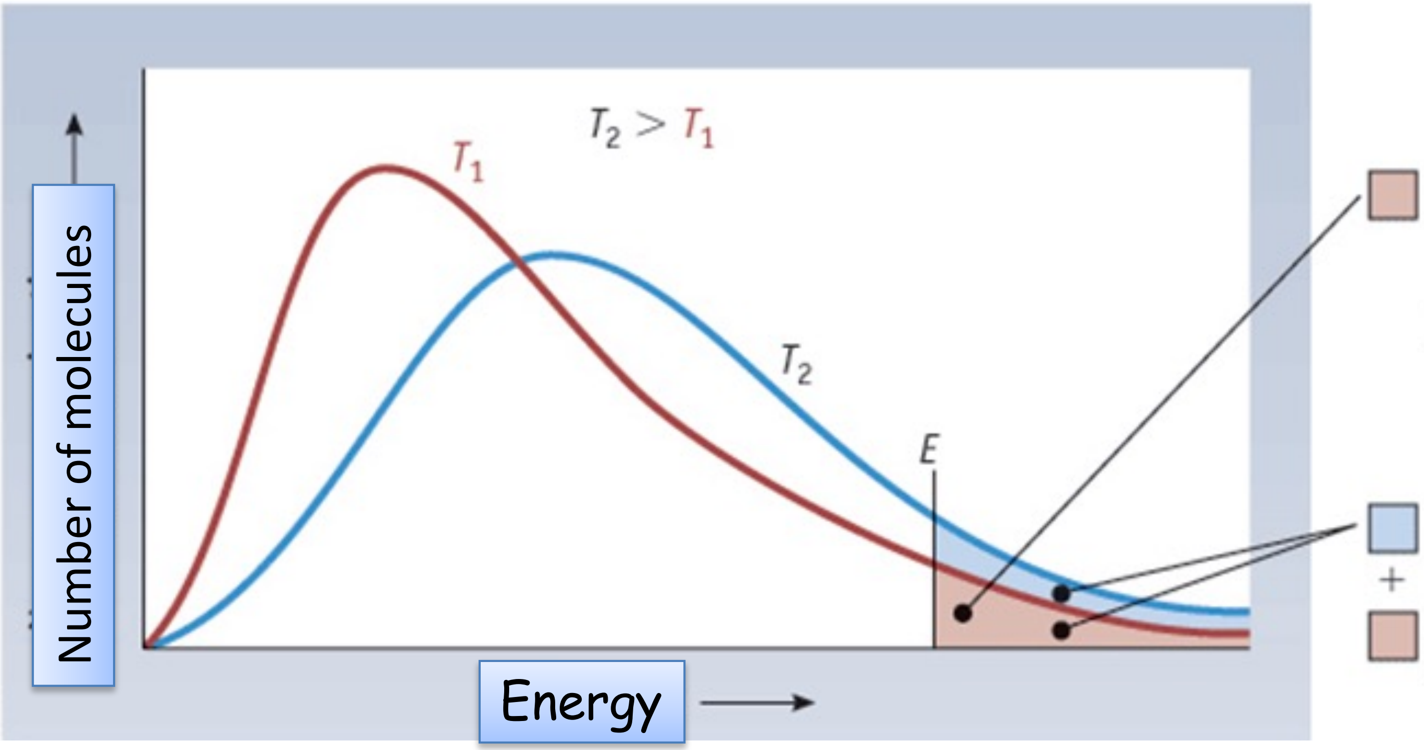
Properties of liquids



a) Fluidity: a liquid is a fluid that, in the absence of external forces, has a spherical shape. The liquids, due to the limited strength of cohesion between the molecules, are sliding, i.e. fluid. However, not all liquids are equally fluid, so it is said that the ether is more fluid than water or that water is more viscous than ether.
b) Elasticity: liquids are very elastic, they are esily deformed and return to their shape if the force is released.
c) Incompressibility: a liquid is a fluid whose volume is constant at constant temperature and pressure. The compressibility of liquids is generally very low.
d) Generally, a compound in the liquid state is less dense than in the solid state, with some notable exception (water).

Evaporation

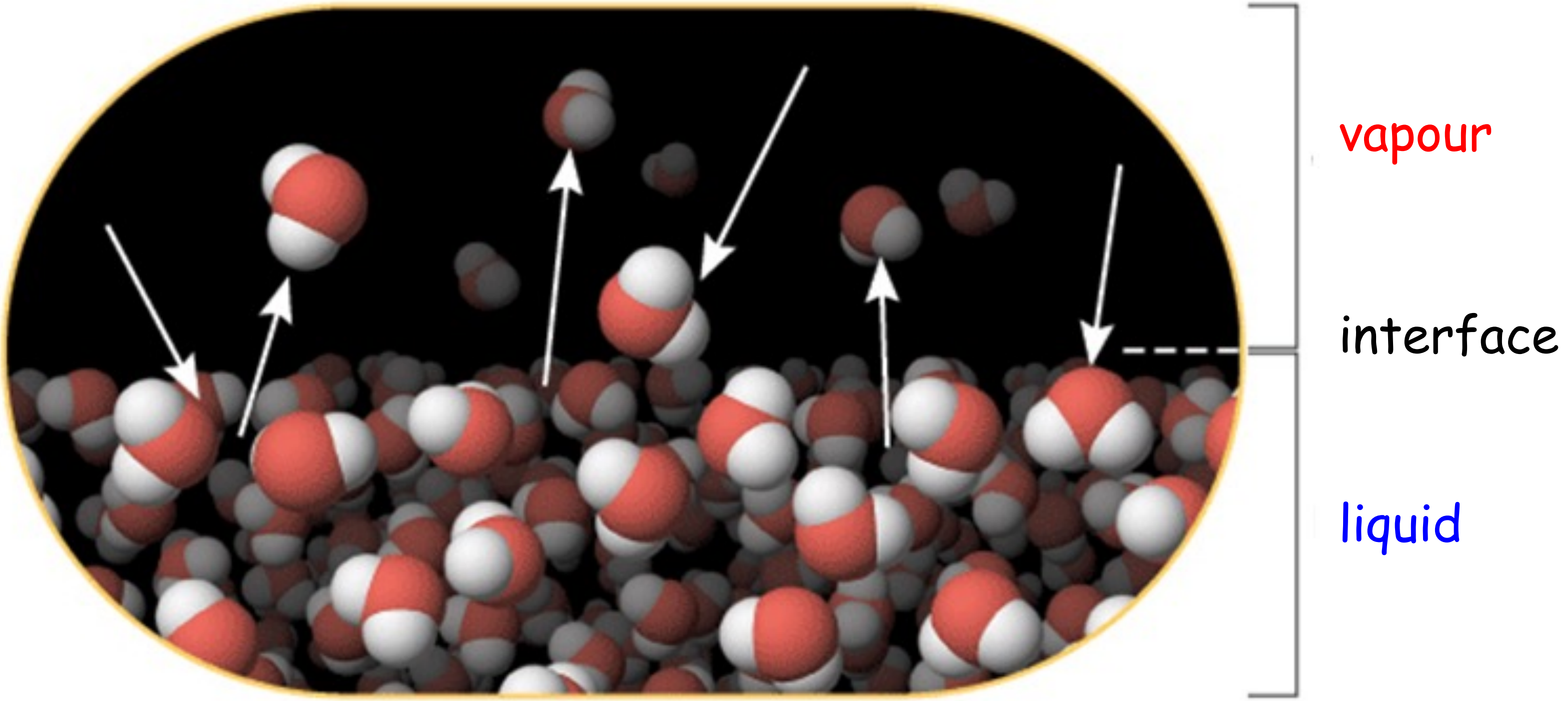
It is the transition from liquid to gas. The distribution of energy in the liquid is similar to that of gases (Maxwell-Boltzmann distribution). Like a gas, the average energy of molecules in a liquid depends only on the temperature: the higher the temperature, the higher the average energy and the fraction of molecules with high kinetic energy.



Number of molecules that have a kinetic energy allowing evaporation at T_1

Number of molecules that have a kinetic energy allowing evaporation at T_2

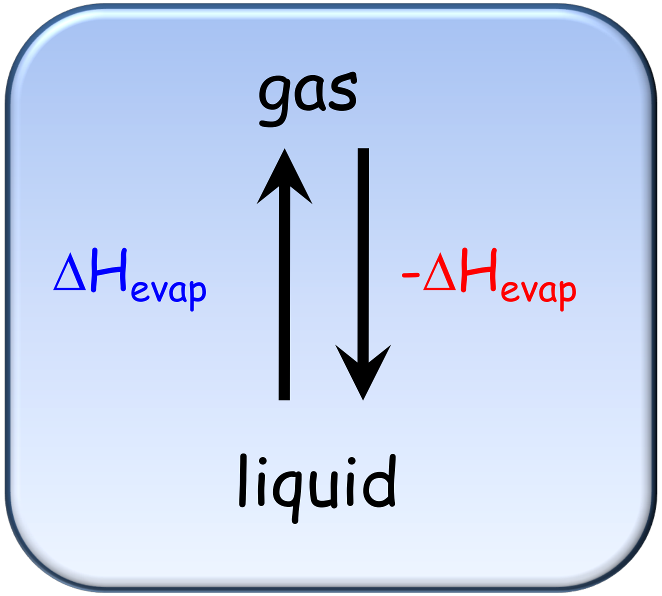
In a liquid there are few molecules with a kinetic energy larger than the energy of intermolecular attractive forces. If these "very fast" molecules are at the surface, they can move into the gas phase.



Evaporation is an endothermic process: energy must be provided to the system to break the intermolecular bonds. Conversely, condensation is an exothermic process.

Molar enthalpy of vaporization and boiling points for some elements and compounds

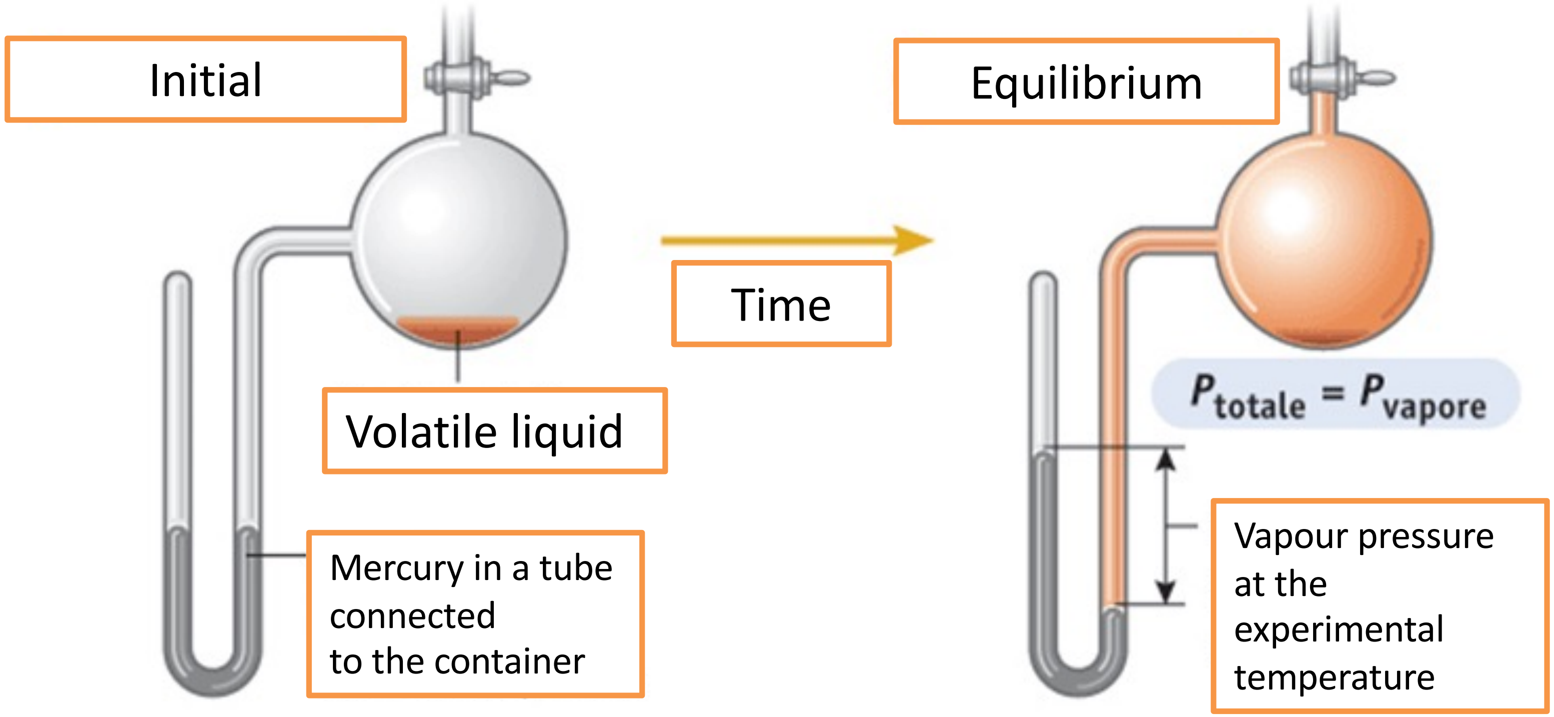
element / compound	molar mass (g/mol)	T_{eb} (° C) (vapour pressure =760 mmHg)	ΔH_{evap} (kJ/mol)
Polar compounds			
HF	20.0	19.7	25.2
HCl	36.5	-84.8	16.2
HBr	80.9	-66.4	19.3
NH_3	17.0	-33.3	23.3
H_2O	18.0	100.0	40.7
Apolar compounds			
CH_4	16.0	-161.5	8.2
C_2H_6	30.1	-88.6	14.7
C_3H_8	44.1	-42.1	19.0
C_4H_{10}	58.1	-0.5	22.4
Monoatomic elements			
He	4.0	-268.9	0.08
Ne	20.2	-246.1	1.7
Ar	39.9	-185.9	6.4
Xe	131.3	-108.0	12.6
Diatomic elements			
H_2	2.0	-252.9	0.9
N_2	28.0	-195.8	5.6
O_2	32.0	-183.0	6.8
Cl_2	70.9	-34.0	20.4



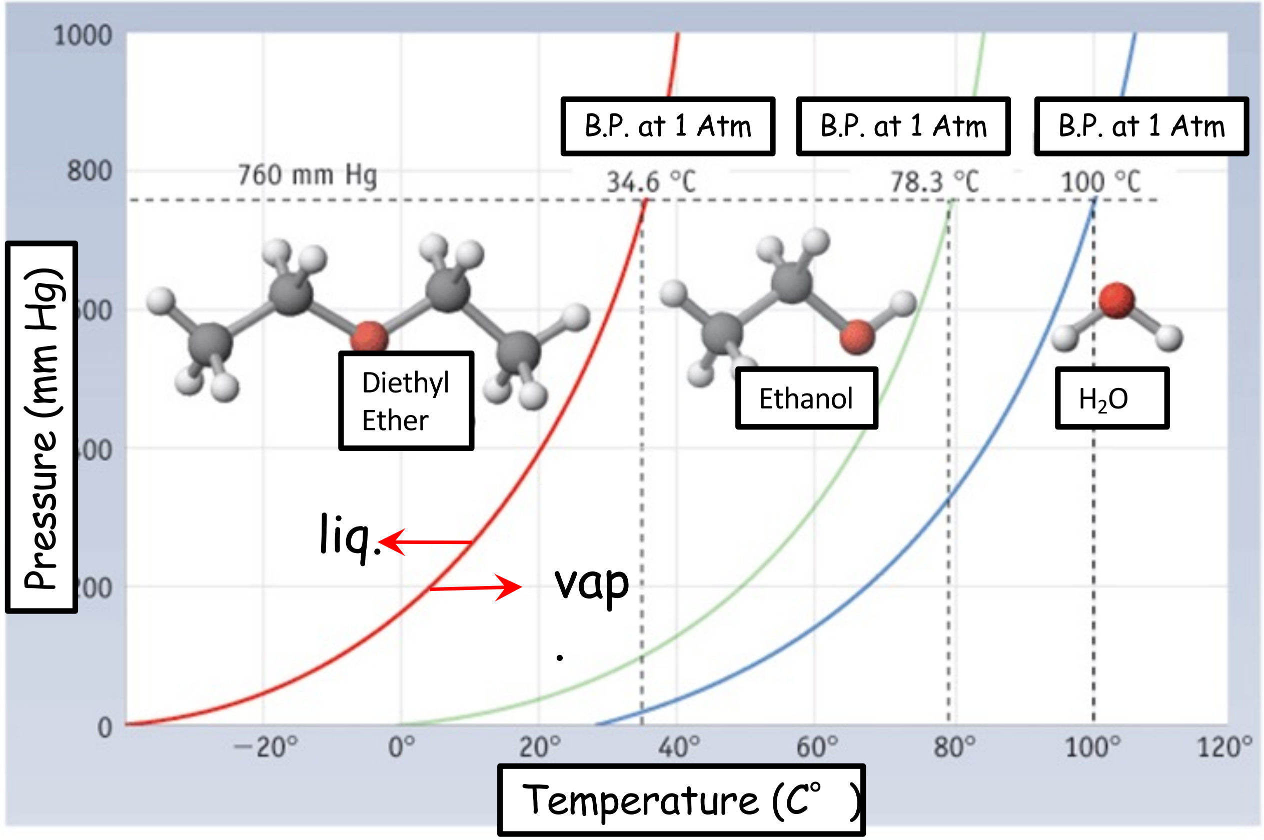
Vapour pressure

If a volatile liquid is placed in a closed container, it evaporates until the evaporation rate equals the rate of condensation. In this final state the system is in dynamic equilibrium. At liquid-vapor equilibrium the equilibrium vapour pressure is measured.

$$\text{liquid} \rightleftharpoons \text{vapor}$$

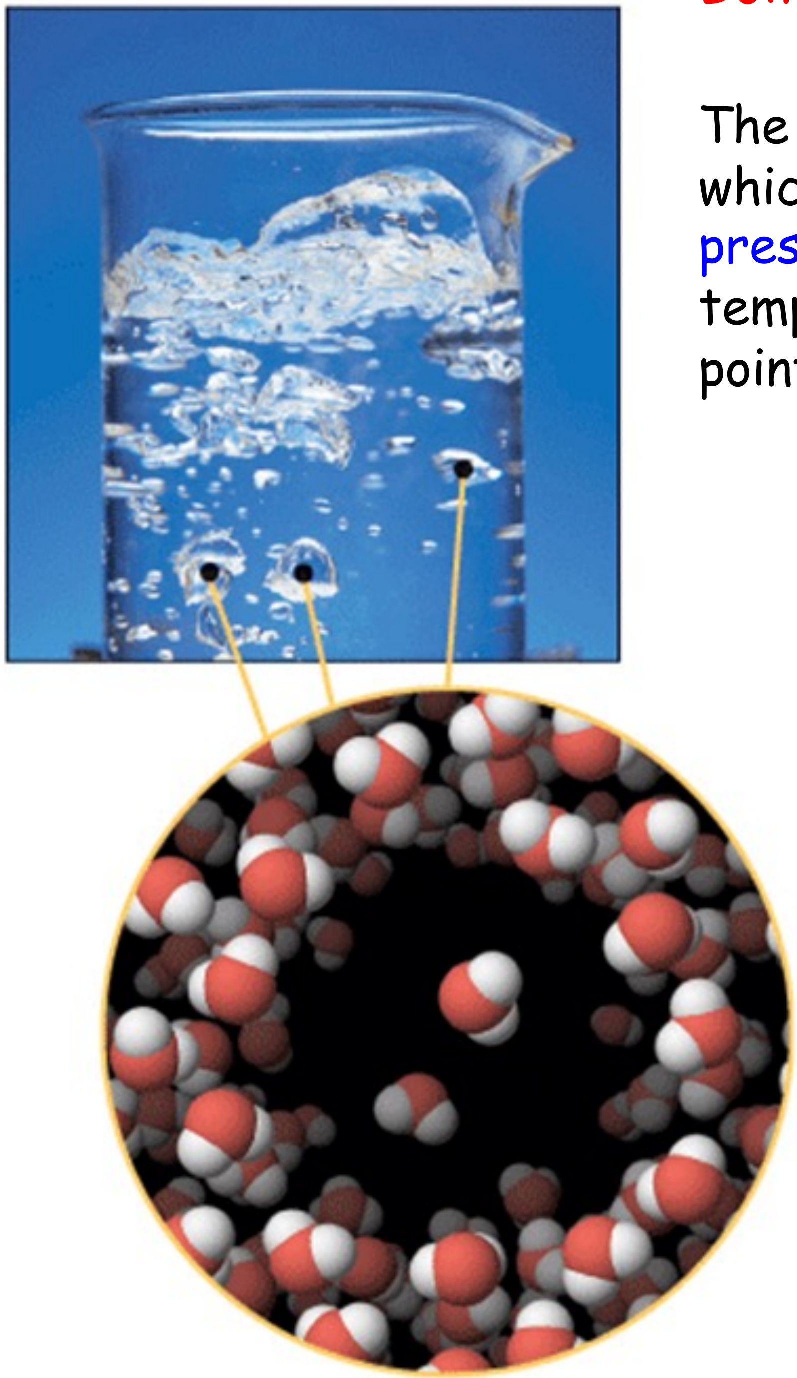


The vapour pressure of a compound is a measure of the tendency of its molecules to escape from the liquid phase into the vapour phase change at a given temperature. The higher the vapour pressure, the more volatile the substance. Vapour pressure increases with temperature: a higher number of molecules have sufficient energy to escape from the liquid surface.

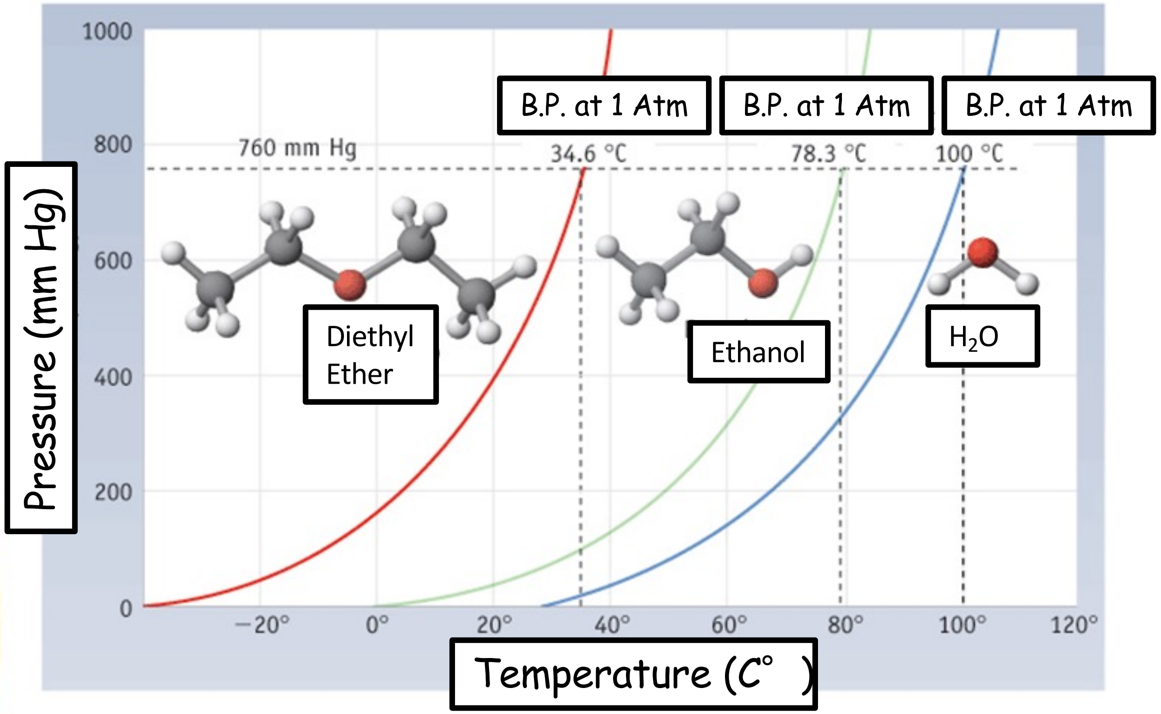


The curves represent the conditions of pressure and temperature at which liquid and vapour phases are in equilibrium (state diagram)

Boiling point



The boiling point of a liquid is the temperature at which the vapour pressure equals external pressure. If the external pressure is 1 atm, this temperature is referred to as the normal boiling point.

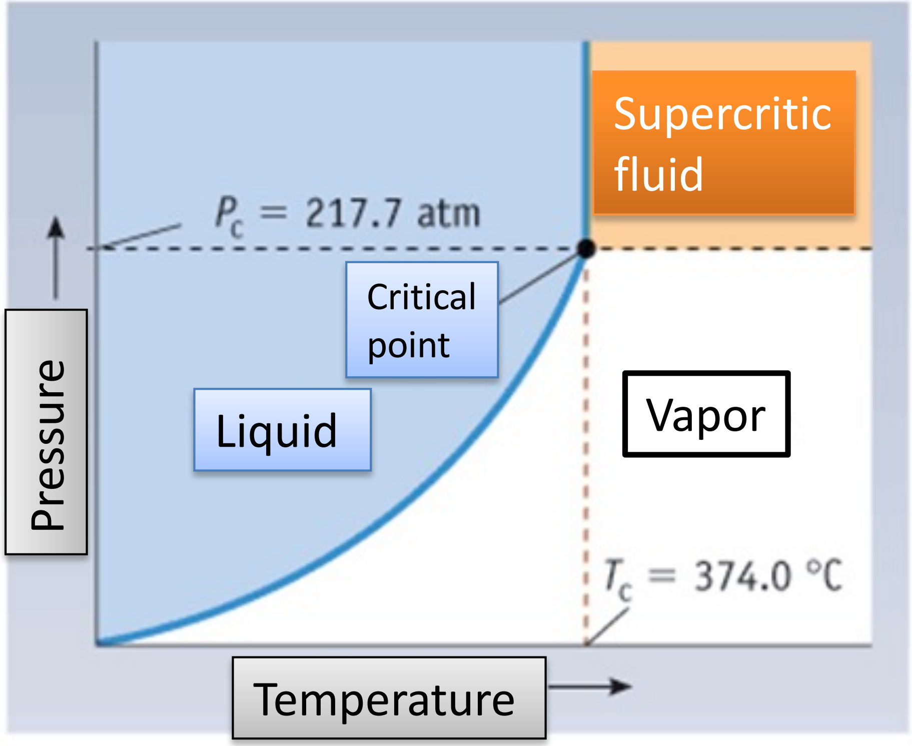


When the vapour pressure equals the external pressure, vapour bubbles start to form within the liquid and it boils.

Critical temperature and critical pressure.

The vapor pressure-temperature curves have an end point.
At specific pressures and temperatures, the interface between the liquid and vapor disappears. This point is called critical point with a critical temperature T_C and the critical pressure P_C. Under these conditions a supercritical fluid is obtained. At the critical point the substance is a gas at a pressure so high that its density is similar to a liquid, while its viscosity is similar to a gas.

Water state diagram (partial)

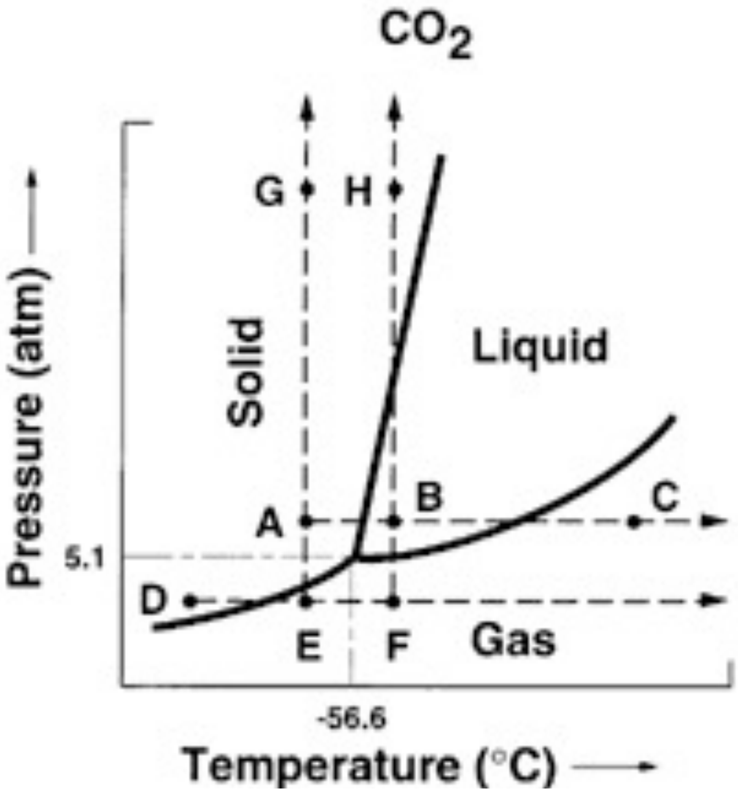


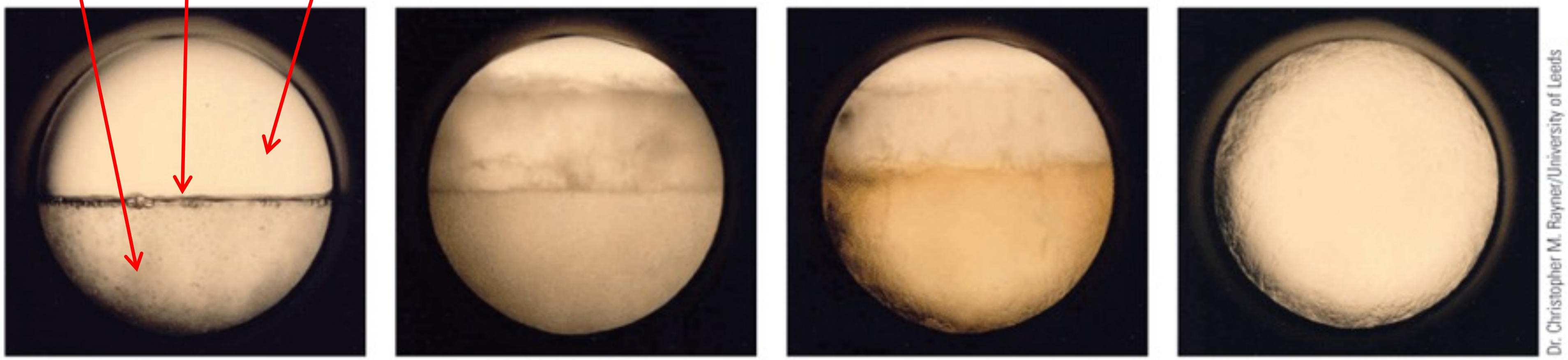
A compound can not be liquid at $T>T_C$

Critical temperatues and pressures.

compound	T_C (° C)	P_C (atm)
CH_4	-82.6	45.4
C_2H_6	32.3	49.1
C_3H_8	96.7	41.9
C_4H_{10}	152.0	37.3
NH_3	132.4	112.0
H_2O	374.0	217.7
CO_2	30.99	72.8
SO_2	157.7	77.8

State diagram of CO_2. When pressure and temperature are “critical” the interface between the liquid and vapour disappears.

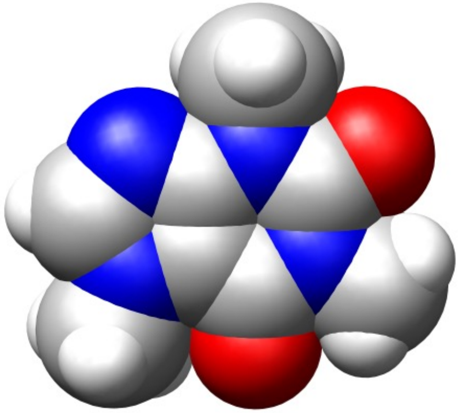


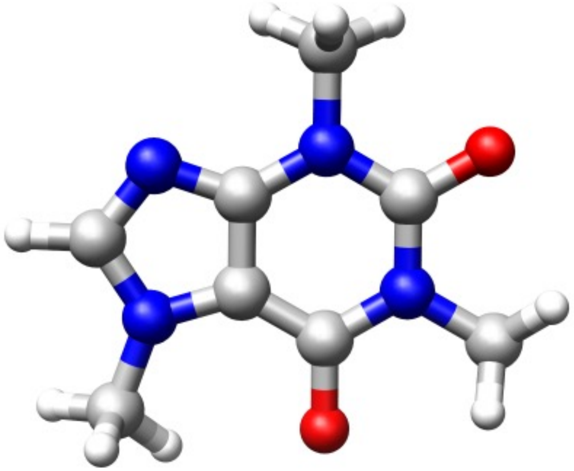


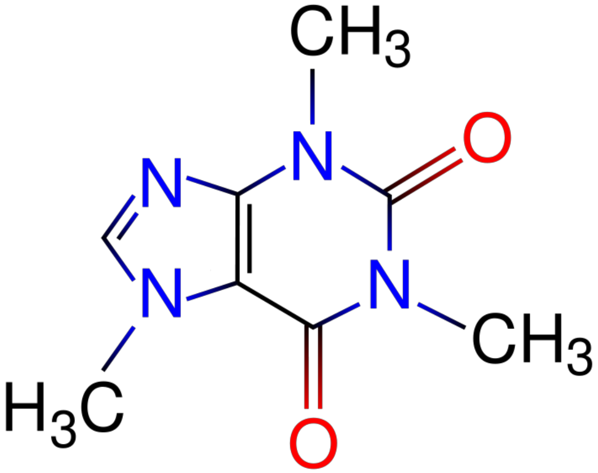
T increases, the interface disappears

Critical point

A supercritical fluid can have unexpected properties such as, for example, the ability to dissolve substances generally insoluble. Supercritical CO_2 is used to extract caffeine from coffee



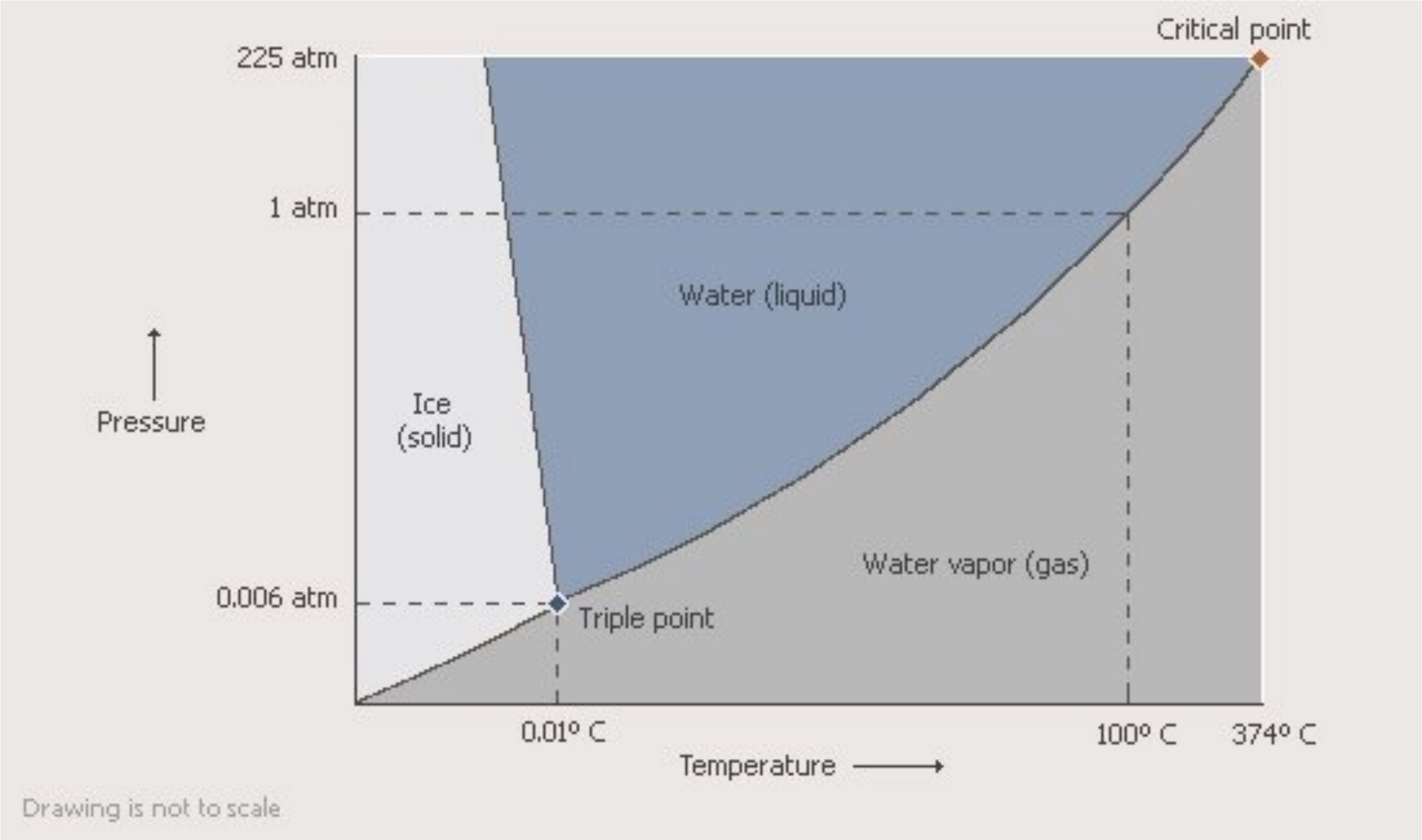


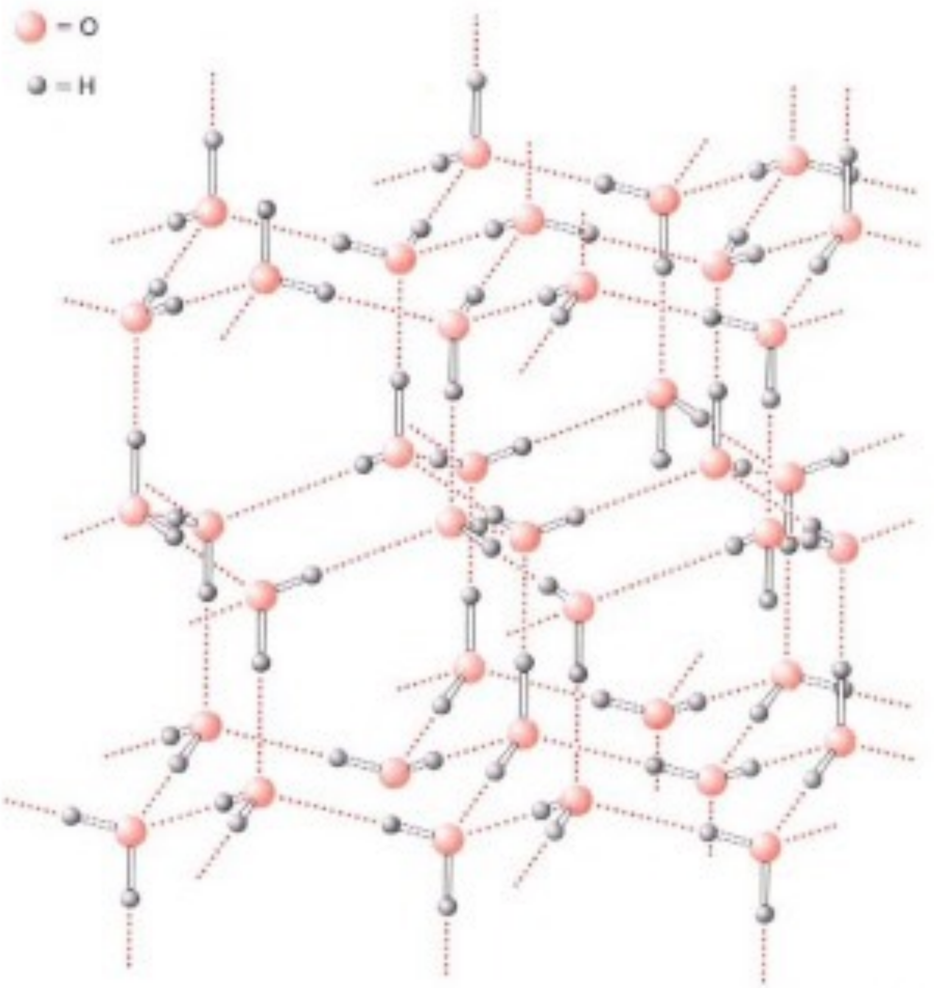


Industrial apparatus for the extraction of apolar compounds by using supercritical CO_2.

Phase diagram

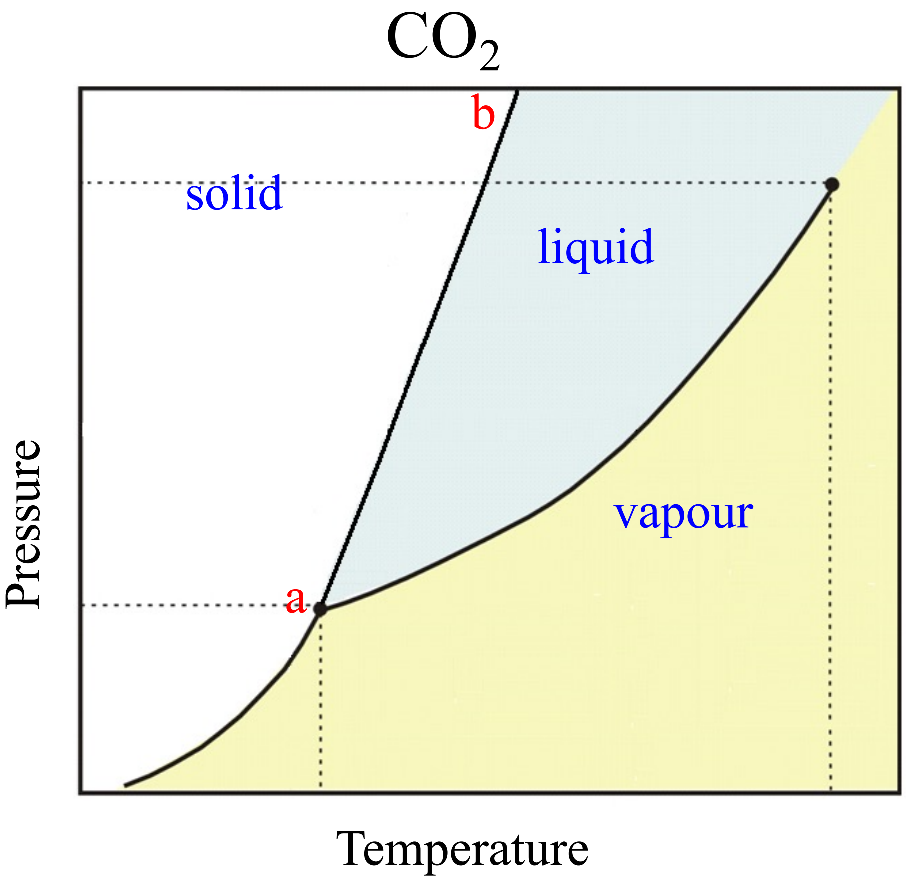
A substance may be solid, liquid or gaseous, depending on the conditions of temperature and pressure. Moreover, under certain conditions, two or even three states can coexist in equilibrium. For water:

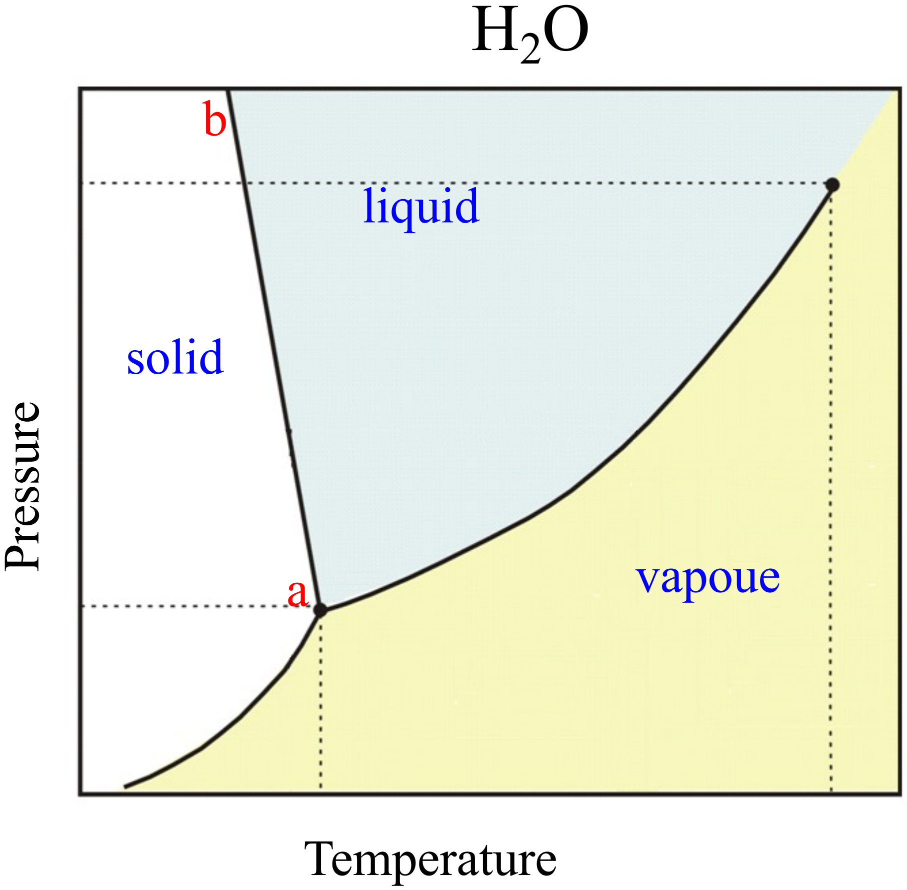




The ice structure is “open”. It is less dense than liquid water.

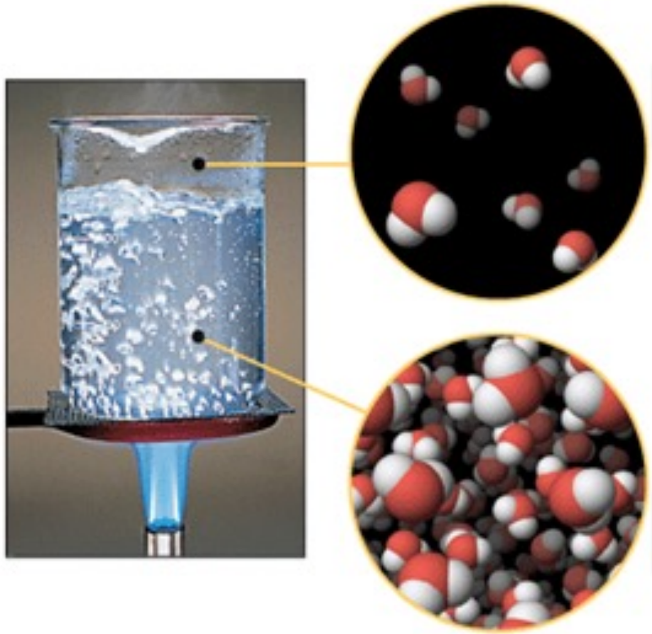
In most substances the melting point increases increasing pressure (the a-b curve has a positive slope): the liquid has a lower density than the solid and melting implies a decrease in volume. Eg CO_2. Some compounds such as H_2O (and bismuth) decrease in volume upon melting, an increase of pressure lowers the melting point (a-b curve has a negative slope).

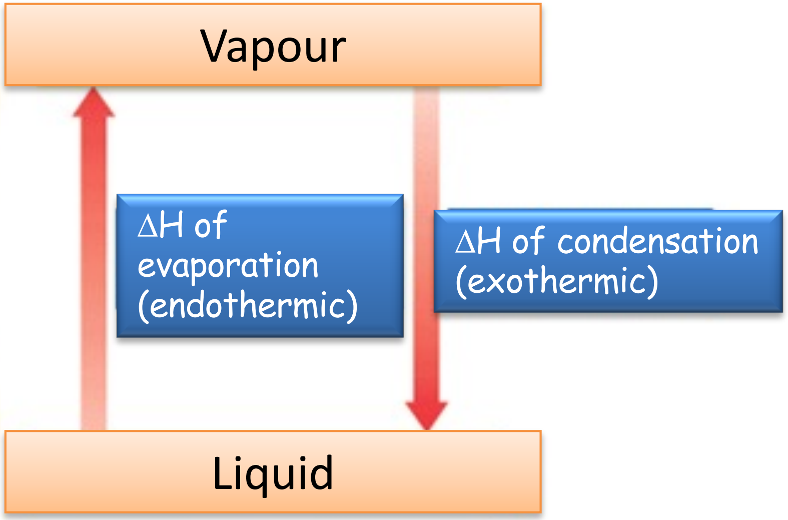




In polar molecules the dipole-dipole interactions affect evaporation and condensation.

$$H_2O\ (l)\ + \text{heat} \rightarrow H_2O\ (g) \quad \Delta H_{evap} > 0$$





Vapour

ΔH of evaporation (endothermic)

ΔH of condensation (exothermic)

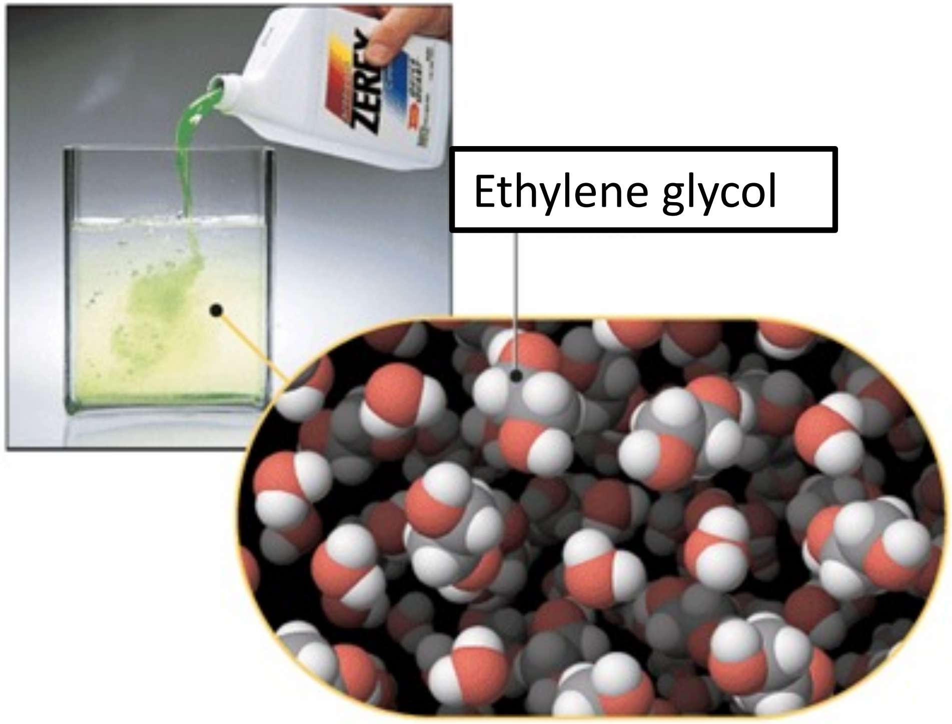
Liquid

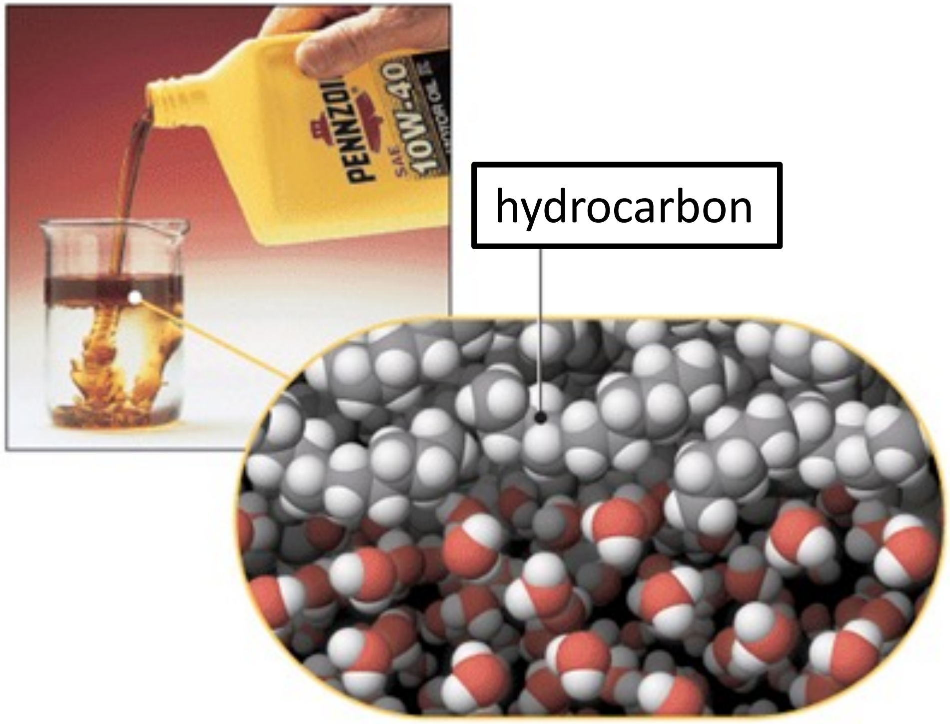
non polar	M (g/mol)	T_{eb} (° C)	ΔH_{evap} (kJ/mol)
N_2	28	–196	5.57
SiH_4	32	–112	12.10
GeH_4	77	–90	14.06
Br_2	160	59	29.96

polar	M (g/mol)	T_{eb} (° C)	ΔH_{evap} (kJ/mol)
CO	28	–192	6.04
PH_3	34	–88	14.05
AsH_3	78	–62	16.69
ICl	162	97	-

Dipole-dipole interactions also affect solubility

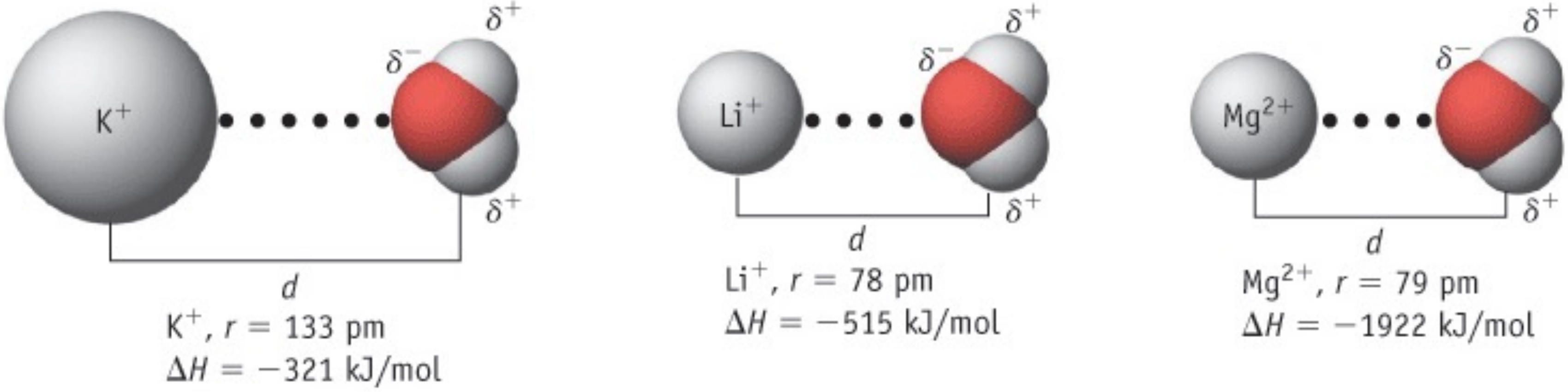
Polar molecules dissolve more easily in a polar solvent and nonpolar molecules dissolve more easily in a nonpolar solvent.





An example of the interaction between ions and polar molecules: the formation of hydrated ions in aqueous solution.

$Na^+(g) + 6\ H_2O\ (l) \rightarrow [Na(H_2O)_6]^+\ (aq)$ + heat $\Delta H_{hyd} = –405$ kJ/mol



cation	Ionic radius (pm)	ΔH_{hyd} (kJ/mol)
H^+	50	~ –1090
Li^+	78	–515
Na^+	98	–405
K^+	133	–321
Rb^+	149	–296
Cs^+	165	–263

As the force of attraction increses ($1/d^2$, ion charge and size of the dipole), the enthalpy of hydration becomes more negative (more esothermic).

Hydrogen bond (5-30 kJ mol^{-1})

- Peculiar dipole-dipole interaction.

-Can be be significantly stronger than a typical dipole-dipole interaction.

-Directional (3 atoms in line).

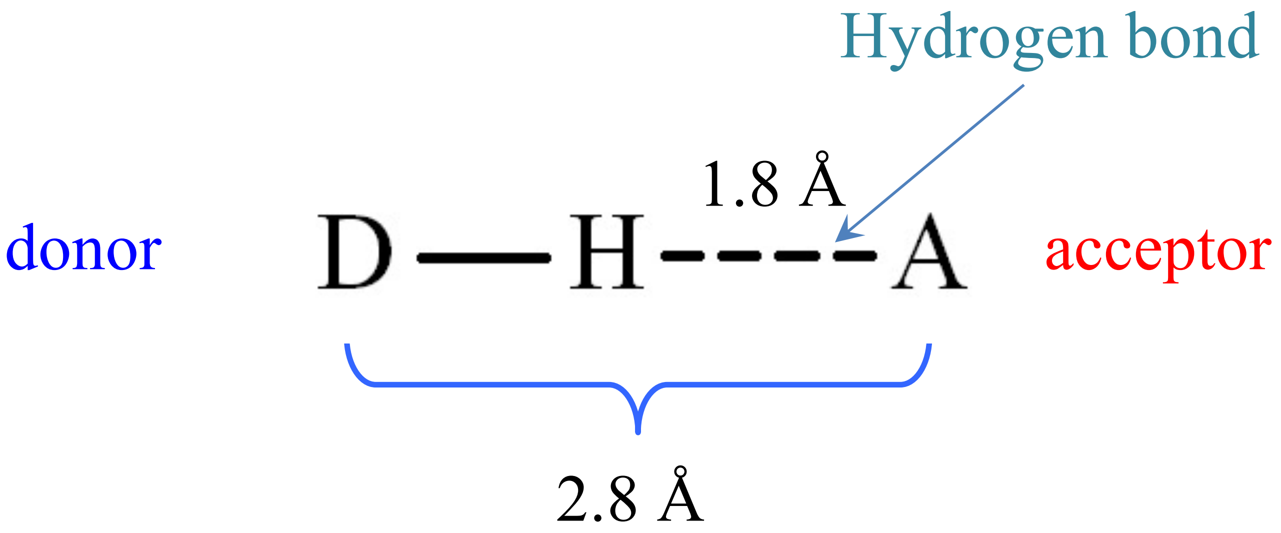
- The most important among non covalent interactions (role in biological macromolecules).

- Short distance range (as in dipole-dipole).

$$D{-}H\cdots A$$

Hydrogen bond (5-30 kJ mol^{-1})

Is formed between a hydrogen atom bound to an electronegative atom called donor and a dipole on a molecule or a functional group.

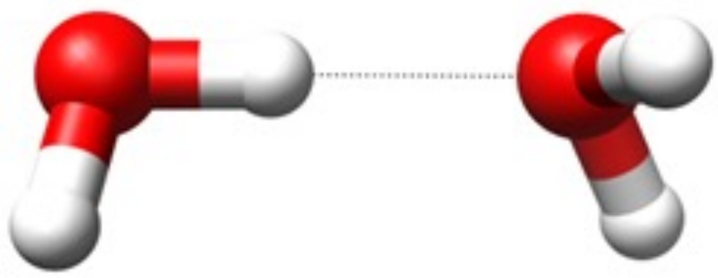


Hydrogen bond

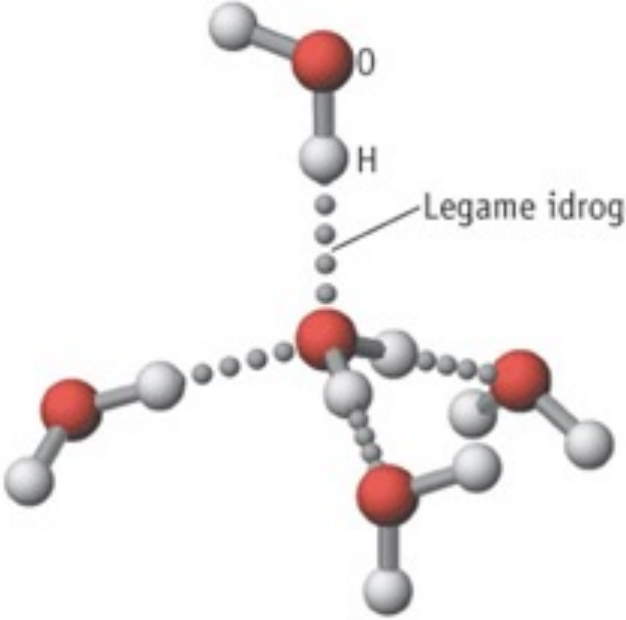
1.8 Å

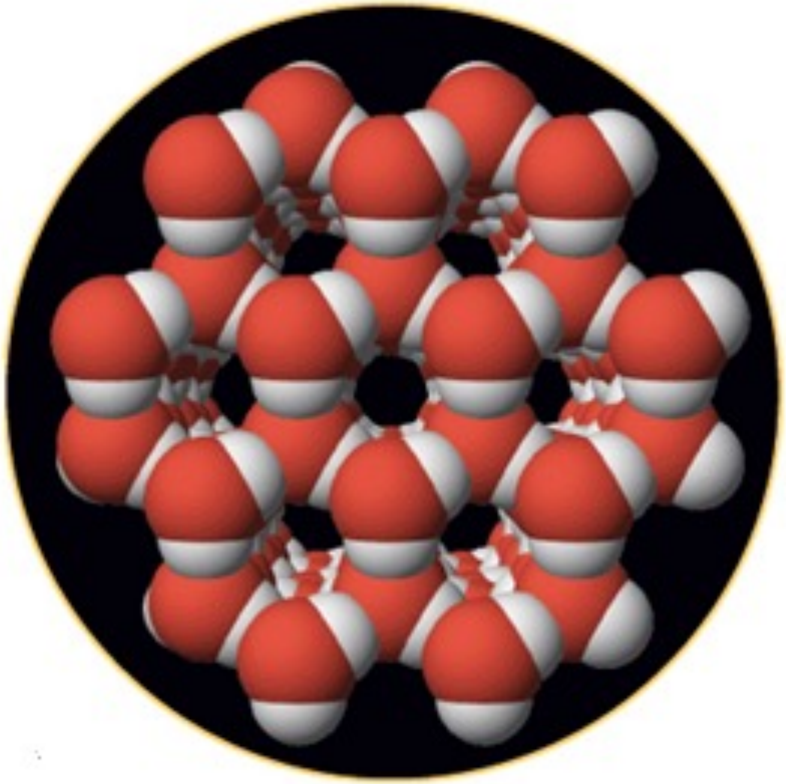
donor D—H----A acceptor

2.8 Å



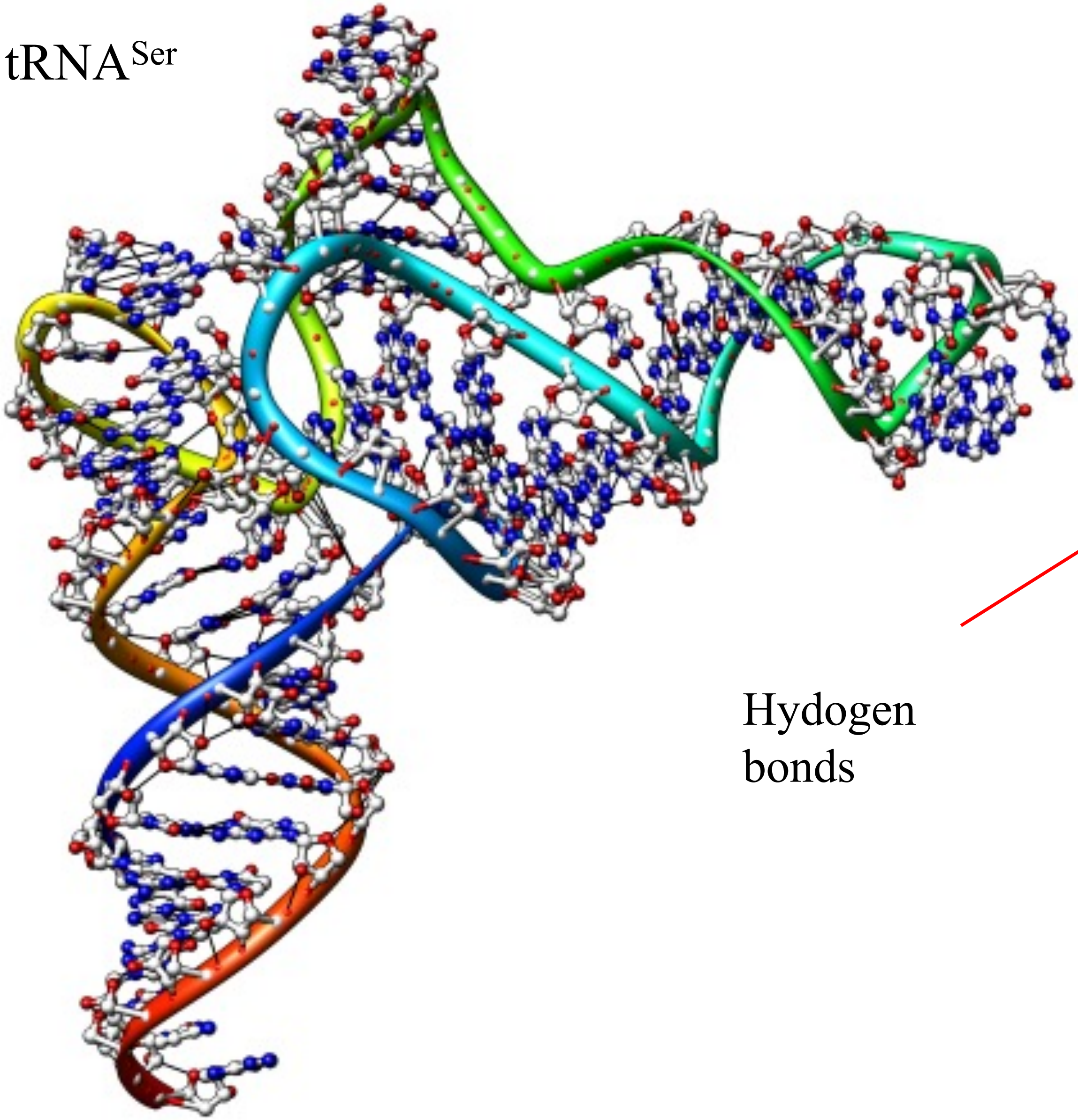
In ice, and to a lesser extent in liquid water, each molecule donates and accepts 2 hydrogen bonds



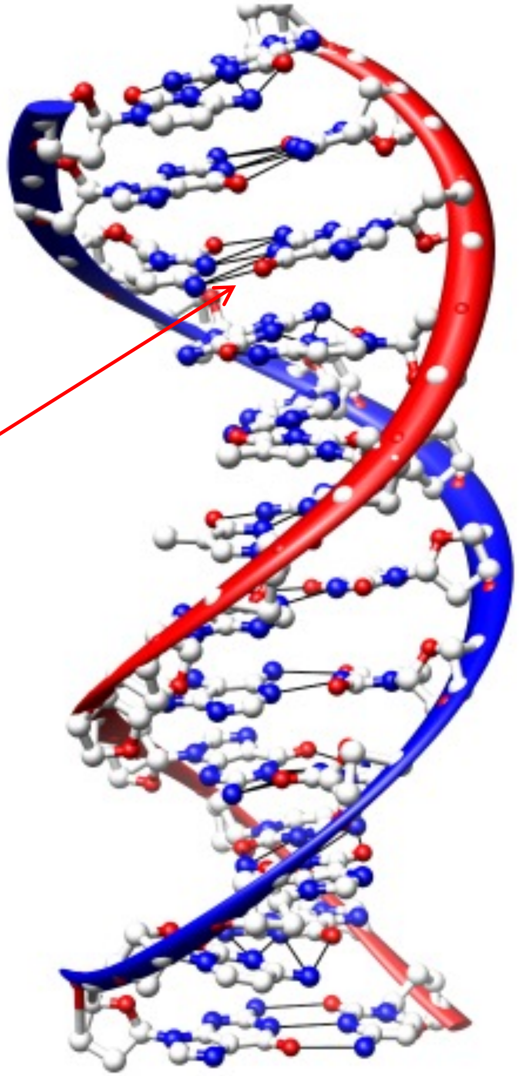


Hexagonal ice structure

tRNA^{Ser}

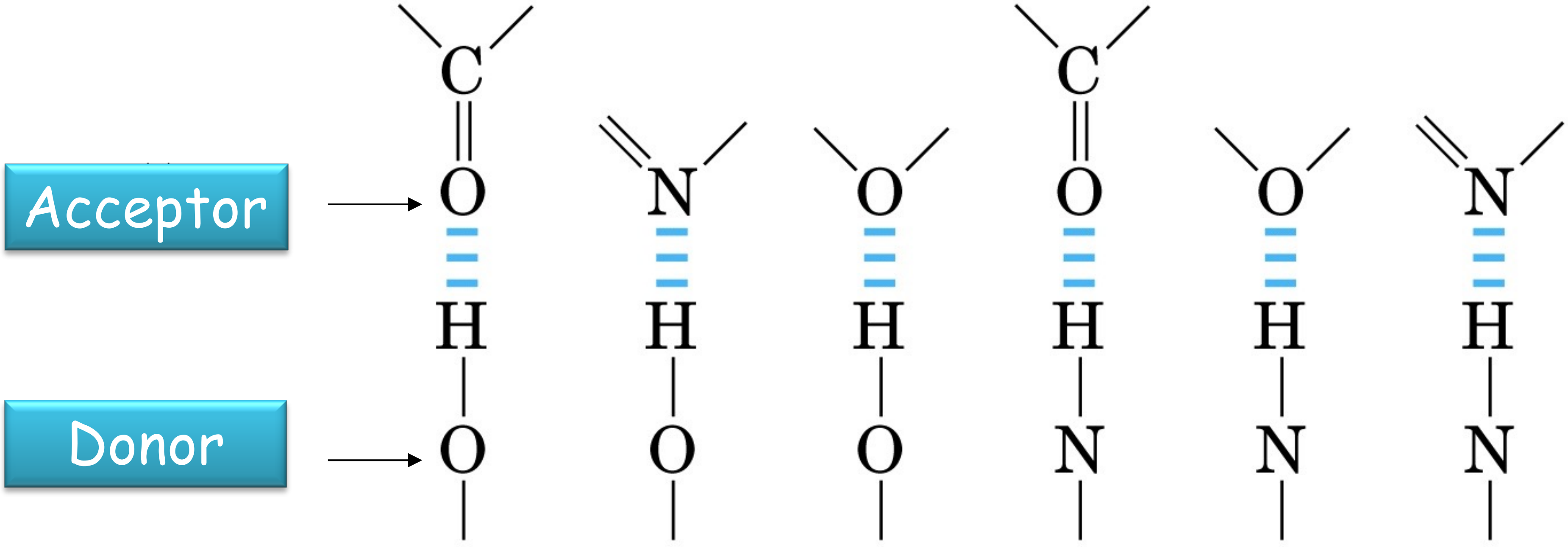


DNA



Hydogen bonds

Examples of hydrogen bonds

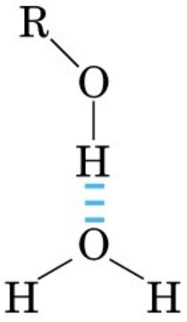


Acceptor

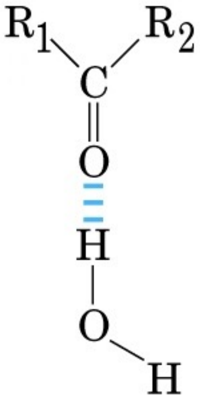
Donor

Some specific examples of hydrogen bond.

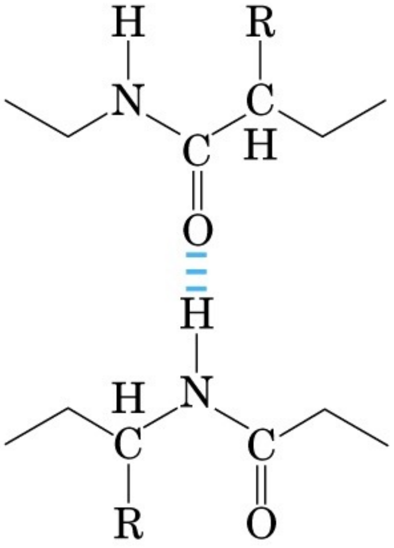
Between hydroxyl groups and water



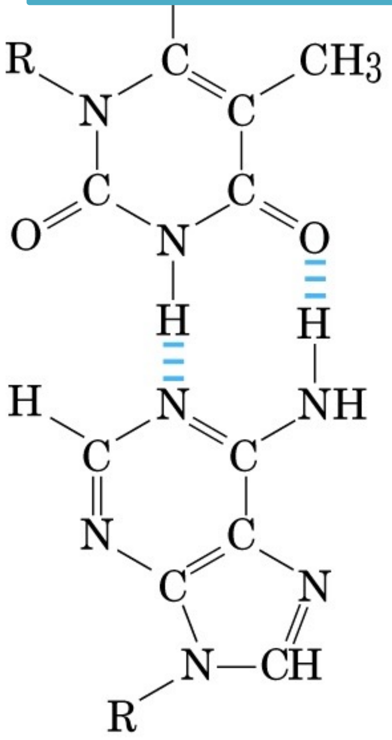
Between a carbonylic group of a ketone and water



Between peptidic bonds of proteins



Between complementary bases of DNA



Thymine

Adenine

The strength of hydrogen bonds depends on its direction.