STATES OF MATTER

- gas
- liquid
- solid crystalline
- solid glasslike, amorphous

CHEMICAL SYSTEMS

open: matter and energy transport possible

closed: only energy transport possible

isolated: no matter or energy transport

order	cohesion	phase
no long-range order	weak	gas
	intermediate	liquid
	strong	amorphous solid
long-range order	weak	———
	intermediate	liquid crystal
	strong	crystalline solid

GASES

Air:

Constituent	% volume	% mass
N_2	78.08	75.52
O_2	20.95	23.14
Ar	0.93	1.29
CO_2	0.037	0.05
Ne	1.82×10^{-3}	1.27×10^{-3}
He	5.24×10^{-4}	7.24×10^{-5}
CH_4	1.7×10^{-4}	9.4×10^{-5}
Kr	1.14×10^{-4}	3.3×10^{-4}

Gases:

- no fixed volume
- no fixed shape
- compressibility
- mixtures are always homogeneous
- most important properties: pressure, volume, temperature
- small particles ⇔ a lot of empty space: only about 0.1% of the total volume is taken up by the particles
- frequent collisions between particles: one H_2 molecule collides 10^{10} times in 1 s at 1 bar and 10°C

Pressure:

$$\text{pressure} = \frac{\text{force (N = kgms}^{-2}\text{)}}{\text{area (m}^{2}\text{)}} \qquad (\text{Pa} = \text{kgm}^{-1}\text{s}^{-2})$$

atmospheric pressure = 1 atm = 101325 Pa =

= 1.01325 bar = 760 mm Hg = 760 torr

barometer: device for measuring atmospheric pressure

manometer: device for measuring pressure in general

Gas laws:

different gases show very similar physical behavior regardless of their chemical makeup

important properties: pressure (p), temperature (T), volume (V), amount of substance (n)

ideal gas: imaginary but very useful model

- gas particles are mass points without volume
- no interaction between particles, only collisions
- known gases behave like an ideal gas at low pressure and high temperature

BOYLE'S LAW

relationship between volume and pressure at constant temperature (isothermal conditions)

Robert Boyle (1627-1691)

Boyle's law: The volume of a fixed amount of ideal gas varies inversely with pressure at constant temperature.

Edme Mariotte (1620-1684)

$V \propto 1/p$ $\qquad$ $pV = \text{constant}$

$$p_1V_1 = p_2V_2$$

CHARLES' LAW

relationship between volume and temperature at constant pressure (isobaric conditions)

temperature: originally °C

$$V = V_0 + \frac{V_0}{273.15} \times t(^\circ\mathrm{C})$$

V_0 : volume at 0 °C

Jacques Alexandre César Charles (1746-1823)

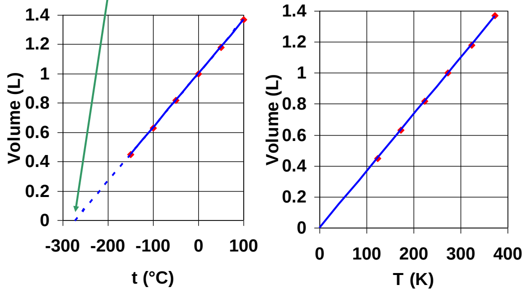
Sample of He gas at constant pressure (760 mm Hg)

Temperature (°C)	Volume (L)
-150	0.45
-100	0.63
-50	0.82
0	1.00
50	1.18
100	1.37

V = 0 hypothesis: -273.15 °C

V = m × T

absolute temperature: T(K) = t(°C) + 273.15



CHARLES' LAW

relationship between volume and temperature at constant pressure (isobaric conditions)

Charles' law: The volume of a fixed amount of ideal gas varies directly with absolute temperature at constant pressure.

$V \propto T$ $\qquad$ $V/T = \text{constant}$

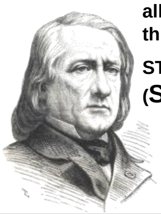
$$V_1/T_1 = V_2/T_2$$

IDEAL GAS LAW

equation of state, valid for any ideal gas

$$pV = nRT$$

R: gas constant $8.3145\ \mathrm{Jmol^{-1}K^{-1}}$



all previous specific laws can be derived from this equation

STANDARD TEMPERATURE AND PRESSURE (**STP**) FOR GASES: 0 °C $\quad p = 101325$ Pa

Henri Victor Regnault (1810-1878)

DENSITY OF GASES

$pV = nRT \qquad n = m/M$

$pV = (m/M)RT \Rightarrow pM = (m/V)RT$

density $\rho = m/V$ $\quad\rho$: *small rho, Greek letter*

$$pM = \rho RT$$

RELATIVE DENSITY OF GASES

$$pM = \rho RT$$

two different gases at the same *p* and *T*

$pM_1 = \rho_1 RT \qquad pM_2 = \rho_2 RT$

relative density $\rho_{rel} = \dfrac{\rho_1}{\rho_2} = \dfrac{M_1}{M_2}$

the ratio of the densities of two different gases at the same temperature and pressure is equal to the ratio of molar weights

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DALTON'S LAW

mixtures of ideal gases behave like a single ideal gas

partial pressure: the pressure exerted by one component of a gas mixture if it alone occupies the same volume at the same temperature

Dalton's law: The total pressure of a gas mixture is the sum of individual partial pressures.

$$p_{total} = p_1 + p_2 + p_3 + ...$$

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a mixture of three gases: n_1, n_2, n_3 **moles**

p_1, p_2, p_3 **partial pressures**

$p_1 = n_1RT/V \qquad p_2 = n_2RT/V \qquad p_3 = n_3RT/V$

$$p_{total} = p_1 + p_2 + p_3 = (n_1 + n_2 + n_3)RT/V$$

mole fraction $X = \dfrac{\text{Moles of component}}{\text{Total moles in mixture}}$

$X_1 = n_1/(n_1+n_2+n_3) \quad X_2 = n_2/(n_1+n_2+n_3) \quad X_3 = n_3/(n_1+n_2+n_3)$

$$p_1 = X_1p_{total} \qquad p_2 = X_2p_{total} \qquad p_3 = X_3p_{total}$$

Average molar weight

$$\overline{M} = \frac{\text{Total weight of mixture}}{\text{Total moles in mixture}}$$

average molar weight for the three-component mixture:

$$\overline{M} = X_1M_1 + X_2M_2 + X_3M_3$$

average molar weight of air:

78 mol% N_2, 21 mol% O_2, 1.0 mol% Ar

$$\overline{M} = 0.78 \times 28.0 + 0.21 \times 32.0 + 0.010 \times 40.0 = 29.0 \text{ g/mol}$$

ATMOSPHERIC PRESSURE

- **normally 101325 Pa at sea level**
- **depends somewhat on the weather**
- **depends markedly on the elevation above sea level**

barometric formula

$$p = p_0 e^{-h\rho_0 g/p_0}$$

h: **elevation above sea level** $\quad p$: **air pressure at elevation h**

g: **gravitational acceleration** $\quad \rho_0$: **air density at sea level**

p_0: **air pressure at sea level**

location	country	elevation	air pressure
Dead sea	Jordan-Israel	– 416 m	106 kPa
sea level	–	0 m	101.325 kPa
Kékes	Hungary	1014 m	91 kPa
Dimlang	Nigeria	2042 m	81 kPa
Hvannadalshnúkur	Iceland	2119 m	80 kPa
Mexico City	Mexico	2300 m	78 kPa
Fan Si Pan	Vietnam	3143 m	71 kPa
Büyük Ağri daği	Turkey	5165 m	57 kPa
Damãvand	Iran	5771 m	53 kPa
Mt. Everest	China-Nepal	8850 m	38 kPa

BASIC ATMOSPHERIC CHEMISTRY

Air Pollution: CO, NO, NO_2, SO_2 from exhaust

formation of smog in industrial areas

smoke + fog

Acid Rain: burning of sulfur present in coal

$S (s) + O_2 (g) \rightarrow SO_2 (g)$

$2SO_2 (g) + O_2 (g) + 2H_2O (l) \rightarrow 2H_2SO_4 (aq)$

sulfuric acid: damage to living organisms and buildings

BASIC ATMOSPHERIC CHEMISTRY

Greenhouse effect: increasing concentrations of CO_2 in the atmosphere ⇒ warming effect on the global weather

Ozone hole: O_3 layer present in the upper atmosphere shields Earth from damaging radiation

freons (used earlier as propellants and refrigerator liquids) cause the decomposition of ozone

Montreal protocol: ban on the use of freons

LIQUIDS

– intermediate attractive forces between particles

– fixed volume: little empty space, particles take up most of the volume

– no fixed shape: particles move relative to one another easily

– volume of different liquids is *NOT ADDITIVE*

1.00 L water + 1.00 L ethyl-alcohol ⇒ ~ 1.9 L mixture

volume contraction

Viscosity of Liquids

Viscosity: The measure of a liquid's resistance to flow.

NOT CONNECTED TO DENSITY!

Example: cooking oil is less dense than water but flows with much more resistance

The attractive forces between particles are different in different liquids ⇒ particles experience different resistance when they move

Attractive forces are temperature-dependent ⇒ viscosity is temperature-dependent

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Thixotropy

Phenomenon: the viscosity of a liquid is sometimes dependent on being shaken, agitated, or otherwise stressed.

Drilling muds

Surface tension of liquids

Surface tension: the resistance of a liquid to spread out and increase its surface area

A liquid particle on the surface interacts with fewer particles than those in the interior ⇒ particles on the surface are drawn toward the interior

Attractive forces are temperature-dependent ⇒ surface tension is temperature dependent

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Viscosities and surface tensions of common liquids at 20 °C

name	formula	viscosity (Ns/m^2)	surface tension (J/m^2)
pentane	C_5H_{12}	2.4×10^{-4}	1.6×10^{-2}
benzene	C_6H_6	6.5×10^{-4}	2.9×10^{-2}
water	H_2O	1.0×10^{-3}	7.3×10^{-2}
ethanol	C_2H_6O	1.2×10^{-3}	2.2×10^{-2}
mercury	Hg	1.5×10^{-3}	4.6×10^{-1}
glycerol	$C_3H_8O_3$	1.5	6.3×10^{-2}

SOLIDS

– strong attractive forces between particles

– fixed volume: little empty space, particles take up most of the volume

– fixed shape: particles do not move relative to one another, only oscillation is possible

– amorphous solids: no long-range order, no well-defined melting point

– crystalline solids: long-range order, well-defined melting point

– one chemical compound or element may have several different crystalline forms with different properties

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CRYSTALLINE SOLIDS

– IONIC SOLIDS: constituent particles are ions, example: common salt = NaCl (s)

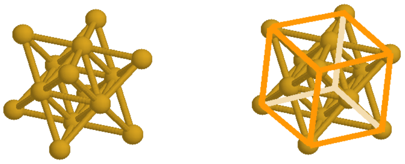
– MOLECULAR SOLIDS: constituent particles are molecules, example ice = H_2O (s)

– COVALENT NETWORK SOLIDS: constituent particles are atoms connected through covalent bonds, example: diamond = C (s)

– METALLIC SOLIDS: constituent particles are metal atoms connected through a large number of shared electrons, example: gold = Au (s)

UNIT CELL

unit cell: the smallest repeating unit of a crystalline solid from which the whole lattice can be constructed



unit cell of gold

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one chemical *element* with several different crystalline forms ⇒ ALLOTROPY

carbon: graphite, diamond, fullerene

sulfur: rhombic, monoclinic

one chemical *compound* with several different crystalline forms ⇒ POLYMORPHISM

SiO_2: α-quartz, β-quartz, α- and β-tridymite, α- and β-cristobalite

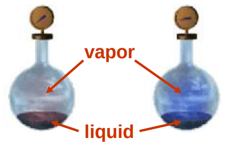
ZnS: zinc blende, wurtzite

PHASE CHANGES

solid → liquid	fusion, melting
liquid → solid	freezing
liquid → gas	vaporization
gas → liquid	condensation
solid → gas	sublimation
gas → solid	deposition

Vapor Pressure

liquid in a closed container with no other gas in it



48 °C

water	methanol
12 kPa	53 kPa

<u>vapor pressure:</u> partial pressure of a liquid vapor at a particular temperature in equilibrium with the liquid

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Vapor pressure

<u>boiling:</u> vapor pressure reaches external pressure

vapor pressure temperature-dependent ⇒

⇒ boiling point (temperature) pressure-dependent

<u>normal boiling point:</u> boiling point when the external pressure is 1 atm = 101325 Pa

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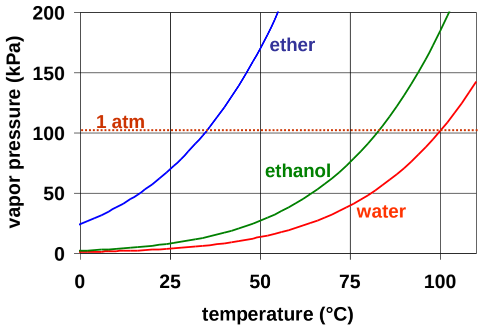
Vapor pressure vs. temperature



PHASE CHANGES

solid → liquid	fusion, melting
liquid → solid	freezing
liquid → gas	vaporization
gas → liquid	condensation
solid → gas	sublimation
gas → solid	deposition

Sublimation

direct 'evaporation' of a solid to form gas

some solids show this behavior under normal conditions:

dry ice = solid CO_2 (carbon dioxide)

iodine

Low pressure: *many substances sublime*

Vapor pressure for solids

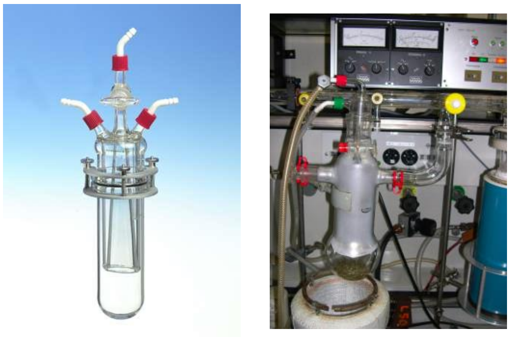
fully analogous to vapor pressure for liquids

<u>sublimation temperature:</u> vapor pressure reaches external pressure

vapor pressure temperature-dependent ⇒
⇒ sublimation temperature pressure-dependent

<u>normal sublimation temperature:</u> sublimation temperature when the external pressure is 1 atm

<u>vacuum sublimation:</u> important method to purify substances



PHASE CHANGES

solid → liquid	fusion, melting
liquid → solid	freezing
liquid → gas	vaporization
gas → liquid	condensation
solid → gas	sublimation
gas → solid	deposition

Melting and freezing

melting point: modest dependence on external pressure

<u>normal melting point</u>: melting point when the external pressure is 1 atm

higher pressure ⇒ higher melting point

Exception: melting point of water decreases with increasing pressure

Water – ice anomaly

melting point of water decreases with increasing pressure

<u>reason:</u> the density of ice is smaller than the density of water at 0 °C

natural waters freeze at the surface first, deeper regions often stay liquid in winter as well (aquatic life!)

skating: very small surface under the blade of a skate ⇒ high pressure ⇒ lower melting point

Phase diagram

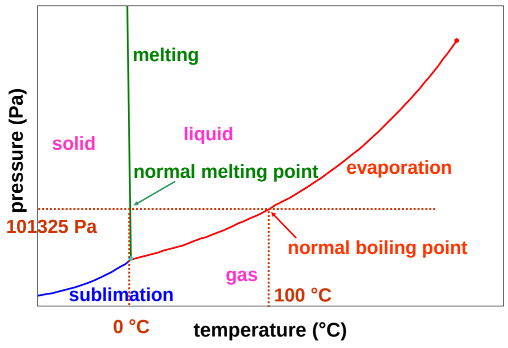
A graph that shows

– the pressure and temperature dependence of a pure substance in a closed system without air or any other substance present.

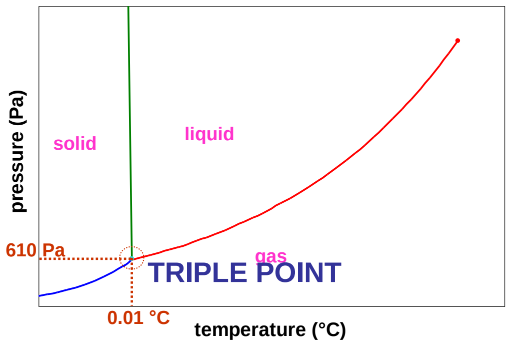
– where the liquid, gas, and solid phases are stable

– the boundaries between phases (vapor pressure curve, pressure dependence of melting point and sublimation temperature)

Phase diagram of water



Phase diagram of water



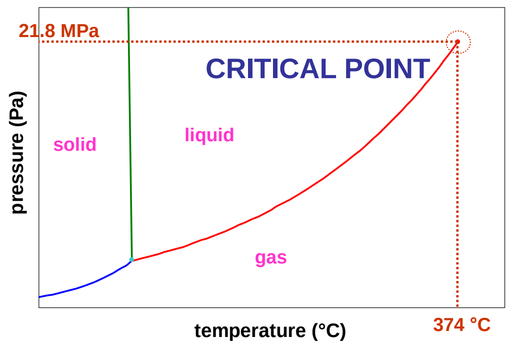
Triple point

All three phases (gas, liquid, solid) coexist in equilibrium.

Unique combination of temperature and pressure.

No liquid can exist at pressures lower than the triple point pressure (610 Pa for water) ⇒ below this pressure ice will sublime

Phase diagram of water



Critical point

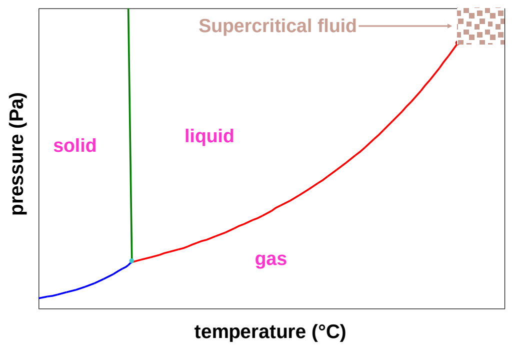
The phase separation between gas and liquid abruptly ends.

Unique combination of temperature and pressure (critical temperature and critical pressure).

No liquid can exist at temperatures above the critical temperature.

A gas cannot be liquefied at temperatures higher than its critical temperature.

Phase diagram of water



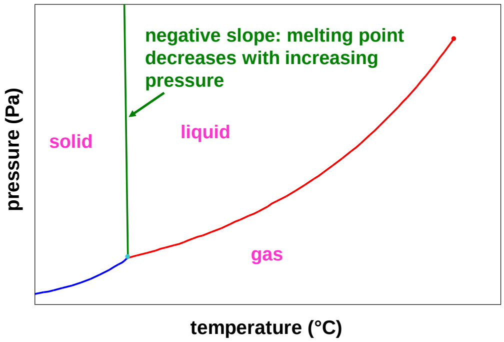
Supercritical fluid

Critical conditions: the liquid and gas phases simply blend into each other

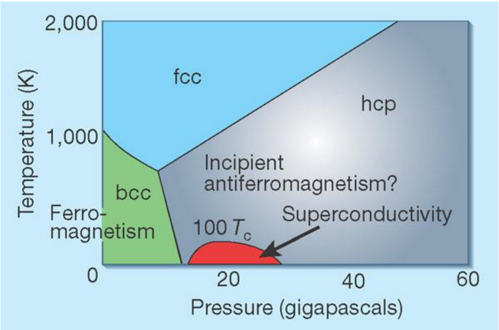
Supercritical state: neither true liquid nor true gas

- **high pressure and temperature**
- **properties are characteristically different from those under normal conditions**

Phase diagram of water



Phase diagram of iron



SOLUTIONS

- **concentration units**
- **solubility of gases**
- **colligative properties: vapor pressure lowering, boiling-point elevation, freezing-point depression, osmotic pressure**
- **reverse osmosis**
- **distillation**

<u>SOLUTION</u> =	**SOLUTE(S)** +	**SOLVENT**
Coca-Cola	**carbon dioxide**	**water**
	sugar	
	(many) other substances	

reminder! **ELECTROLYTES**
NON-ELECTROLYTES
WEAK ELECTROLYTES
STRONG ELECTROLYTES

Concentration Units

MOLARITY (c) = $\dfrac{\text{Moles of solute}}{\text{Volume of solution}}$ **unit:** molL^{-1}, mol/dm^3, M

MOLE FRACTION (X) = $\dfrac{\text{Moles of component}}{\text{Total moles making up the solution}}$

MASS PERCENT = $\dfrac{\text{Mass of component}}{\text{Total mass of solution}} \times 100\%$

MASS PERCENT ≡ WEIGHT PERCENT

$$\text{Parts per million (ppm)} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$$

$$\text{Parts per billion (ppb)} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^9$$

$$\text{MOLALITY } (m) = \frac{\text{Moles of solute}}{\text{Mass of } \textit{SOLVENT}} \qquad \text{unit: mol/kg}$$

MOLALITY ≡ Raoult concentration

HENRY'S LAW

relationship between the solubility and the partial pressure of a gas

Henry's law: The solubility of a gas in a liquid at a given temperature is directly proportional to the partial pressure of the gas over the solution.

William Henry
(1774–1836)

$$\overset{\text{mol/L}}{Solubility} = \overset{\text{mol/(L×Pa)}}{k} \times \overset{\text{Pa}}{p}$$

partial pressure of the gas

Henry's law constant

COLLIGATIVE PROPERTIES

colligative: 'bound together in a collection'

Colligative properties depend on the amount (number of particles) of dissolved solute but not on its chemical identity

Quantitative laws: only for *IDEAL DILUTE SOLUTIONS*

– relatively small concentration

– further addition of solvent does not change the solvation of solute

BOILING POINT ELEVATION

the vapor pressure of a solution is lower than the vapor pressure of the pure solvent ⇒

⇒ the boiling point of a solution is higher than the boiling point of the solvent

$$\Delta T_b = K_b \times m$$

molality

change in boiling point

molal boiling-point-elevation constant

FREEZING POINT DEPRESSION

the triple point pressure of a solution is lower than the triple point pressure of the pure solvent ⇒

⇒ the freezing point of a solution is lower than the freezing point of the solvent

$$\Delta T_f = K_f \times m$$

molality

change in freezing point

molal freezing-point-depression constant

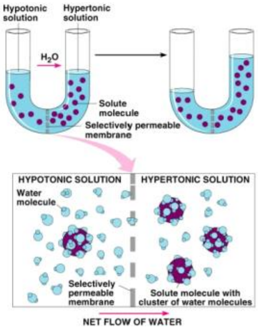
OSMOSIS

special type of diffusion between two different solutions

semipermeable membrane: small solvent molecules pass through, but large solute molecules are blocked

osmosis: movement of solvent molecules from less concentrated solutions to more concentrated solutions

OSMOSIS



hypotonic solution:
low concentration,
low osmotic pressure

hypertonic solution:
high concentration,
high osmotic pressure

OSMOTIC PRESSURE

the amount of pressure necessary to stop the process of osmosis

Π: capital pi, a Greek letter (small π used for 3.14159...)

units: Pa, all other pressure units

$$\Pi V = nRT \quad \Rightarrow \quad \Pi = cRT$$

analogy with the ideal gas law!!

IMPORTANCE OF COLLIGATIVE PROPERTIES

– freezing point depression

using salt to make roads less slippery in winter

– osmotic pressure

life: cell membranes are semipermeable

isotonic solution: **has the same osmotic pressure as body fluids, e.g. 0.15 M NaCl solution**

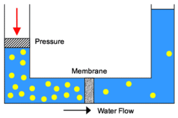
hypotonic solution: **osmotic pressure lower than that of body fluids**

hypertonic solution: **osmotic pressure higher than that of body fluids**

REVERSE OSMOSIS

osmosis: **spontaneous movement of solvent molecules from less concentrated solution to more concentrated solution**

reverse osmosis: **movement of solvent molecules from more concentrated solution to less concentrated solution forced by external pressure**



almost the same as *FILTRATION*, but the filter has very small pores

IMPORTANCE: **making drinking water from seawater**

DISTILLATION

purification of a liquid by boiling it and condensing the vapors

FRACTIONAL DISTILLATION: **separation of a mixture of liquids using the difference in boiling point**

petroleum: complex mixture of hydrocarbons

fractional distillation of petroleum: gasoline (bp. 30 – 200 °C), kerosene (bp. 175 – 300 °), gas oil (bp. higher)