Seawater

The oceans cover 70% of the planet with a solution of salts in water. The video below shows how seawater composition affects ocean currents and, in turn, affects global climate change.

Outline

The Liquid State

Properties

We've seen that in the gaseous state, all molecules or atoms in the gas are individual units that are unconnected to others. They are rapidly moving to fill all available space and there are no strong interactions between them. The volume of the particle is insignificant relative to the total volume of the gas so the volume of 1 mole of gas depends on temperature and pressure but not on the nature of the gas.

Liquids are different. Like gases, liquids flow and the shape of a liquid depends on the shape of its container. Gases always fill their container but liquids don't. A sample of liquid will have a particular volume at a set temperature. This is measured as **density**, usually in units of g/mL.

Molecules (or atoms) in a liquid are in motion within the liquid but they are held in the liquid phase by strong interactions between the particles. The particles in a liquid "stick" together. This means that there is little empty space between molecules and the volume of 1 mole of liquid depends very much on the nature of the molecules or atoms that make it up. Liquids have significantly higher density than gases.

Molecule	Molar volume of gas	Molar volume of liquid	Density (at 25 deg C)
H_2O	24 L	1.8×10^{-2} L	1.0 g/mL
CH_2Cl_2	24 L	6.4×10^{-2} L	1.33 g/mL
C_6H_{14}	24 L	13×10^{-2} L	0.648 g/mL

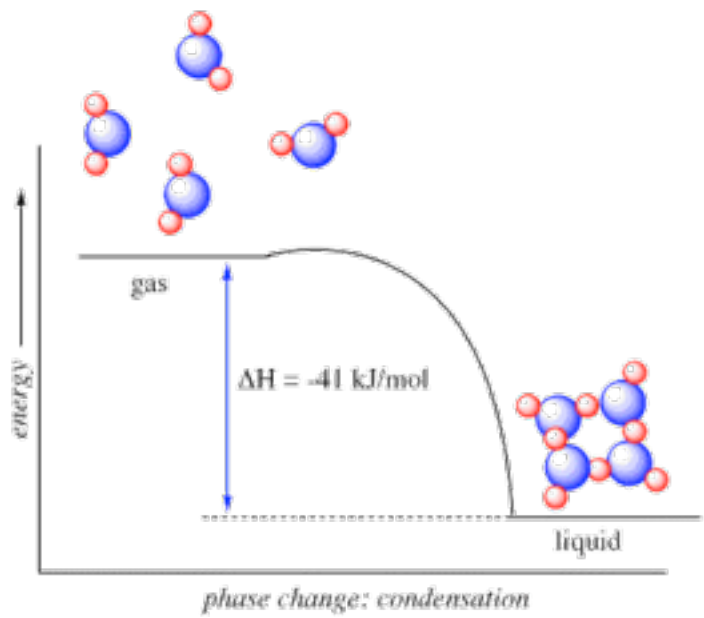
Go to the simulation to see the differences between gas, liquid, and solid phases of neon, argon, molecular oxygen, and water.

What happens to the particles in each phase when you add heat?

What happens when you increase or decrease the pressure?

Energy changes

Condensation of any gas leads to a liquid with a lower energy content. The enthalpy change is a negative number. The interactions between molecules stabilizes the liquid molecules relative to the gas phase molecules and the difference in heat energy is released from the system to the surroundings.



For water, about 41 kJ of heat is released for every mole of water that goes from the gas phase to the liquid phase.

Liquid properties

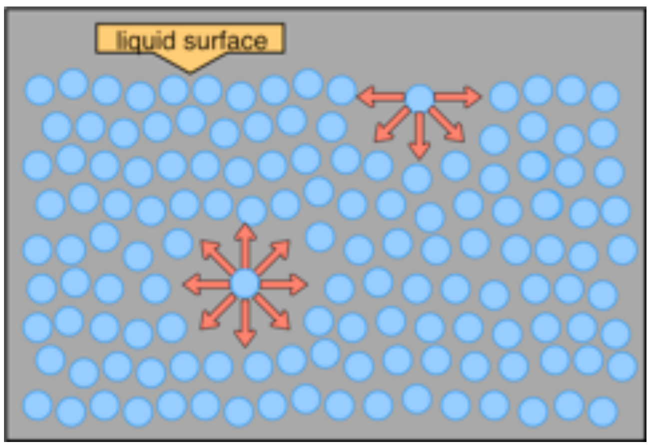
One property of a liquid is its **viscosity**, that is its resistance to flow. This relates to the forces between molecules and the size of the molecules. If water has a viscosity of 1, the molecule benzene C6H6 (a component of gasoline) has a viscosity of only 0.65. This is because water molecules form hydrogen bonds or O-H---O interactions between molecules but benzene molecules don't. Motor oil consists of very large molecules with long chains of CH_2 groups and has a viscosity of 200. Viscosity decreases with temperature.

Temperature (deg C)	0	10	20	40	60	80	100
Water viscosity	1.8	1.3	1.0	0.65	0.47	0.36	0.28

You may have tried to float a paper clip on the surface of water, or watched an insect walk on this surface. The **surface tension** is another property of liquids.

A molecule of a liquid interior to the liquid has equal forces all around it from interaction with other atoms. The molecules on a surface, however, have these energy-reducing interactions only below and on the sides so they are less stable. Surface molecules must interact with each other more strongly to stabilize the surface. This results in a surface film.

Water, a liquid with a high surface tension, forms spherical drops when poured to minimize the surface area.



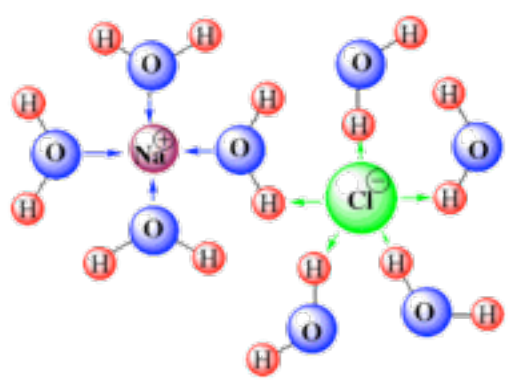
Prof. Steven Lower, Simon Fraser University
http://www.chem1.com/acad/webtext/states/liquids.html#SEC1

Seawater Composition

Salinity

Seawater is a solution of salts.

When a mineral such as NaCl dissolves in water, the ions separate and are surrounded by water molecules. The lone pair electron orbitals on the oxygen of water interact with the electron-poor cations and the anions donate some of their excess electron density to the electron-poor hydrogen atoms of water.

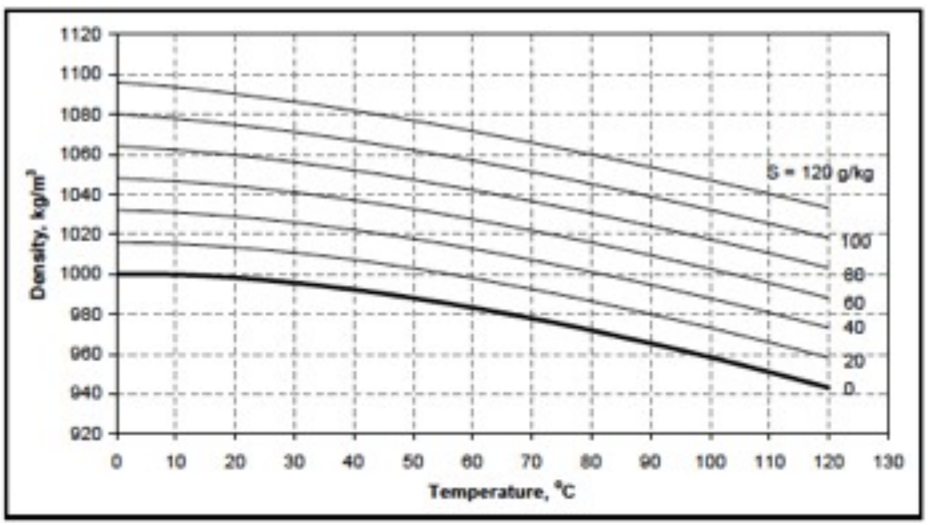


The salinity of seawater is measured by the number of grams of ions in a kilogram of the water. For seawater of salinity 35, the major ions are:

Ion	Concentration (mol/L)	g/kg seawater
Cl^-	56×10^{-2}	19.353
Na^+	48×10^{-2}	10.784
SO_4^{2-}	2.9×10^{-2}	2.712
Mg^{2+}	5.4×10^{-2}	1.284
Ca^{2+}	1.1×10^{-2}	0.412
K^+	1.0×10^{-2}	0.399

Density

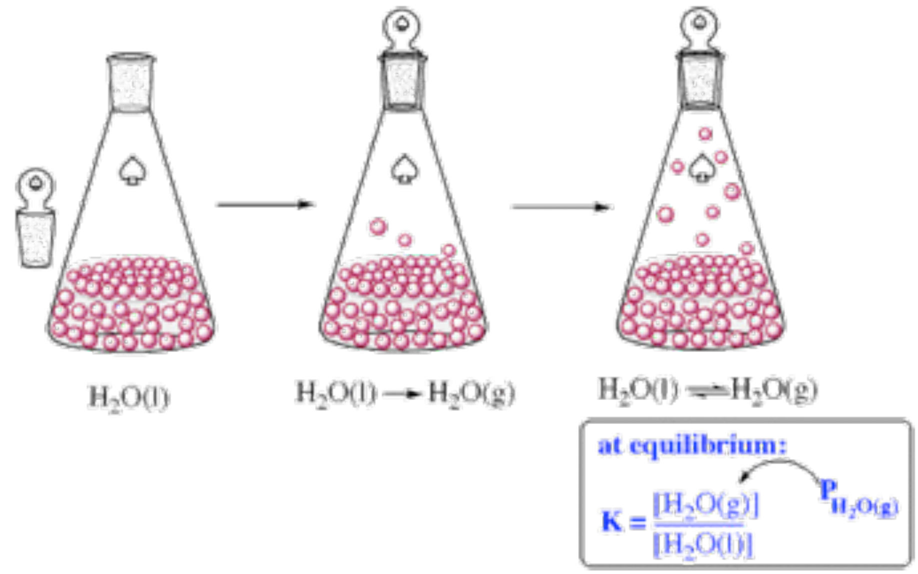
The density of seawater depends increases with increasing salt content and decreases with increasing temperature. This is a key influence on ocean currents.



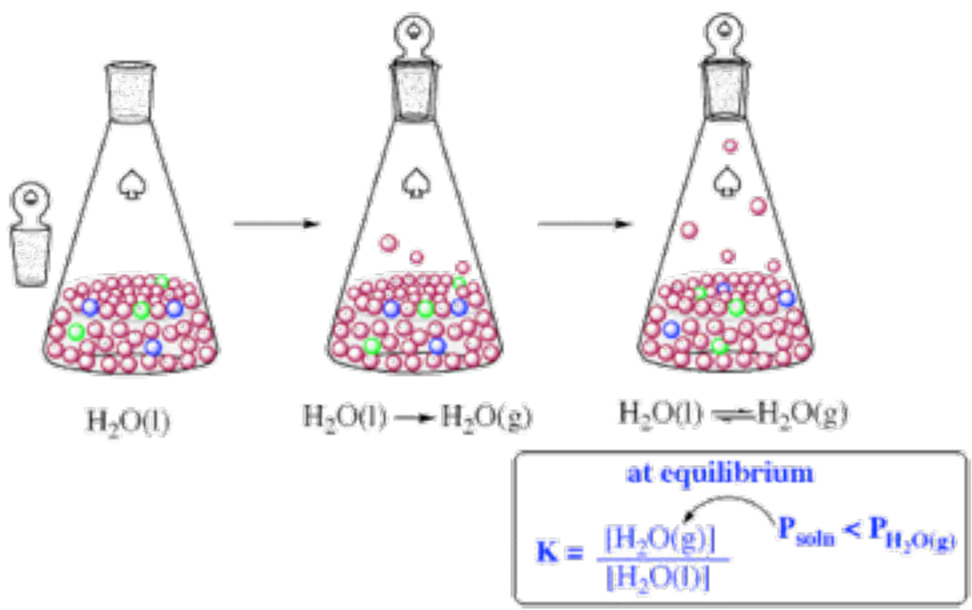
Colligative Properties

Some properties of a salt solution like seawater are due to the number of particles (anions + cations) that are present. These are the colligative properties.

Pure liquids, including water, are in equilibrium with the gas phase molecule. Consider what would happen if we added some liquid water to an empty flask. Water molecules on the surface with sufficient energy would escape to the gas phase. Gas phase water molecules would condense and become part of the liquid water. Evaporation and condensation processes would continue rapidly but the concentration of water vapor above the liquid water would reach a constant value, the equilibrium vapor pressure. This vapor pressure would increase with increasing temperature and decrease with increased external pressure.

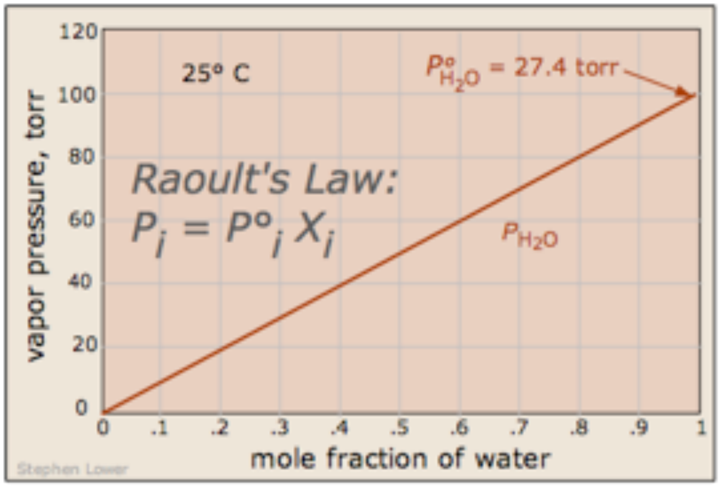


When substances that can't evaporate are dissolved in water, the concentration of water in the liquid is reduced and the equilibrium concentration of water in the gas phase is reduced.



Partial pressure of water, the part of the total gas pressure that is due to water vapor, is a measure of the concentration of water gas.

The vapor pressure of any solution, P_i, is equal to the product of the vapor pressure of the pure solvent, P^0_i, and the mole fraction of the solvent.



In pure water, all of the molecules in the liquid are water molecules so the mole fraction is 1 (100 % H_2O, 55 mol/L). In sea water, the concentration of water molecules in the solution is less than that of pure water so the vapor pressure of sea water is also lower. The vapor pressure of pure water at 20 deg C is 0.0231 atm while the vapor pressure of seawater with the composition listed above is 0.0226 atm.

There are several other colligative properties that we see in seawater:

1. **Boiling point elevation**
2. The higher the concentration of ions (or molecules) in solution, the higher is the boiling point of the solution. For seawater with a salinity of 35, the boiling point is higher by about 0.3 deg C.
3. **Freezing point depression**
4. Seawater freezes at a temperature about 2 deg C lower than freshwater.

$$\Delta T = K_{bp} \text{ (mol of solute/kg solution)}$$

$$\Delta T = K_{fp} \text{ (mol of solute/kg solution)}$$

Air-Sea Equilibrium

All atmospheric gases are in equilibrium with those gases in solution. In the equation below, the concentration of a gas is given by its partial pressure (P_i). We rearrange the equilibrium expression so that the ratio of the partial pressure of gas in the atmosphere divided by its concentration in solution is a constant, the Henry's Law constant or K_H.

$$\text{gas} + H_2O(l) \rightleftharpoons \text{gas(aq)}$$

$$K_{eq} = \frac{[\text{gas(aq)}]}{[\text{gas}][H_2O]} \qquad K_H = \frac{P_i}{[\text{gas(aq)}]} = \frac{1}{K_{eq}\,[H_2O(l)]}$$

P_i (→ [gas])

Below is a table of Henry's Law constants for some common gases.

Henry's Law: gases in air and water

$$\frac{P_g}{k_{H,pc}} = C$$

What is the concentration of $O_2(aq)$?

0.21 atm/769.23 atm M^{-1} = 2.7E-4 M

What is the concentration of $N_2(aq)$?

0.78 atm/1639.34 atm M^{-1} = 4.8E-4 M

equation:	$k_{H,cp} = \frac{c_{aq}}{p_{gas}}$	$k_{H,pc} = \frac{p_{gas}}{c_{aq}}$	$k_{H,px} = \frac{p_{gas}}{x_{aq}}$	$k_{H,cc} = \frac{c_{aq}}{c_{gas}}$
dimension:	$\left[\frac{mol_{gas}}{L_{soln} \cdot atm}\right]$	$\left[\frac{L_{soln} \cdot atm}{mol_{gas}}\right]$	$\left[\frac{atm \cdot mol_{water}}{mol_{gas}}\right]$	[dimensionless]
O_2	1.3 E-3	769.23	4.259 E4	3.180 E-2
H_2	7.8 E-4	1282.05	7.099 E4	1.907 E-2
CO_2	3.4 E-2	29.41	0.163 E4	0.8317
N_2	6.1 E-4	1639.34	9.077 E4	1.492 E-2
He	3.7 E-4	2702.7	14.97 E4	9.051 E-3
Ne	4.5 E-4	2222.22	12.30 E4	1.101 E-2
Ar	1.4 E-3	714.28	3.955 E4	3.425 E-2
CO	9.5 E-4	1052.63	5.828 E4	2.324 E-2