

In gases, distances between atoms and molecules are relatively large compared to the actual size of atoms and molecules. Consequently, physical properties of gases are almost independent of the type of gas, and depend primarily on the number of gas molecules present. Consequently, $PV=nRT$, works reasonably well for all gases.

In liquids and solids, atoms and molecules are considered to be in contact with each other, and their physical properties are much more dependent on the chemical nature of the substance and consequent interactions between molecules.

Intermolecular Forces

Dispersion forces. These are the most weak attractive forces, and are present in all substances. Other factors being equal, dispersion forces increase with increasing molar mass. Consider "normal" boiling temperatures of the halogens:

Cl ₂	- 34.6	Br ₂	59	I ₂	184	deg.C
MW =	71	160	254	g / mole		

Due to its higher mole mass, dispersion forces are greater in I₂ (MM= 254) than Br₂ (MM=160). More massive iodine molecules require more energy to "escape" from the liquid solid to the vapor state.

Dipole forces. In addition to dispersion forces, polar molecules carry partial charges. They tend to orient themselves among neighboring polar molecules to maximize interactions between partial charges of opposite signs. This preferred alignment offers an extra "dash" of stabilization that is not available to non-polar molecules. Consequently, boiling point temperature of polar molecules are higher than those of non-polar molecules of similar molar masses. Carbon monoxide (CO) and nitrogen (N₂) have the same MW. However, the boiling point temperature of polar CO is 81 deg.K, as compared to that of 77 deg.K for N₂.

Hydrogen bonding. In addition to dispersion forces and polar forces, molecules in which H is bonded to F, or O, or N, can "hydrogen bond". The difference in electronegativities between H and F, O and N makes such bonds especially polar and results in significant molecular orientations leading to even greater stabilization than available from dipole forces alone. Consider the "normal" boiling temperatures of hydrides for the oxygen family of elements:

H ₂ O	100	H ₂ S	- 61.8	H ₂ Se	-42	H ₂ Te	- 1.8	deg.C
MW =	18	34	81	130		g / mole		

Boiling temperatures for hydrides of S, Se and Te follow a pattern expected for dispersion forces (higher b.p. with larger MW), However, water is "out-of-line". Water, because of hydrogen-bonding, has much larger intermolecular forces at play, and more energy is needed to overcome this additional stabilizing force causing in the "out-of-line" and much higher b.p. temperature for water.

LIQUIDS: The liquid/gas interface.

Substances can exist exclusively in the gas state. Many substances can also exist exclusively in the solid state. However, every substance in the *liquid* state will **always** have some of its molecules present in the *gas* phase; TWO phases will be present. Many examples of liquid and associated gas phases are met in everyday life. Acetone is a liquid at normal conditions, but the odor of acetone molecules *in the gas phase* is readily detected near the liquid. The odor of ethanol molecules *in the gas phase* is readily detected near a glass of wine. Water *in the gas phase* is the source of "seeing" ones breath in winter, or in summer - the source of liquid droplets forming on a can of cold soda. Perfume bottles are kept tightly closed so the solvent in the liquid phase has less opportunity to escape (evaporate) into the gas phase.

Volatility expresses the relative ease that liquids furnish their molecules to the gas phase. Acetone is more volatile than ethanol. Ethanol is more volatile than water. Volatility depends on the magnitude of intermolecular forces (stronger forces means lower volatility) and temperature (more heat energy available at higher temperature means higher volatility). Given a collection of liquids at some specified temperature, the more volatile liquids will be closer to their boiling point temperatures.

Equilibrium gas pressures (i.e., vapor pressures) are a measure of volatility. Liquids in a closed container furnish molecules to the gas phase in the space above the liquid. At a given temperature this gas phase attains a maximum vapor pressure value and the two phases enter a condition of dynamic equilibrium. This equilibrium vapor pressure can not be exceeded at the specified temperature. Recall that humidity is a ratio of actual partial pressure of water vapor in the atmosphere, compared to its maximum equilibrium vapor pressure. 100 % humidity means the gas phase is at its maximum possible pressure (at this specific temperature) and is on the verge of condensing to form liquid, i.e., for water, it is about to start to rain or precipitate.

Equilibrium vapor pressure is similar to solubility in that both are temperature dependent and represent maximum quantities:

- eq.vap.pressure = maximum partial pressure of a gas above a liquid phase.
- solubility = maximum amount of solute that can be present in a solution.

If conditions change causing the amount of solute in a solution to exceed the maximum (such as a temperature change) then the excess solute will precipitate out of solution. Similarly, if conditions change causing the amount of substance present in the vapor phase to exceed the maximum (such as a decrease in volume, or lowering of temperature) then the excess substance will precipitate out of the gas phase - it condenses to the liquid phase.

Toluene, C_7H_8 (liquid), has an equilibrium vapor pressure of 80 torr at 47 deg.C. For any sample of toluene at 47 deg.C, this is the maximum pressure that the gas phase will exert. The "solubility" of toluene in the gas phase above the liquid is 80 torr. Any amount in the gas phase beyond 80 torr must condense to the liquid phase.

Consider the following set of problems which involve toluene at 47 deg.C. They are intended to exercise thinking and facilitate understanding about equilibrium vapor pressures.

- Find the maximum volume of a flask if it is to contain 0.370 g of toluene in an equilibrium condition between liquid and vapor phases at 47 deg.C.
- Calculate the pressure exerted by 0.370 g of toluene in a 1.50 L flask at 47 deg.C.
Will any liquid be present?
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Values for equilibrium vapor pressures of the gas phase, as a function of temperature, are related by the

Clausius-Clapeyron equation.
$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{(vap.)}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right].$$
 It uses $R = 8.31 \text{ J / mol-deg}$

- Water has a vapor pressure of 23.76 torr at 25°C. What is its vapor pressure at 80°C?

More often this expression is used to determine the enthalpy of vaporization of substances after measuring the equilibrium vapor pressures at two different temperatures. For example:

- At 10°C ethyl ether has a vapor pressure of 275 torr, whereas at -12°C it is 90 torr.
What is the heat of vaporization of ethyl ether?

When liquids are in contact with the atmosphere (as in an open container), then atmospheric pressure acts as the "lid" on the container; it is the opposing force keeping volatility in check. If enough heat energy is furnished to the liquid so its vapor pressure matches atmospheric pressure, then the liquid is in a boiling condition. The normal b.p. is that temperature at which the vapor pressure of the liquid is equal to an atmospheric pressure of 760 mm Hg or 1 atm. Water has a normal b.p. of 100. Ethyl alcohol has a normal b.p. of 78.5. Acetone has a normal b.p. of 56.2°C.

Raoult's Law Consider the vapor pressure of *solutions* containing solutes that are non-volatile, i.e., the solute does not contribute to the vapor pressure of the liquid solvent in the gas phase above the solution. For such cases, it is found that the vapor pressure of the gas phase in such a solution is LOWER than that of the pure liquid. Applicable mathematical expressions are: $P_{(solution)} = c_{(solvent)} P_{(solvent)}^0$ or $\Delta P_{(solution)} = c_{(solute)} P_{(solvent)}^0$

Other consequences of the lowering of v.p. in solutions w/ non-volatile solutes are:

- the boiling point of the solution is HIGHER than that of the pure solvent, and
- the freezing point of the solution is LOWER than that of the pure solvent.

The boiling point elevation, or freezing point depression, i.e., the change in temperature, is given by $\Delta T = K * m$; where m is molality, and K is a constant unique to each solvent. K also depends on whether the solution is at its boiling or freezing temperature. For liquid water as solvent, $K_b = 0.52 \text{ deg/molal}$, $K_f = 1.86 \text{ deg/molal}$; please remember these values. This expression offers another way to determine molar masses of substances as solutes in solutions. (And also accounts for why cities in Northern climes salt their ice-covered streets in winter.)

$$\text{molality} = m = \frac{\text{moles}(\text{solute})}{\text{kg}(\text{solvent})}$$

- (f) Aqueous solutions of ethylene glycol, $\text{C}_2\text{H}_6\text{O}_2$, are used in automobile radiators to prevent their freezing in winter. What is the freezing point temperature (in deg.F) of a 50% solution?
- (g) The normal boiling point of the solvent para-dichlorobenzene is 174.1 C. When 1.413 g of a solute of unknown molar mass is dissolved in 46.3 mL of p-dichlorobenzene, the resulting solution boils at 175.5 C. What is the molar mass of the solute? (density of p-dichlorobenzene is 1.25 g/mL, and $K_b = 6.2$ deg/molal)
- (h) Nitromethane, CH_3NO_2 , has an equilibrium vapor pressure of 295 torr at 50deg.C. What is the molality of an acetonitrile solution having a vapor pressure 0.303 atm at 50deg.C?

Osmotic pressure is measured by the difference in levels of a solution that is separated by a SPM from the pure solvent. Osmotic pressure effects are particularly useful for determining MM of substances with very large MM, like proteins.

- (i) When 7.364 g of a protein are dissolved in enough water to prepare 1 L of solution, the osmotic pressure of the solution is measured to be 3.10 torr, at 25deg.C. Sketch a diagram of the system used for measuring the osmotic pressure. What is the difference in levels of the solution and pure solvent (density of mercury = 13.6 g/cm³, density of water = 1.00 g/cm³). Estimate the MM of the protein.

Colligative properties depend on the number of particles present, rather than on their type. For solutions of electrolytes (i.e., solutes are ionic compounds) colligative properties depend on the numbers of ions present. So solutions of NaCl, for example, will have twice the colligative effect, as those of sugar or alcohol solutions of same molality.

Walls of living cells are sort of like SPM. Cell walls can burst when immersed in solutions of lower concentrations, or shrink when immersed in solutions of higher concentrations. In RBC, cell walls are at an osmotic pressure of about 7.7 atm, measured against solvent water. Aqueous solutions to be introduced into the blood stream must have the same osmotic pressure as RBC. Otherwise... Such solutions are said to be isotonic with blood.

- (j) What are the molarities, at 25 deg C, of an isotonic lactose solution? of an isotonic saline solution?

Colligative properties collected:

$$P_1 = P_1^0, \quad \Delta P = c_2 P_1^0, \quad \Delta T = km, \quad \Pi = MRT \quad (\Pi = \text{osmotic pressure})$$

SOLIDS: type of bonding and properties

Molecular solids are composed of neutral molecules packed in such a manner to make most efficient use of space. They generally have relatively low melting points (often below 100°C), do not conduct electricity, and dissolve in non-polar solvents such as benzene and CCl_4 (but not in water). Sugar is a molecular solid that dissolves in water because it contains polar H-O bonds. The crystals are relatively soft.

Ionic solids are composed of ions packed in very specific arrays to maximize interactions between ions of opposite charges. They usually have relatively high m.p., often above 500°C, and tend to dissolve in polar solvents. Although the solids are non-conductors of electricity, their aqueous solutions often are. The crystals are brittle.

Network covalent solids are composed of atoms continuously bonded throughout the entire crystal, so the whole crystal may be considered as one giant molecule. In general they have relatively high m.p.'s, are non-conductors of electricity and do not form solutions. Diamond and quartz (SiO_2) are common examples of three dimensional network solids. Graphite is an example of a two dimensional network covalent solid and it is a conductor of electricity in selected dimensions.

Metal solids are composed of metallic atoms embedded in a sea of valence shell electrons. In general metals do not form solutions, although alloys may be considered as solutions of metal solute or non-metal solute in a metal as solvent. Metals conduct electricity, are ductile, malleable, and can be polished to display a lustrous surface.

(a) (b) (c) (d) (e) worked out in class - answers not provided here.

(f) Assume 50% by weight composition, so 50 g glycol (as solute) for every 50 g water (as solvent).

$$\text{moles solute} = 50 / 64 = 0.781 \quad \text{kg solvent} = 50 / 1000 = 0.05$$

$$\text{molality} = m = 0.806 / 0.05 = 15.6 \text{ molal}$$

$$\Delta T = (1.86) 15.6 = 29.1 \text{ deg.C (this is the freezing point temperature LOWERING)}$$

The freezing point temperature w/b 30 deg.lower than that of pure water, or ... - 30 deg.C.

$$\text{deg.F} = (9 / 5)[-30] + 32 = -20.2 \text{ deg F}$$

(g) $\Delta T = (175.5 - 174.1) = 1.4 \text{ deg.C}$ $k_b = 6.2$?g = 46.3 mL solvent $\left[\frac{1.25\text{g}}{\text{mL}} \right] = 57.875 \text{ g}$

$$\Delta T = k_b (\text{molality})$$

$$\text{molality} = \Delta T / k_b = 1.4 / 6.2 = 0.226 \text{ molal} \quad m = \frac{\left(\frac{\text{mass}(\text{solute})}{\text{MW}(\text{solute})} \right)}{\text{kg}(\text{solvent})}, \quad 0.226 = \frac{1.413}{0.0579}$$

$$\text{MW (solute)} = 108 \text{ g / mole}$$

(h) $\Delta P(\text{solution}) = c(\text{solute}) P_{\text{solvent}}^0$ $\Delta P = 295 - (0.303 \times 760) = 64.7 \text{ torr}$

$$64.7 \text{ torr} = c(\text{solute}) 295 \text{ torr} \quad c(\text{solute}) = 0.2194$$

recall $\sum c = 1$, and for a two-component system, $c(\text{solvent}) = 1 - c(\text{solute}) = 0.7806$

$$\text{?g solvent} = 0.7806 \text{ moles CH}_3\text{NO}_2 \left[\frac{61\text{g}}{1\text{mole}} \right] = 47.6 \text{ g CH}_3\text{NO}_2, \text{ or } 0.0476 \text{ kg CH}_3\text{NO}_2$$

$$\text{molality} = \text{moles solute} / \text{kg solvent} = 0.2194 / 0.0476 = 4.61 \text{ molal}$$

(i) $\Pi = MRT$ $(3.10 / 760 \text{ atm}) = \frac{\left(\frac{7.364\text{g}}{\text{?MW}} \right)}{1\text{L}} (0.082 \text{ L-atm/deg-mol})(298 \text{ K})$ $\text{MW} = 44,120 \text{ g/mole}$

(j) $M = \Pi / RT = 7.7 / (0.083 \times 298) = 0.315 \text{ molar}$ for a lactose solution, but 0.157 molar for a saline solution.