

Solubility and Precipitates

- Everything dissolves in everything else, but to what extent?
- *Rule of thumb*: If solubility limit < 0.01 M, it is considered insoluble

Solubility rules (guidelines)

- **All** NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$, ClO_4^- , Group IA metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and NH_4^+ salts are **soluble**.
- **Most** Cl^- , Br^- , and I^- salts are **soluble**.
 - *Exceptions*: Pb^{2+} , Ag^+ , and Hg_2^{2+}
- **Most** SO_4^{2-} salts are **soluble**.
 - *Exceptions*: Sr^{2+} , Ba^{2+} , Pb^{2+} and Hg_2^{2+} (Ca^{2+} is slightly soluble)
- **Most** CO_3^{2-} , OH^- , PO_4^{3-} , and S^{2-} salts are **insoluble**.
 - *Exceptions*: Group IA metal ions (Ca^{2+} , Ba^{2+} and Sr^{2+} are slightly soluble)

If you're not part of the solution...

- You're part of the precipitate!
- In net ionic equations, the precipitate does not dissociate (stays as one entity)
- Example: $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{NaNO}_3$ (overall)
- $\text{Ag}^+ + \text{NO}_3^- + \text{Na}^+ + \text{Cl}^- \rightarrow \text{AgCl} + \text{Na}^+ + \text{NO}_3^-$ (ionic)
- $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$ (net ionic)

Empirical Gas Laws

- Early experiments conducted to understand the relationship between P , V and T (and number of moles n)
- Results were based purely on observation
 - No theoretical understanding of what was taking place
- Systematic variation of one variable while measuring another, keeping the remaining variables fixed

Boyle's Law (1662)

- For a closed system (i.e. no gas can enter or leave) undergoing an isothermal process (constant T), there is an inverse relationship between the pressure and volume of a gas (regardless of the identity of the gas)

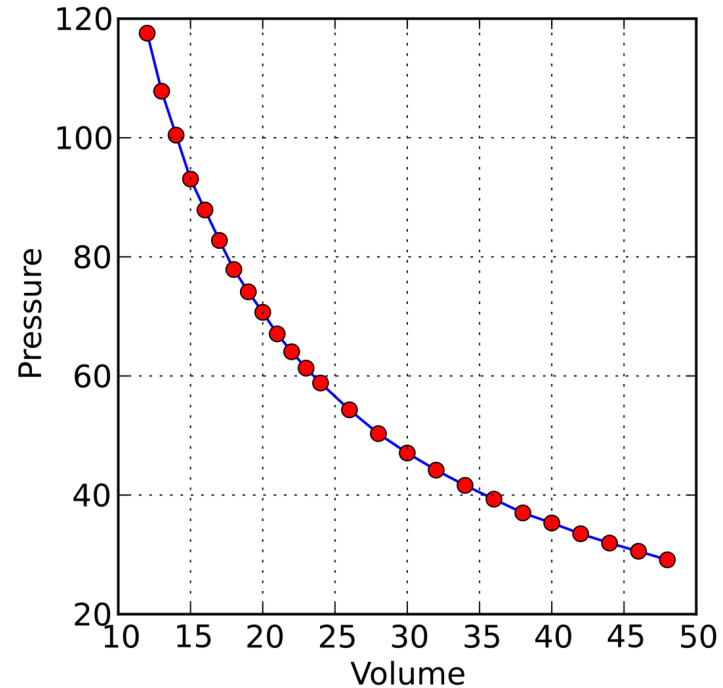
$$V \propto 1/P$$

- To turn this into an equality, introduce a constant of proportionality (a)
→ $V = a/P$, or $PV = a$
- Since the product of PV is equal to a constant, it must **UNIVERSALLY** (for all values of P and V) be equal to the same constant

$$P_1V_1 = P_2V_2$$

Boyle's Law

- There is an *inverse* relationship between P and V (isothermal, closed system)



Charles' Law (1787)

- For a closed system undergoing an isobaric process (constant P), there is a direct relationship between the volume and temperature of a gas.

$$V \propto T$$

- Proceeding in a similar fashion as before, we can say that $V = bT$ (the constant need not be the same as that of Boyle's Law!) and therefore $V/T = b$

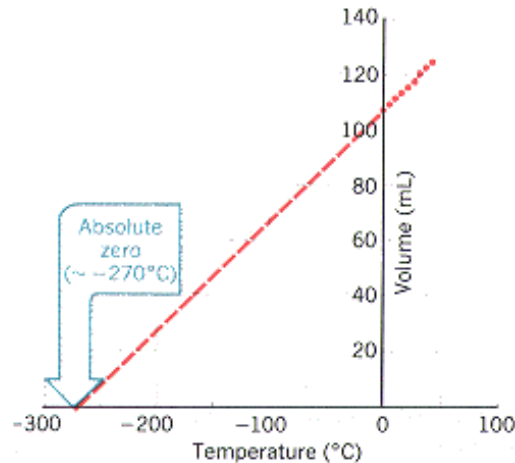
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles' Law (continued)

- This equation presumes a plot of V vs T would give a straight line with a slope of b and a y -intercept of 0 (i.e. equation goes through the origin).
- However the experimental data did have an intercept!
- Lord Kelvin (1848) decided to extrapolate the data to see where it would cross the x -axis (T)
 - Regardless of the nature of the gas, the data always would yield the same value:
-273.15°C
 - Therefore to make it go through zero, just add 273.15 to each point!
- This established the Kelvin (absolute) scale

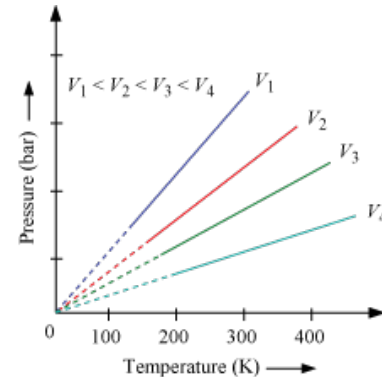
Absolute temperature (Kelvin)

- The establishment of an absolute temperature scale was based on experiments



Gay-Lussac's Law (1809)

- For a closed system undergoing an isochoric process (constant V), there is a direct relationship between the pressure and temperature of a gas
- $P \propto T$
- Or proceeding as for Charles' Law, $P/T = c$
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
- In this relation, we also must use absolute temperature



Avogadro's Law (1811)

- For an open system (mass is allowed to be transferred in or out), the volume of gas is directly proportional to the amount of gas present (given isothermal and isobaric conditions)

$$V \propto n$$

- Mathematically this can be written as $V = dn$ (yet another constant)

Avogadro's Law (continued)

- Since the T and P must be constant, it would be useful to define a reference state (T and P) so that gases can be compared to each other
- STP (standard temperature and pressure)
 - T = 0 °C and P = 1 atm
- Standard state
 - T = 25 °C and P = 1 bar

Combined Gas Law (?)

- It would appear that all the relationships can be combined into one equation. For example, volume is seen to be inversely proportional to pressure, directly proportional to the temperature and directly proportional to the number of moles of gas. Therefore

$$V \propto nT/P$$

- Or $\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$
- This will eventually lead to the ideal (perfect) gas law, $PV=nRT$, as well.

Kinetic Molecular Theory

- Provides a theoretical explanation for the behavior of gases
- KMT is simply a model – it is not a perfect description of reality
 - Good enough! (if not we will fix it later)

Postulates of the KMT

- A gas is composed of particles (molecules or atoms) that are perfect spheres
- Gas particles are in constant, random motion
- Gas particles move in straight lines (i.e. not accelerating)
- Gas particles are very far apart
 - $V_{\text{gas}} \ll V_{\text{container}}$ (most of a gas is empty space)
- The **temperature** is proportional to the average kinetic energy of the motion

More postulates of the KMT

- Gas particles move **independently** of each other
 - The position and momentum of one particle are not affected by the position/momentum of another.
 - *There are no forces of attraction or repulsion between particles*
- Eventually gas particles will collide.
 - Collisions with other particles will be perfectly elastic
 - Collisions with the walls of the container will result in **pressure**.

Determine the number of moles of compound and the number of moles of each type of atom in 3.06×10^{-3} g of the amino acid glycine, $\text{C}_2\text{H}_5\text{NO}_2$.

1 IA										18 VIIIA												
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3 Li Lithium 6.94	4 Be Beryllium 9.0121831																					
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Applications of the Ideal Gas Law

- Determination of the molar mass of a gas
- Since $PV=nRT$ we can say that $n=PV/RT$
- We can also say that the number of moles is given by $n=m/M$
- Setting these expressions equal to each other yields $PV/RT = m/M$, which can be rearranged to solve for the molar mass:

$$M = \frac{mRT}{PV}$$

Applications of the Ideal Gas Law

- Determination of the density of a gas
- Let's use the fact that $\rho = m/V$ and rearrange the ideal gas law to yield $V=nRT/P$
- Combining this with $n=m/M$ and doing some algebra gives

$$\rho = \frac{MP}{RT}$$

**What is the molar mass
of a gas if 0.0494 g of the
gas occupies a volume of
0.100 L at a temperature
26 °C and a pressure of
307 torr?**

What is a mole?

- Small furry animal



- Facial blemish



What is a mole?

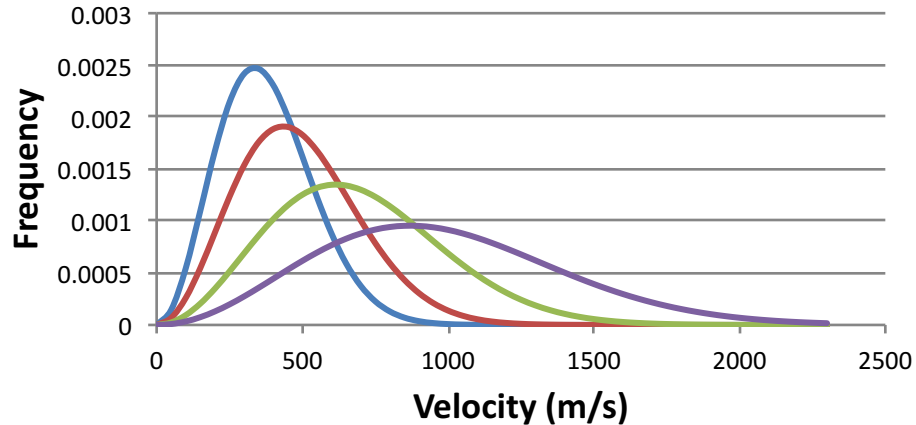
- A mole represent the number of “particles” (elementary entities) present in a sample.
- Avogadro’s Number (N_A)
 - $6.022 \times 10^{23} / \text{mol}$
- The mole can also be related to mass
 - $n = m/M$
 - $n = \# \text{ of moles}$
 - $m = \text{mass}$
 - $M = \text{molar mass (or formula mass or atomic mass)}$

Molecular velocities

- The KMT can be used to calculate the root-mean-square velocity

$$u_{rms} = \sqrt{\frac{3RT}{M}}$$

Maxwell-Boltzmann Distribution of CO₂ at Various Temperatures



Graham's Law of Diffusion/Effusion (1831)

- Diffusion – movement due to a driving force (i.e. concentration gradient)
- Effusion – movement through a small hole
- Both are a “spreading out”, and their behavior is based on KMT
- If two gases are at the same temperature, then they must have the same average kinetic energy

$$\frac{1}{2}M_1u_1^2 = \frac{1}{2}M_2u_2^2$$

- Rearranging this, $\frac{u_2}{u_1} = \sqrt{\frac{M_1}{M_2}}$

Describe what happens to the average kinetic energy of ideal gas molecules when the conditions are changed as follows:

(a) The pressure of the gas is increased by reducing the volume at constant temperature.

(b) The pressure of the gas is increased by increasing the temperature at constant volume.

(c) The average velocity of the molecules is increased by a factor of 2.

Real gases

- There are a number of reasons why the ideal gas law might break down
 - Molecular forces
 - Attractive and repulsive forces do exist, and may be substantial (i.e. polar molecules)
 - Conditions
 - Under extreme cases of “high” pressure and/or “low” temperature gases start to behave more like condensed phases (liquids and solids) and intermolecular forces cannot be ignored

van der Waals equation

- First account for the finite volume that a gas molecule occupies
 - $V \rightarrow V-nb$
- Since this will decrease the volume “available” for the molecules to collide, they should collide more often. This will mean that the pressure should *increase*.
- Mathematically a collision is defined as two particles in the same place at the same time. We can think of the “particle density” as being n/V . Thus the number of collision should be proportional to $(n/V)(n/V) = n^2/V^2$
 - $P \rightarrow P + an^2/V^2$

van der Waals equation

- Putting all of this together leads to

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

where $v = V/n$. v is known as the specific volume, or molar volume.

It is important to note that the constants (a and b) are different for each substance.

van der Waals equation

- Typically corrections are “small” but can improve agreement
 - $v=22.4$ L/mol for ideal gas at STP so b/v is $\ll 1$
- Corrections tend to be larger for larger molecules, as well as for polar molecules

Substance	a (L ² atm/mol)	b (L/mol)
He	0.0341	0.02370
Ar	1.34	0.0322
H ₂	0.244	0.0266
O ₂	1.36	0.0318
CO ₂	3.59	0.0427
CCl ₄	20.4	0.1383

Under which of the following sets of conditions does a real gas behave most like an ideal gas, and for which conditions is a real gas expected to deviate from ideal behavior? Explain.

(a) high pressure, small volume

(b) high temperature, low pressure

(c) low temperature, high pressure

A comparison of the three main phases of matter

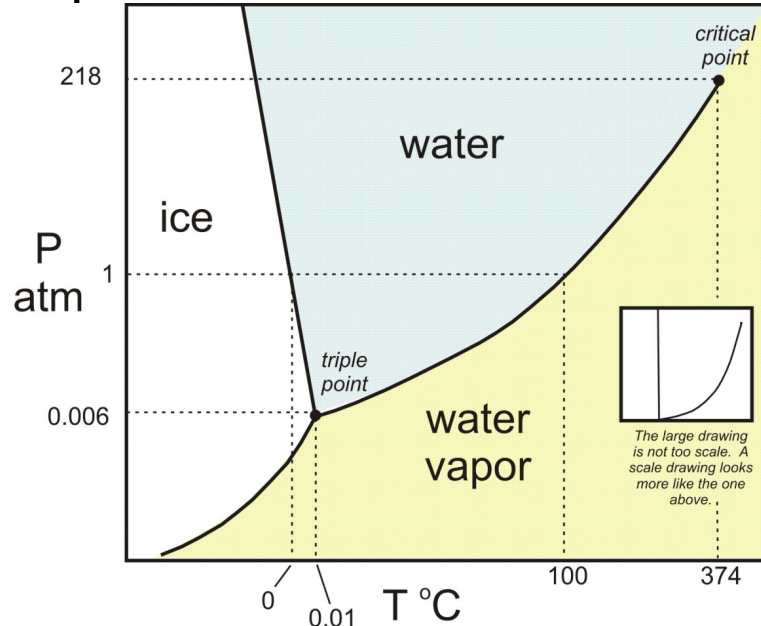
- Gases, liquids and solids differ from each other in the relative magnitudes of *inter-* and *intramolecular* forces

Phase	Volume	Shape	Compressibility	Fluidity
Gas	Indefinite	Indefinite	High	High
Liquid	Definite	Indefinite	Low	High
Solid	Definite	Definite	Low	Low

A 2.50-L volume of hydrogen measured at $-196\text{ }^{\circ}\text{C}$ is warmed to $100\text{ }^{\circ}\text{C}$. Calculate the volume of the gas at the higher temperature, assuming no change in pressure.

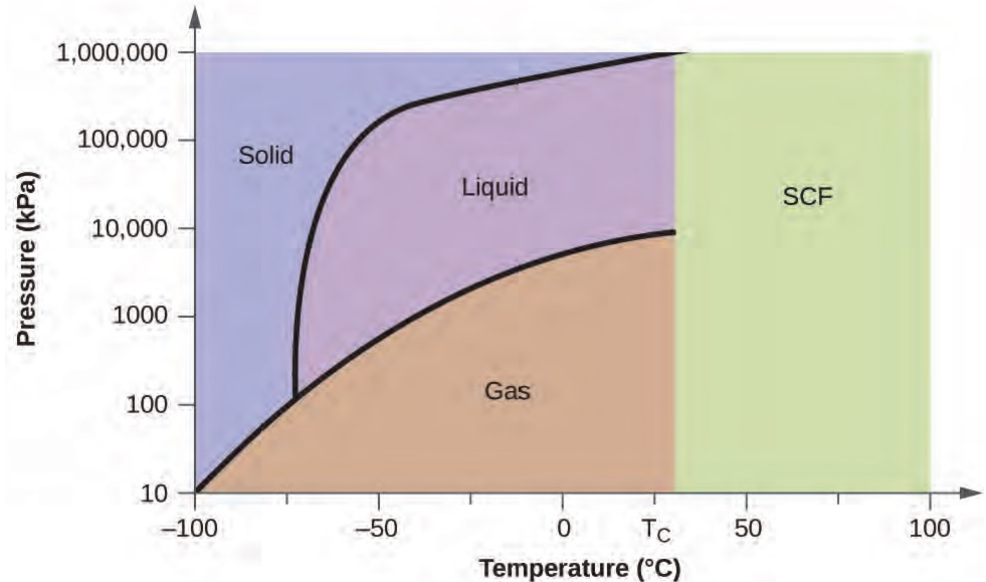
Phase diagrams

- Graphical representation of the states of matter as a function of temperature and pressure



From the phase diagram for carbon dioxide, determine the state of CO₂ at:

- (a) 20 °C and 1000 kPa
- (b) 10 °C and 2000 kPa
- (c) 10 °C and 100 kPa
- (d) -40 °C and 500 kPa
- (e) -80 °C and 1500 kPa
- (f) -80 °C and 10 kPa

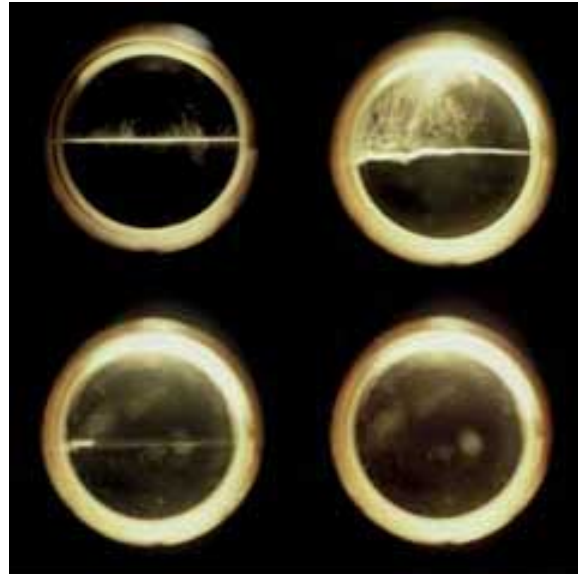


Critical Points

- Critical Temperature (T_c)– highest temperature that liquid and gas can exist as distinct phases
 - A liquid can be produced by simply increasing the pressure of the gas
- Critical Pressure (P_c) – highest pressure that liquid and gas can exist as distinct phases
 - A liquid can be produced by simply decreasing the temperature of the gas
- Beyond the critical point, supercritical fluid exists

Critical Point – in pictures

- Phase boundary disappears, so the two phases are indistinguishable



Triple Point

- For a one component system, there exists a **unique** temperature and pressure where *all three phases coexist at equilibrium*
- It is a physical property of the substance and can't be varied!
- Ex. H_2O $T = 0.0098^\circ\text{C}$ and $P = 4.58 \text{ mm Hg}$



Solids

- Most difficult phase to model because particles (ions, atoms, molecules) are in very close contact
 - Strongest intermolecular forces
- *Amorphous* – disorganized clusters with no long-range order
- *Crystalline* – highly ordered lattice-like assemblies

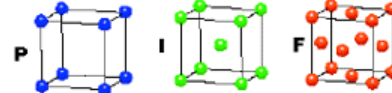
Types of Crystalline Solids

- Molecular
 - Nonpolar
 - Polar
 - H-bonded
- Network covalent
- Ionic
- Metallic

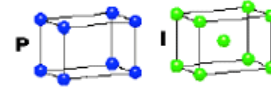
Crystal lattices

- 14 different types
- Lengths (a,b,c)
- Angles (α, β, γ)
- Different types of symmetry
- Cubic has the greatest degree of symmetry ($a=b=c, \alpha=\beta=\gamma=90^\circ$)

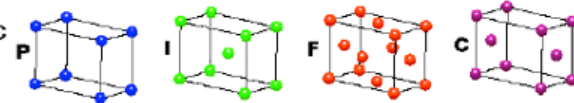
CUBIC
 $a=b=c$
 $\alpha=\beta=\gamma=90^\circ$



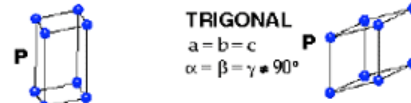
TETRAGONAL
 $a=b \neq c$
 $\alpha=\beta=\gamma=90^\circ$



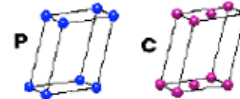
ORTHORHOMBIC
 $a \neq b \neq c$
 $\alpha=\beta=\gamma=90^\circ$



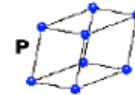
HEXAGONAL
 $a=b \neq c$
 $\alpha=\beta=90^\circ$
 $\gamma=120^\circ$



MONOCLINIC
 $a \neq b \neq c$
 $\alpha=\gamma=90^\circ$
 $\beta \neq 120^\circ$



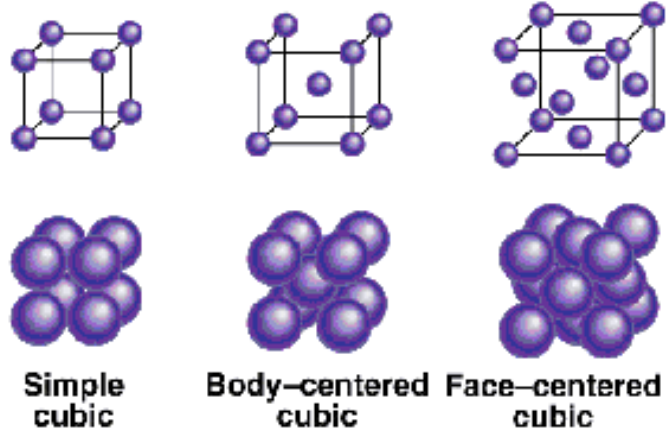
TRICLINIC
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$



4 Types of Unit Cell
 P = Primitive
 I = Body-Centred
 F = Face-Centred
 C = Side-Centred
 +
 7 Crystal Classes
 → 14 Bravais Lattices

Cubic Arrangements

- Simple cubic cell
 - Has its constituents only at the edges (corners) of a cube
- Body-centered cubic (bcc)
 - Has an additional constituent at the center of the cube
- Face-centered cubic (fcc)
 - Has an additional constituent at the center of each face of the cube



Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

(a) SiO_2

(b) KCl

(c) Cu

(d) CO_2

(e) NH_4F

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Types of solutions

Solute	Solvent	Solution Phase	Examples
Gas	Gas	Gas	Air, natural gas
Gas	Liquid	Liquid	Club soda (CO_2 in H_2O), artificial blood (O_2 in perfluorodecalin)
Liquid	Liquid	Liquid	Vodka
Solid	Liquid	Liquid	Saline
Gas	Solid	Solid	H_2/Pd
Solid	Solid	Solid	14-karat gold (Ag in Au)

Energetics of solution formation

- 1) Pure solvent \rightarrow separated solvent molecules
 - $\Delta H_1 > 0$ because intermolecular forces are being broken
- 2) Pure solute \rightarrow separated solute molecules
 - $\Delta H_2 > 0$ because intermolecular forces are being broken
- 3) Separated solvent and solute molecules \rightarrow solution
 - $\Delta H_3 < 0$ because intermolecular forces are being formed

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

What it means to be ideal

- For condensed phases, we know that there are intermolecular forces, which may be fairly significant. Considering the case of just two different types of molecules in a solution (A and B), there are really **three** types of interactions: A-A, A-B and B-B.
- If the solution is *ideal*, then the magnitudes of these interactions are all equal – i.e. it doesn't really matter who your neighbor is!
- $\Delta H_{\text{solution}} = 0$, $\Delta V_{\text{solution}} = 0$

Ways to measure concentration

- Relative/qualitative terms
 - Dilute or concentrated
- Solubility – usually based on g of solute / 100 mL of water
 - Unsaturated – under solubility limit
 - Saturated – at solubility limit
 - Supersaturated – over solubility limit

Ways to measure concentration

- % by mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{total mass of solution}} \times 100\%$$

– Total mass = mass of solute + mass of solvent

- % by volume

$$\% \text{ by volume} = \frac{\text{volume of solute}}{\text{total volume of solution}} \times 100\%$$

– Total volume \approx volume of solute + volume of solvent

Ways to measure concentration

- Molarity

- Most common unit of concentration in chemistry

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume of solution (in L)}}$$

- $M = n/V$

- Molality

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent (in kg)}}$$

- $m = n/m$

- Better because with molarity you are unsure of the actual volume of liquid being added

Ways to measure concentration

- Normality

- Used almost exclusively for acids and bases

- $N = M \cdot E$, where M is the molarity and E is the # of equivalents (# of H^+ that will dissociate in an acid, or # of OH^- that will dissociate in a base)

- Useful for titrations

- Mole fraction

$$X_A = \frac{n_A}{n_{tot}} = \frac{n_A}{\sum n_i}$$

- Useful for colligative properties, chemical processes

**Determine the molarity
when 98.0 g of
phosphoric acid, H_3PO_4 ,
is dissolved in 1.00 L of
solution.**

1 IA										18 VIIIA											
1 H Hydrogen 1.008																		2 He Helium 4.002602			
3 Li Lithium 6.94	4 Be Beryllium 9.0121831																				
11 Na Sodium 22.98976928	12 Mg Magnesium 24.305																				
State of matter (color of name) GAS LIQUID SOLID UNKNOWN		Subcategory in the metal-metalloid-nonmetal trend (color of background)																			
		Alkaline metal					Alkaline earth metal					Metalloid		Noble gas							
		Lanthanide					Actinide					Polyatomic nonmetal									
		Transition metal					Post-transition metal					Diatomic nonmetal									
								Unknown chemical properties													
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955908	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938044	26 Fe Iron 55.845	27 Co Cobalt 58.933194	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921595	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798				
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90584	40 Zr Zirconium 91.224	41 Nb Niobium 92.90637	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.750	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293				
55 Cs Caesium 132.90545196	56 Ba Barium 137.327	57 - 71 Lanthanoids		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.592	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)			
87 Fr Francium (223)	88 Ra Radium (226)	89 - 103 Actinoids		104 Rf Rutherfordium (261)	105 Db Dubnium (268)	106 Sg Seaborgium (269)	107 Bh Bohrium (270)	108 Hs Hassium (278)	109 Mt Meitnerium (278)	110 Ds Darmstadtium (285)	111 Rg Roentgenium (282)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flerovium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (293)	117 Ts Tennessine (294)	118 Og Oganesson (294)			

Atomic Number → 1

Symbol ← H

Name → Hydrogen

Atomic Weight ← 1.008

57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93033	68 Er Erbium 167.259	69 Tm Thulium 168.93422	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.0377	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (260)

Raoult's Law

- Consider a solution made up of solvent A (large purple spheres) and solute B (small green spheres).
- The rate at which A leaves the surface (vaporization) is proportional to how many you have on the surface, which is proportional to the mole fraction: $r = kx_A$
- The rate at which A comes back (condensation) is proportional to the concentration of the gas, which is proportional to the partial pressure: $r = k'P_A$
- Since these two rates must be the same:

$$P_A = \frac{k}{k'}x_A$$

For a pure liquid $x_A = 1$ so $k/k' = P_A^*$. This means that

$$P_A = x_A P_A^*$$

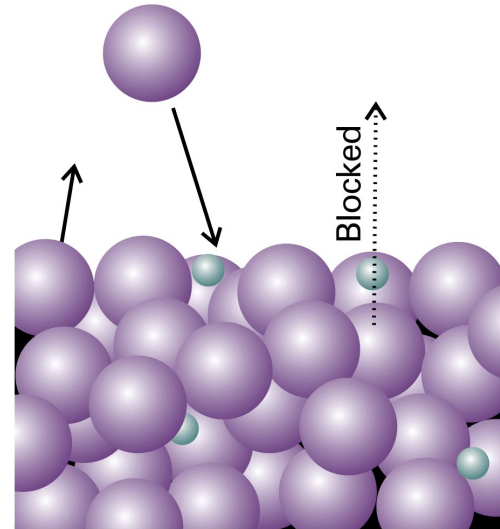


Figure 5-13
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Ideal solutions

- An ideal solution is one where Raoult's Law is obeyed.
- Since $P = P_A + P_B$, and the vapor pressure for a liquid is the same as that for a gas, for an ideal solution we can say that

$$P = P_A^* x_A + P_B^* x_B$$

- Furthermore, since $x_A + x_B = 1$,

$$P = P_A^* x_A + P_B^* (1 - x_A) \text{ or}$$

$$P = (P_A^* - P_B^*) x_A + P_B^*$$

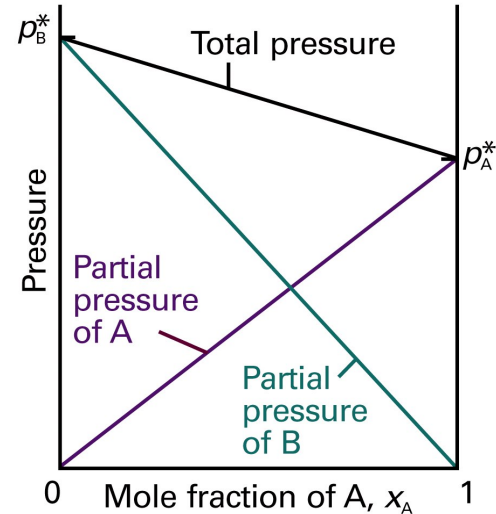


Figure 5-11
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Example of an ideal solution

- Solutions tend to behave ideally when the solvent (A) and solute (B) are “similar” to each other in terms of molecular structure, polarity, intermolecular forces, etc.
- Ex. Benzene and toluene (methylbenzene)

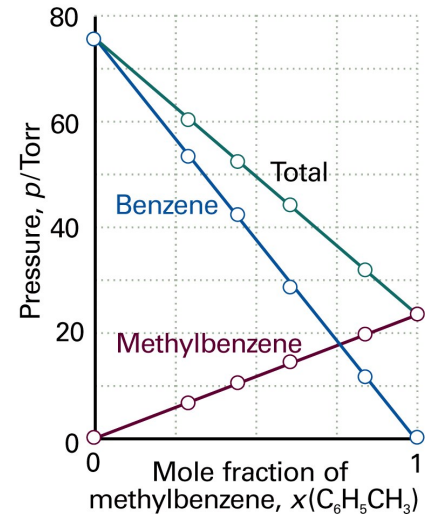
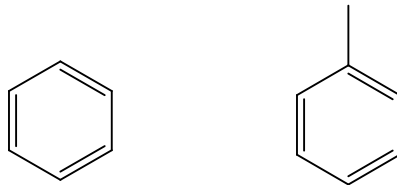


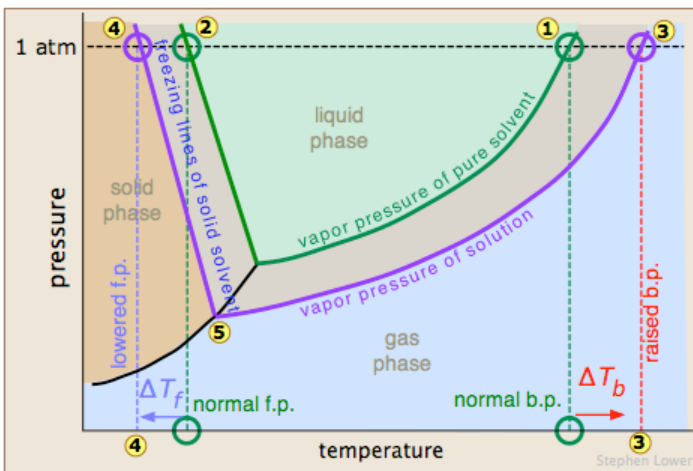
Figure 5-12
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Colligative properties

- The presence of a solute can affect the properties of a solution
- This effect is (primarily) due to the amount of solute (i.e. concentration) but not necessarily on the nature of the solute
- Three main colligative properties:
 - Boiling point elevation
 - Freezing point depression
 - Osmotic pressure

Freezing point depression and boiling point elevation

- Consider solutions where only the solvent is volatile, and the solute only dissolves in the liquid phase of the solvent



- $\Delta T_f = -iK_f m$

- $\Delta T_b = iK_b m$

i = van't Hoff factor ($i = 1$ for a non-electrolyte, ≈ 1 for a weak electrolyte, or # of particles for a strong electrolyte)

K_f = freezing-point depression (cryoscopic) constant

K_b = boiling-point elevation (ebullioscopic) constant

m = molality

Osmotic pressure

- Osmosis - net flow of solvent molecules through a semipermeable membrane
 - Solvent molecules go from a solution of lower concentration to a solution of higher concentration (solute is not able to pass through)
- Osmotic pressure (π) = pressure required to stop osmosis
- $\pi = MRT$, where M = molarity

