Lecture 7

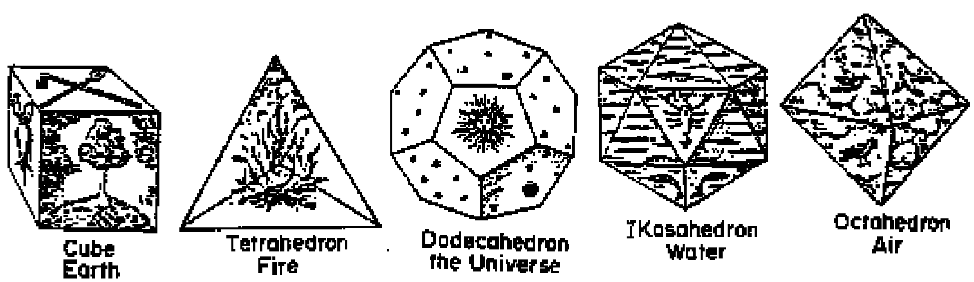
The Material Universe

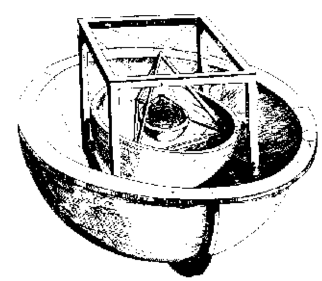
Outline of Lecture 7

- History of Ideas about Elements:
  - Water, fire, earth, air, and quintessence (Greek)
  - Water, fire, earth, metal, and wood (Chinese)
  - Solid, liquid, and gaseous phases.
- Metallurgy and the Path to Alchemy/Chemistry:
  - Metals as true elements
  - Rise and fall of alchemy
- Atoms/Molecules and the Paths to Microscopic and Macroscopic Physics:
  - Democritus: atoms and the void.
  - Ideal gases and Boyle's law
  - Explanation in terms of atoms/molecules by Daniel Bernoulli
  - Determination of Avogadro's number through Brownian motion by Einstein & Perrin
  - Law of integer proportions found by Gay-Lussac & Dalton for atoms to form molecules.
  - Modern conception of solids, liquids, gases, and changes of phases of matter.

History of Western Philosophical Ideas about Elements

- Babylonians: primal element is *water,* giver of life and capable of solid, liquid, vapor transformations.
- Greeks (Heraclitus) added *fire* to oppose water, then *earth* (Xenophanes) to mediate between hot and cold (cf. Taoism: yin and yang).
- Hero (ca. 150 BC), a Greek scientist, proved that *air* is a substance.
- Fire is subsequently delegated to celestial realm. Terrestrial elements are earth, water, and air, representing fundamental solid, liquid, gas.
- Plato connected four Greek elements to four of the five "Platonic" solids.
  - Aristotle proclaimed that "nature abhors a vacuum," and postulates a fifth element, quintessence, to fill the space between Heaven and Earth.
  - Later, during Renaissance, Shakespeare (in *King Lear*) wrote: "I tax not you, the elements, with unkindness. I never gave you kingdom, called you children. You owe me no subscription." The "elements" to which Lear was referring was that of Greek tradition, namely, the wind (air), rain (water), lightning (fire), and cold ground (earth) of the storm that he was in.
  - By relating the Euclidean solids to the spacing of planetary orbits in *Mysterium Cosmographicum*, Kepler reprised the classical ideas more literally:





History of Eastern Philosophical Ideas about Elements

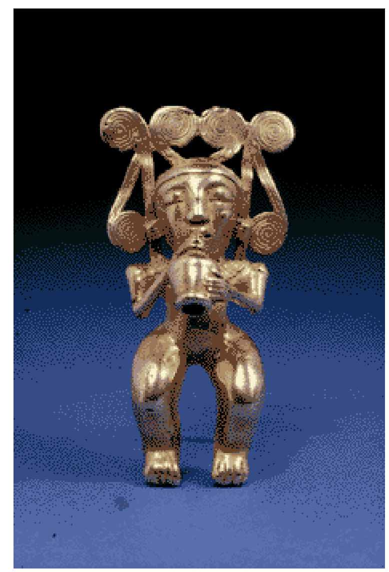
- “Five elements” of classical antiquity play important role in Chinese ideas about “feng-shui,” which is relic of old mystical way of thinking.
- Association with planets: Water-Mercury; Metal-Venus; Fire-Mars; Wood-Jupiter; Earth-Saturn.
- Idea that all seven metals of antiquity -- gold, silver, copper, tin, iron, lead, quicksilver -- are the same metal leads to alchemy.
- Experimentation with nitrogen and sulfur compounds led to invention of gunpowder in ninth century AD.
- Alchemy becomes mixed with search for elixir that gives everlasting life.
  - Potions to aid the digestion of gold.
  - More Emperors had life foreshortened than prolonged.
  - Jabir Ibin Hayan in eighth century discovers that a mixture of nitric and sufuric acid (“aqua regia”) can dissolve gold.
  - Discovery of zinc in China and India (from the smelting of copper and the making of brass) in eleventh century lead to dying of interest in alchemy in Far and Middle East.

National Palace Museum, Taiwan

Chinese practicality: objects d’art made from water, fire, earth (top); metal (middle); wood (bottom). Contrast with Greek theoretical abstraction of air and quintessence.

Metallurgy and Civilization

- Metal technology defined progress of early human cultures:
  - Old stone age →New stone age → Copper Age
  - Paleolithic → Neolithic → Civilizations dominant in warfare
- Copper Age → Bronze Age → Iron Age → Age of brass & silicon …
- Sumerians: *copper* + *tin* = bronze (an alloy).
- Egyptians: *gold, silver, asem*, meteoritic *iron*.
- Austria (ca. 750 BC): iron from charcoal blast furnaces. Carbon enters iron → steel.
- Greeks: asem = alloy of gold & silver, *lead*.
- Ancients did not consider *quicksilver* (*mercury*) to be a metal because it is a liquid at room temperature without smelting.
- Chinese and Indians: Brass = copper + zinc (valued for yellow gold-like color); discovery of zinc destroys alchemical ideas linking metals and planets (next slide).



Seven Metals for Seven Planets

Metal	Planet
Gold	Sun
Silver	Moon
Tin	Mercury
Copper	Venus
Iron	Mars
Asem	Jupiter
Lead	Saturn

Alchemical (i.e., fake) gold coin showing astronomical symbol *h* for Saturn (lead) rising to Sun (gold).

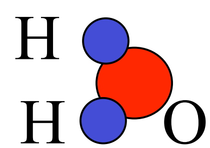
Mystic Beliefs: Alchemy

- In some sense, Greeks had transformed (by careful refinement) asem into silver (small art) and gold (great art). Can other metals, which have similar properties, e.g., malleability, ductility, conductivity, shininess, etc. also be transformed one into another, for example, worthless lead to valuable gold?
- First act, blacken the metal to hide its true color; thus, the first name for alchemy is the "black art."
- In the Fujian dialect (and Korean), the name for gold is "kim." The Arabs translate this to "alchemy" ("the gold"), which eventually becomes "chemistry."
- Newton practiced alchemy more than he did astronomy, mathematics, or physics. His later neurological disorders are sometimes blamed on mercury poisoning. One way to make dull metals (like lead) shiny is to rub them with mercury.
- Quicksilver, a liquid at room temperature, is not originally considered a metal. Later quicksilver replaces asem (an alloy) and is assigned to Mercury, the planet, acquiring its name (because both move quickly). Tin goes to Jupiter. But with discovery of zinc, etc., metals begin to outnumber planets. Alchemy, like astrology, thus has no basis in fact.

Roger Bacon, Franciscan Friar, Philosopher, & Alchemist

The Beginnings of European Chemistry

- Joseph Priestly (1733-1804):
  - Heats up an oxide of mercury and releases a colorless. odorless gas which is refreshing to breathe, finding in this way that an important constituent of air is *oxygen* -- vital for the respiration of animals.
  - Rats placed inside bell jar of pure oxygen survive 5 times longer than rats in bell jar with same amount of air. Thus, air is only 20% oxygen; the rest is mostly nitrogen. Air is not a pure substance, i.e., not an element. (Note also the first hint that life processes are a matter of chemistry.)
- Antoine Lavoisier (1743-1794): water is also a compound substance = H_2O, not an element.



  - Gas (hydrogen) given off when some acids react with metals can combine with oxygen to give water. ("Hydrogen" = "can generate water.")
  - Combustion (fire) results when things that can burn combine with oxygen. Thus, fire is also not an element.
  - Law of conservation of mass (approximately true for chemical reactions).
  - Beheaded by guillotine during Reign of Terror.
  - Tribute by Lagrange: "It took but a moment to sever that head. How many centuries must pass before we see its like again?"

The Periodic Table in 1871

- By1789, besides the classical metals, Lavoisier had identified hydrogen, nitrogen, oxygen, sulfur, phosphorus, and zinc as true elements.
- None of the Greek candidates: water, fire, earth, air, quintessence turn out to be true elements. The Chinese substitution of "metal" as one of the five elements of antiquity was more fruitful for turning alchemy to chemistry.
- In 1871, Dimitri Mendeleev (1834-1907) published a list of the then known 63 elements in the form of a periodic table, which subsequently became the most basic tool of the chemist.
- Elements in the vertical groups I through VIII behave similarly in chemical reactions. Their approximate molar amounts in gm are given by the "Arabic" numbers, H = 1, etc.
- Notice that Mendeleev's original table did not contain a column for noble gases, because these do not participate in chemical reactions. Their discovery by astronomical and physical means was to come later.

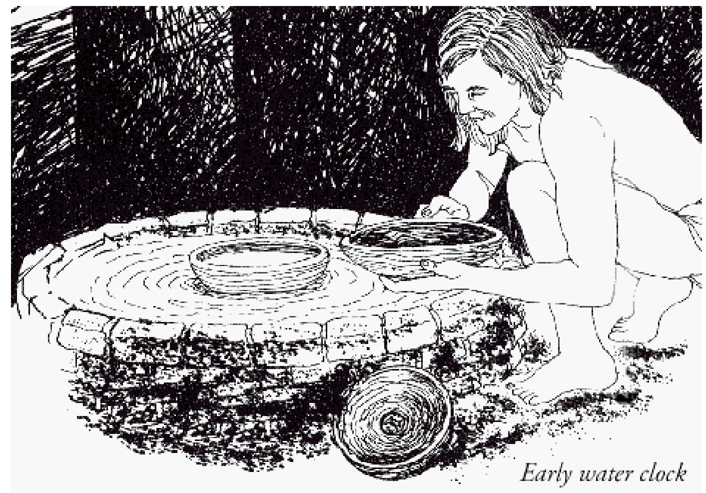
Period \ Group	I	II	III	IV	V	VI	VII	VIII
1	H=1							
2	Li=7	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	K=39	Ca=40	?=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56,Co=59 Ni=59
5	Cu=63	Zn=65	?=68	?=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	?=100	Ru=104,Rh=104 Pd=106
7	Ag=108	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140				
9								
10			?Er=178	?La=180	Ta=182	W=184		Os=195,Ir=197 Pt=198
11	Au=199	Hg=200	Tl=204	Pb=207	Bi=208			
12				Th=231		U=240		

Mendeleev (1871)

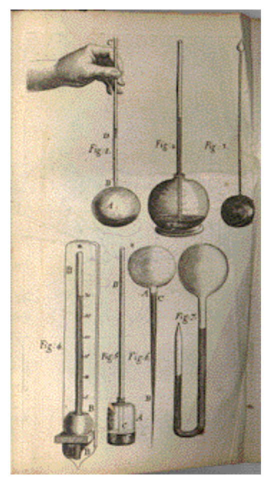
A Radically Different Approach: Atoms and the Void

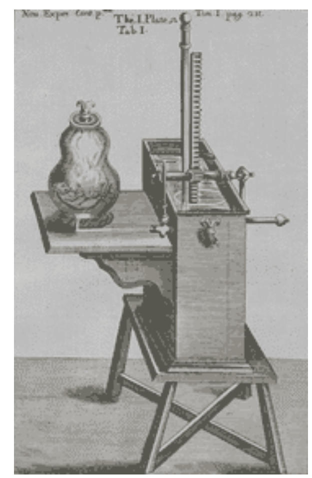
- Leucippus, pondering Zeno's paradox (tortoise and hare), wonders if matter is infinitely divisible.
- Democritus (460-370 BC) proposes a radically different view of matter and its transformations: "nothing but atoms and the void." Hooks and eyelets to form compounds (molecules).
- Using a water clock, Hero (ca 150 BC) proves that air is a substance.
- Hero performs experiments on the compressibility of air supporting Democritus's view of "atoms and the void."
- Experiments of Robert Boyle (1627-1691) with the help of Robert Hooke demonstrate Boyle's law:

  $PV = \text{constant}$.
- Jacques Charles and Joseph Gay-Lussac show the right-hand side is proportional to (absolute) temperature T.

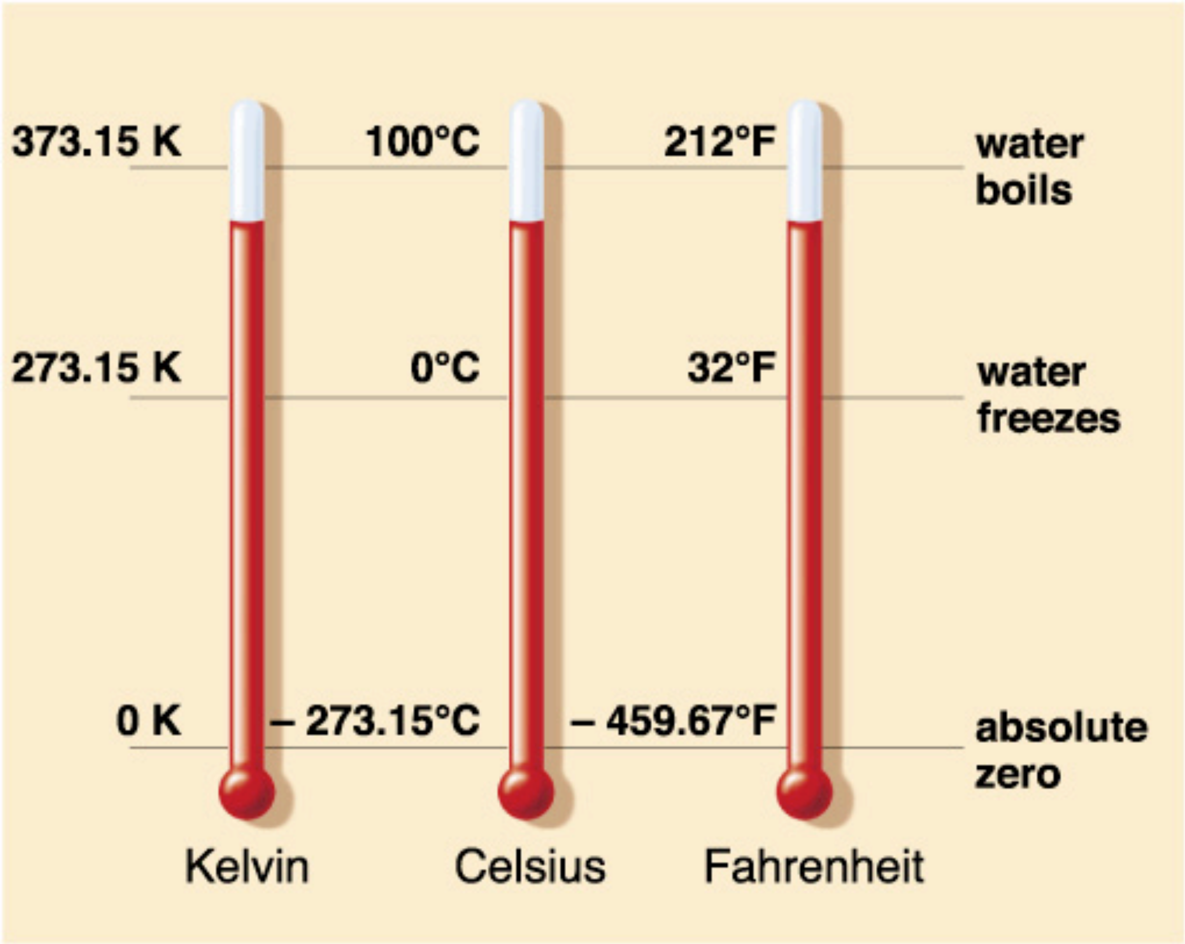


Early water clock



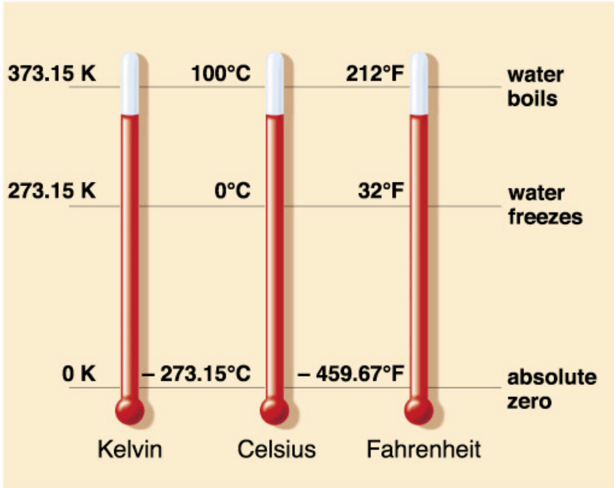


Temperature Scales



Ideal Gas Law: $PV = \nu\Re T = NkT$

- Pressure P = force per unit area exerted on container wall of volume V by gas.
- T = temperature in Kelvin units
- RHS must also be proportional to how much gas there is since at given P and T, doubling V must double the amount of gas.
- ν expresses the amount of gas in moles (chemists' concept). Approximately, one mole of H atoms = 1 gm of H; one mole of C atoms = 12 gm of C; one mole of O atoms = 16 gm of O, one mole of water molecules = 18 gm H_2O, etc.
- N expresses the amount in number of gas particles or molecules (physicists' concept).
- The proportionality constant, $\Re$ (gas constant) or k (Boltzmann's constant) then depends on whether we use number of moles ν or the number of molecules N. The numerical values of $\Re$ and k depend on the definition of T, which was historically chosen arbitrarily based on the properties of water (the "primal element"). What must always be true is $\nu\Re = Nk$, i.e., the number of molecules per mole = $N/\nu = \Re/k = \text{const} \equiv$ Avogadros' number $\equiv N_A$.



Determination of Gas Constant

- At standard pressure and temperature (STP), P = 1 atmosphere = 1.01×10^5 kg m^{-1} s^{-2}.

  and T = 273 K (0 C), one can measure that the volume occupied by $\nu = 1$ mole of any gas is V = 22.4 liters = 0.0224 m^3.
- Thus,

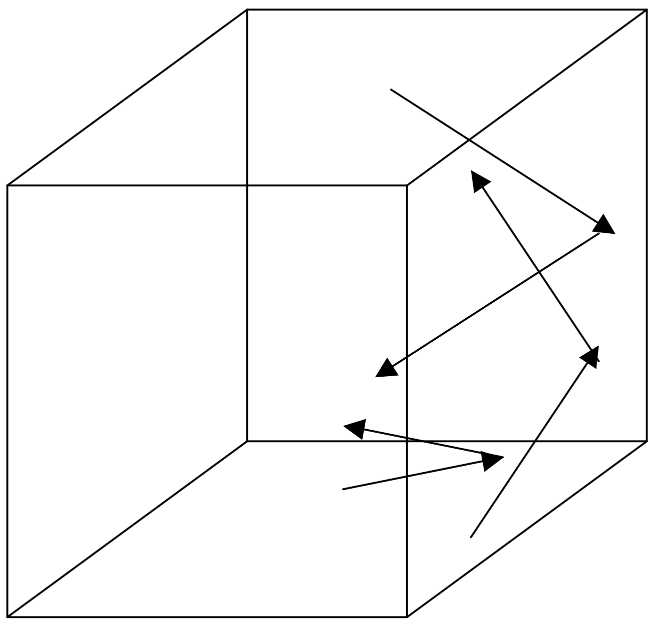
$$\Re = \frac{PV}{\nu T} = 8.31 \text{ kg m}^2 \text{ K}^{-1} \text{ s}^{-2} \text{ mole}^{-1}.$$

Explanation of Ideal Gas Law by Daniel Bernoulli (1700-1782)

- Gas is made of large numbers of particles (atoms or molecules) that are moving freely in space except when they have collisions with each other, or when they collide with the walls of a container.
- The pressure P is the momentum transferred per unit time (force) on average by gas particles of number density $n = N/V$ colliding elastically with a unit surface area of the wall.
- If we write the ideal gas law in the form

$$P = \frac{N}{V} kT = nkT,$$

then it is possible to identify the combination kT as 2/3 the mean kinetic energy of the colliding gas particles. Thus T = absolute zero corresponds to when gas particles stop moving altogether and are unable to bounce off surfaces (real or imaginary) to exert a gas pressure on vessel walls.



Derivation of Ideal Gas Law (extra material)

- In an isotropic gas, every direction is the same; therefore,

$$\langle v^2 \rangle \equiv \langle {v_x}^2 + {v_y}^2 + {v_z}^2 \rangle = 3\langle {v_x}^2 \rangle.$$

- Consider now the direction perpendicular to a wall, which we will call the *x* direction. Half of the molecules to one side of the wall are moving toward it on average. If these molecules all have a single value for the velocity component, then the number of molecules that will hit an area *A* on the wall in time Δt is given by the number *N* of molecules of number density *n* in the volume $V = A v_x \Delta t$

$$N = \frac{1}{2} nV = \frac{1}{2} nA v_x \Delta t.$$

- Each molecule of mass *m* will bounce elastically from the wall and transfer an amount of *x*-momentum to the wall equal to

$$\Delta p_x = 2m v_x.$$

- The total momentum transferred in time Δt is therefore

$$N \Delta p_x = nAm {v_x}^2 \Delta t.$$

- If we divide by Δt, we get the rate of transferring momentum, or the perpendicular force exerted on the piece of wall of area *A*. Dividing by *A* then gives the perpendicular force per unit area, which is the pressure *P* exerted by the gas on the wall:

$$P = nm\langle {v_x}^2 \rangle = \frac{1}{3} nm \langle v^2 \rangle,$$

where we have made use of the first of the equations on this slide. We have also replaced squared velcities by their average value because the molecules are moving in reality with a variety of speeds instead of only a single value. If we compare the last expression with the ideal gas law, $P = nkT$, we obtain the identification:

$$kT = \frac{1}{3} m \langle v^2 \rangle \Rightarrow \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT,$$

i.e., 3/2 times *kT* is simply the average kinetic energy of gas molecules in an ideal gas (*kT*/2 in each of 3 directions). On a microscopic level, the combination that matters is *kT*, not *k* or *T* by itself.

Moles, Molecules, Atoms, and Avogadro's Number

- Mole = large mass (Latin)
- Molecule = small mass
- Atom = cannot cut (Greek)
- N_A = number of atoms in one mole of any atomic substance = $\Re / k$.
- In lab, can measure $\Re = 8.31 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mole}^{-1}$.
- How to measure k without ability to see atoms or molecules?
- Einstein in 1905 explains Brownian motion in terms of individual water molecules randomly and incessantly striking a pollen grain suspended in water. Perrin uses Einstein's theory to determine $k = 1.38 \times 10^{-23} \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1}$.
- Avogadro's number: $N_A = \frac{\Re}{k} = 6.02 \times 10^{23}$ (molecules per mole).
- Therefore, 18 gm (1 mole) of liquid water (18 cc = roughly 1 cubic inch) contains 600 billion trillion molecules of H_2O!

Perrin, *Atoms* (1913)

Law of Integer Proportions Discovered by Gay-Lussac & Dalton

Gay-Lussac's empirical findings (extra material):

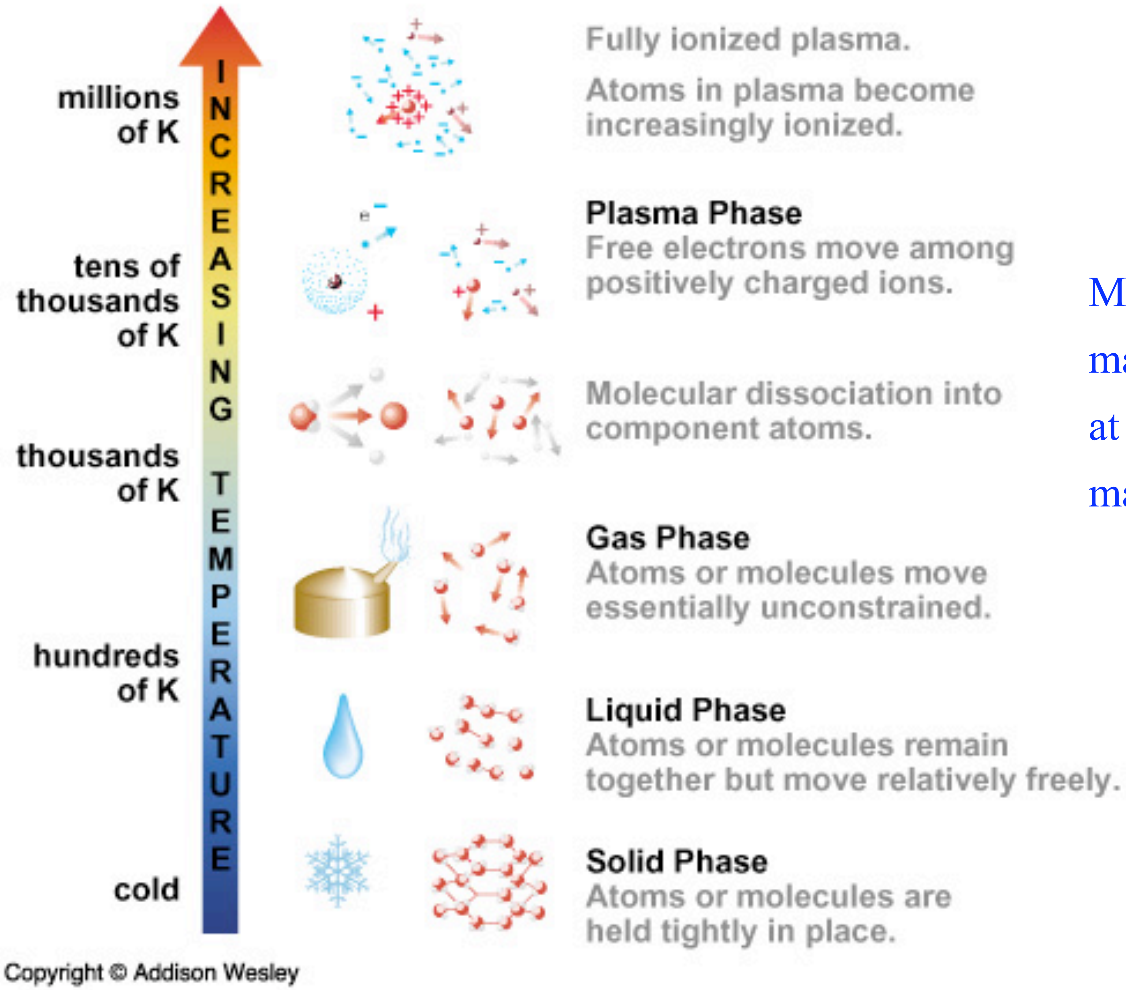
Volume of nitrogen gas	Volume of oxygen gas	Volume of Compound gas
22.4 liters	22.4 liters	44.8 liters NO
44.8 liters	22.4 liters	44.8 liters N_2O
22.4 liters	44.8 liters	44.8 liters NO_2

- Above can happen only if nitrogen gas and oxygen gas exist naturally as N_2 and O_2. Then 1 mole of N_2 combines with 1 mole of O_2 to form 2 moles of NO, etc.
- At first, the Englishman Dalton did not want to believe the Frenchman Gay-Lussac's findings
  - Dalton did not believe that like atoms can combine with themselves, N with N, O with O, or with each other in multiple ways. He was wrong.
  - Dalton thought that molar amount should be proportional to mass, not volume. Dalton is correct, but relationship in mass does not result in integer proportionalities because of effects of isotopes and mass deficit (more elsewhere). Fortunately, for ideal gases at STP, number of moles is strictly proportional to volume.

Dalton's later atomic credo:

- All matter is composed of indivisible particles called atoms.
- Atoms are indestructible and unchangeable.
- All atoms of a given element are identical chemically. Atoms of different elements have different properties.
- Molecules are formed when atoms of different elements combine chemically. When elements react to form compounds, they do so, by numbers of atoms, in well-defined, whole number ratios.
- Chemical reactions occur by atoms or smaller molecules coming together and binding to form larger molecules, or by larger molecules coming apart to form smaller molecules or atoms. These too occur only in integer proportions.
- Thus, as far as the material universe of atoms and molecules go, Pythagoras was right: "All things are numbers."

Changes of Phase
When Temperature Increases



Mnemonic: At low temperatures,
matter wants to be more bound;
at high temperatures,
matter wants to have more particles.

Summary

- In hindsight, we see that the contrasting philosophies of Plato and Democritus were both right:
  - Matter does form ordered states (crystalline solids) with regular 3-D geometric shapes (cosmos)
  - Matter also forms irregular states (gases) which correspond to atoms moving randomly in a void (chaos)
- The Oriental path of regarding metals as elements led to alchemy and then to chemistry. The Occidental path of gases as atoms in the void led to microscopic and macroscopic physics which ultimately also led to chemistry (atoms combining into molecules).
- Thus, the distinction made between chemistry and physics is a historical accident and is not intrinsic to these subjects. Later, westerners were to learn the even more disturbing fact that there is no true distinction between biology and chemistry. For Asians, the revelation comes as less of a surprise, since they have always regarded humans as comprising a part of nature (the material world), not standing apart from it.