History of Gas Laws

(***from*** http://web.fccj.org/~ethall/gaslaw/gaslaw.htm)

The gas laws started to evolve in 1643 with the invention of the barometer and continued until 1873 with the van der Waals equation. Note that this is well before the birth of the modern atomic theory. The gas laws led to numerous concepts including the mole, temperature, formula weight, absolute zero, kinetic energy, and stoichiometric coefficients. This brief history highlights some of the early pioneers.

Barometer

Evangelisto Torricelli (1608-1647)

Torricelli served as Galileo's secretary (1641-1642) and succeeded him as court mathematician to Grand Duke Ferdinando II. Torricelli used mercury to make the first barometer in 1643. Mercury is more than 13 times as dense as water; a water barometer would require a tube more than 30 feet long. Under standard conditions at sea level, the height will be 29.92 inch or 760 millimeters. The invention of the barometer allowed Boyle to discover the relationship between pressure and volume. (Torricelli letter to Michelangelo concerning the Barometer)

Boyle's Law: $P_1V_1=P_2V_2$

(*appelée loi de Boyle par les anglophones, mais loi de* ***Mariotte*** *ou loi de* ***Boyle*** --***Mariotte*** *par les francophones*)

Robert Boyle (1627-1691)

Boyle had the good fortune to have Robert Hooke as an assistant and together they made an air pump. Recognizing its scientific possibilities, Boyle conducted pioneering experiments in studying the role of air in combustion, respiration, and the transmission of sound. In 1662, Boyle published what is now known as Boyle's law: At constant temperature the volume of a gas is inversely proportional to the pressure.

Boyle was aware that a gas expands when heated but no temperature scale existed and he could not determine the relationship between "hotness" and volume.

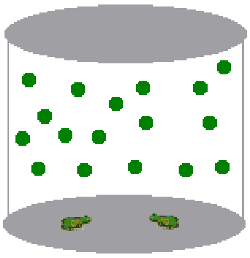
Amontons' Law: $P_1T_2=P_2T_1$

Guillaume Amontons (1663-1705)

Amontons developed the air thermometer--it relied on increase in volume of a gas with temperature rather than the increase in volume of a liquid. Amontons failed to discover Charles' law for the same reason as Boyle: a temperature scale did not exist. Using the air thermometer, Amontons (1702) devised a method to measure change in temperature in terms of a proportional change in pressure. Although Amontons' law became the most obscure of the gas laws, it was this work that eventually led to the concept of absolute zero in the 19th century.

As a consequence of becoming deaf as a young boy, Amontons worked on inventions to benefit the deaf. One of his inventions, the first telegraph, relied on a telescope, light, and several stations to transmit information over large distances. Although not adopted in Amontons lifetime, the ideas were later refined and put into use.

Kinetic Theory of Gases



Daniel Bernoulli (1700-1782)

Bernoulli studied medicine at the insistence of his father Johann Bernoulli, chair of mathematics in Basel Switzerland. However the younger bernoulli became interested in his father's theories of kinetic energy and even applied these theories to his doctoral dissertation on the mechanics of breathing. While practicing medicine in Venice, Bernoulli published his first mathematical work consisting of four separate parts: (1) Probability,(2) flow of water from a hole in a container, (3) the Riccati differential equation, and (4) a geometry question concerning figures bounded by two arcs of a circle. These paperswon him a position at the influential Academy of Sciences in St. Petersburg, Russia. At the academy Bernoulli lectured in medicine, mechanics, and physics. He developed what is nowcalledBernoulli's principle: The pressure in a fluid decreases as its velocity increases.

The modern kinetic molecular theory of gases essentially started with Bernoulli's suggestion in 1734 that the pressure exerted by a gas on the walls of its container is the sum of the many collisions by individual molecules, all moving independently of each other. Bernoulli derived the basic laws for the theory of gases and gave, although not in full detail, the equation of state discovered by van der Waals a century later.

Temperature Scale

Measurement of temperature has developed relatively recently in human history. The invention of the thermometer is generally credited to Galileo who developed the first known thermometer (1592) based on the expansion/contraction of air. German physicist Fahrenheit made a mercury thermometer (1714) ranging from the freezing of water (32°) to body temperature (96°). Swedish astronomer Celsius (1742) devised a scale ranging from the boiling of water (0°) to the freezing of water (100°)--this inverted scale (centigrade) gained widespread use and in 1948 the name was changed to Celsius. In 1848 British physicist William Thomson (Lord Kelvin) proposed a system using degree Celsius but starting at zero Kelvin (-273°C).

Charles' Law: $V_1T_2=V_2T_1$

Jacques Charles (1746-1823)

The physical principle known as Charles' Law states that the volume of a gas equals a constant value multiplied by its temperature as measured on the Kelvin scale. The law's name honors the pioneer balloonist Jacques Charles, who in 1787 did experiments on how the volume of gases depended on temperature. The irony is that Charles never published the work for which he is remembered, nor was he the first or last to make this discovery. In fact, Amontons had done the same sorts of experiments 100 years earlier, and it was Gay-Lussac in 1808 who made definitive measurements and published results showing thatevery gas he tested obeyed this generalization.

Law of Combining Volumes

Joseph Gay-Lussac (1778-1850)

Gay-Lussac carefully investigated the ratio of the volume of hydrogen gas that combined with a given volume of oxygen gas to form water. He found the oxygen could combine with exactly twice its own volume of hydrogen. There were similar simple volumetric ratios for other reactions between gases and if the product of the reaction was also a gas, it filled a volume simply related to those of the combining gases.

Gay-Lussac combined research with his passion of hot air balloons. Because nitrogen is lighter than oxygen, Gay-Lussac reasoned there might be proportionately less oxygen in the air at higher elevations. To find out, in 1802 he went up in a balloon to 23,000 feet (a record for 50 years). He found the proportions nearly the same.

Law of Partial Pressures: $P_T = P_1 + P_2 + P_3 + \cdots$

John Dalton (1766-1844)

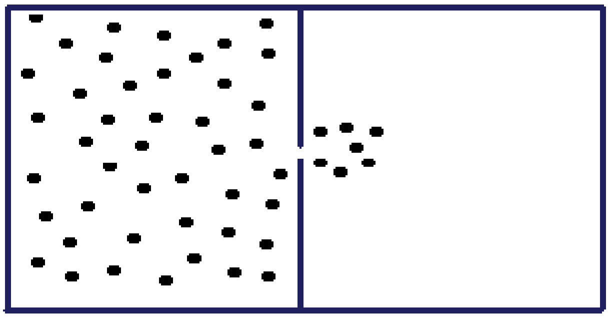
Dalton's law of partial pressures was stated by John Dalton in 1801: The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual component gases. The partial pressure is the pressure that each gas would exert if it alone occupied the volume of the mixture at the same temperature.

Avogadro's Principle

Amedeo Avogadro (1776-1856)

After practicing law for three years, Avogadro began to study mathematics and physics. Eventually he was appointed Professor of Natural Philosophy at the College of Vercelli. Based on the work of Gay-Lussac, all gases when subjected to an equal rise in temperature expand by the same amount, Avogadro published an article (1811) stating that at the same temperature and pressure, equal volumes of different gases contain the same number of molecules. The science community was not ready to accept such a radical idea and Avogadro's Principle went ignored for the next 50 years. Avogadro's work was finally recognized when countryman Stanisalo Cannizaro presented the work at a Conference in 1860. Today, one mole (6.022E23) is called Avogadro's number. At the time Avogadro's principle was becoming acceptable, Bernoulli's 1738 kinetic model of tiny gas molecules moving about in otherwise empty space was also reexamined; our modern view of gases began to emerge in 1860.

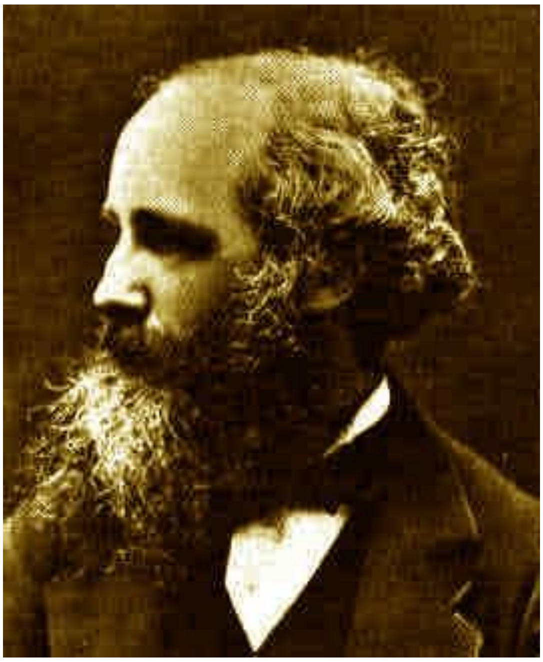
Graham's Law of Effusion: $\frac{u_1}{u_2} = \sqrt{\frac{m_2}{m_1}}$



Thomas Graham (1805-1869)

Graham was professor of chemistry at University College in London and later became Master of the Mint. He is best known for Graham's law (1846) which states that the rate of effusion of a gas is inversely proportional to the square root of its molecular weight. Graham also devised the technique known as dialysis to separate colloids from crystalloids and coined many of the terms used in colloid chemistry.

Molecular Speed: $u^2 = 3\frac{RT}{M}$



James Clerk Maxwell (1831-1879)
Maxwell treated gases statistically (1866) and formulated what has become known as the root-mean-square molecular equation ($u = [3RT/M]^{½}$). This represents a relationship between molecular mass, average speed, and temperature (R is the familiar gas constant). Because two gases with two different masses must have the same average kinetic energy at the sametemperature, the heavier gas molecules must possess lower average speed. On another front, Maxwell's mathematical equations expressing the behavior of electric and magnetic fields are considered one of great achievements of the 19th century.

Boltzmann Distribution

Ludwig Boltzmann (1844-1906)
The distribution of velocities among molecules of a gas was first developed by Maxwell (1859) and later generalized by Boltzmann (1871). The Maxwell-Boltzmann theory explained the gasl aws in terms of the motion of individual molecules. Previously it was assumed heat flowed from hot to cold. The Maxwell-Boltzmann theory treated molecules at high temperature as havinga high probability of moving toward those at low temperature. Consider the distribution of velocities for oxygen at 25°C shown in the figure: Boltzmann worked out a statistical approach to show more molecules moving at 400 m/s than at any other speed. This type of curve is called a Maxwell-Boltzmann distribution. All systems observed to date appear to obey the distribution law.

Van der Waals Equation: $(P + \frac{a}{V^2})(V-b) = RT$

Johannes van der Waals (1837-1923)
van der Waals began as an elementary school teacher (1856-1861) but continued with his studies of math and physics. At age 36 (1873) van der Waals obtained his doctorate and published the famous equation: $(P + a/V^2)(V-b) = RT$ [for a = b = 0, the equation becomes PV =RT] The equation considers the specific volume of gas molecules and predicts critical temperature for condensation. The equation also assumes a force (van der Waals forces) between molecules. In 1910 van der Waals awarded Nobel Prize for Physics.