**Handout Origins**

**Origins: Thermodynamic science in the making – The difficult birth of the law of energy conservation**

*Questions to keep in mind while reading:*

1. *Which of the earlier concepts have survived into the modern theory?*
2. *Which aspects of nature did the caloric theory explain successfully and how was it eventually falsified?*
3. *How did the scientific process work in the progression from early forms to the caloric theory, and on to the kinetic gas theory?*

The history of the Kinetic Theory of Gases begins in the 17th century when Torricelli, Pascal, and Boyle established the physical nature of the air. They persuaded other scientists that the earth is surrounded by a sea of gas that exerts a pressure and explained many phenomena previously accounted for by ‘nature abhors a vacuum’.

It was well known in the time of Galileo that water will not rise more

than 34 ft in a pump. His student Torricelli devised an experiment to

illustrate the effect in the laboratory. Since mercury is about 14 times

as dense as water, one might expect that it can be lifted only a 14th

times as much, and this is what is observed. Taking a yard long glass

tube, partially filled with mercury, and placing a finger to close one end

of it, the other being properly closed, and then inverting the tube, the mercury fell to about 30 inches

when the finger is removed. Between the top of the mercury column

and the end of the tube was an empty space, which became known as

Torricellian vacuum. According to Torricelli, it is just the mechanical

pressure of the air that raises the mercury in the tube.

Blaise Pascal then pointed out that by analogy the pressure of the air on a mountain top should be less than at sea level. An experiment was devised, which confirmed this prediction.

Robert Hooke devised a pneumatic engine for Robert Boyle, who devised experiments based on the laws of impact (collisions), which built the kinetic theory of billiard balls (atoms represented by elastic spheres). Boyle is credited with the discovery that the pressure exerted by a gas is inversely proportional to the volume in which the gas is confined. His main achievement was to introduce a new variable, pressure. Boyle also proposed a theoretical explanation of the elasticity of air (upon compression): The atoms are said to behave like springs, which resist compression. To a modern reader this seems hardly satisfactory. Boyle also tried the crucial experiment, which was some 200 years later responsible to overthrow his own theory in favor of the kinetic gas theory: A pendulum in an evacuated chamber shows hardly any difference in its period or in the time needed to come to rest than with air.

In 1859, Maxwell deduced from the kinetic theory that the viscosity of a gas should be independent of its density, a property difficult to explain based on Boyle’s theory. In Boyle’s own day, his work was criticized by Thomas Hobbes, who postulated a subtle matter filled space (the ether), a view that hampered the development of kinetic theory right up to the 20th century.

In the 18th century, Daniel Bernoulli formulated an early version of a kinetic theory as a billiard ball model, much like the ones in introductory texts today, involving the application of the principle of energy conservation, then often known as the *vis viva*, the living force. Bernoulli’s kinetic theory, which is in accord with modern views, was a century ahead of his time, when heat was still envisaged as a substance, not as atomic motion. Bernoulli’s assumption that heat was nothing but atomic motion was unacceptable, especially in the study of radiant heat. Bernoulli’s model neglected the drag of the ether and the interaction between atoms. The best that could be said about this theory was that it explained some properties of gases, which were already well understood anyway.

It was not possible for the kinetic theory to be fully accepted until the doctrine that heat is a substance, or *‘caloric’*, was overthrown. From the standpoint of the early 19th century scientists, there were many valid reasons to retain the caloric theory and to reject the mechanical theory (what we now call *thermodynamics*).

Caloric was a fluid composed of particles that repel each other but are attracted to the particles of ordinary matter. Caloric is able to diffuse into and penetrate the interstices of all matter, and each particle of matter is surrounded by an atmosphere of caloric whose density increases with temperature. These atmospheres cause two particles to repel each other at small distances (where the atmosphere reaches). At larger distances gravitational attraction dominates and there is thus an intermediate point of equilibrium. As the temperature rises more caloric is added to the substance, the equilibrium point shifts outward, and the average distance between particles becomes greater, causing a (thermal) expansion of the body. If the body is instead compressed, caloric is squeezed out and appears as heat. In this context, Black postulated the doctrines of latent and specific heats: He showed that various substances absorb different amounts of caloric (heat) when their temperature is raised by the same amount and that they require large amounts of heat to be added during the process of melting or vaporization. Thus, a clear distinction was made between caloric (heat) and temperature.

Opinions differed on the question: Does caloric have weight? The American Benjamin Thompson, later created Count Rumford, performed a series of experiments from which he concluded that the weight of caloric would be undetectable. This became one of his arguments against the caloric theory. Rumford also pointed out that an indefinite amount of heat can be produced from matter by doing mechanical work on it (hw 1), which is consistent with an energetic nature of heat, but not with a subtle particle one (caloric), because the particles would have to exhaust at some point.

The opponents of this view stated that heat could be transferred across a vacuum, as radiant heat, and this could only be achieved by particles (caloric). At this time, the history of this science adopted some national flavor: a French school stayed with the strict caloric view, the British school accepted the main idea of caloric but added Black’s discoveries, and an emerging German school would eventually diverge completely from the caloric view.

To illustrate how the caloric theory explained the properties of gases, I summarize the derivation of the gas laws by Pierre Simon, Marquis de Laplace (1825). Laplace is also known for his mathematical development of Newton’s theory of planetary motion and for his work on the theory of probability (which was mainly developed to appease rich benefactors with gambling problems). The kinetic theory of gases and statistical mechanics owe much to Laplace’s development of probability theory.

Denoting by c the amount of caloric in a molecule, Laplace assumed that two similar molecules at a distance r would repel each other with a force $F=H c^{2}ϕ\left(r\right)$. Where H is a constant and expresses the rapid decrease of the repelling force with distance.

The total pressure due to such forces becomes

 $P=2π H K ρ^{2}c^{2}$ where  is the density and K is the sum of all forces exerted on a given molecule by all the others.

It appears that the pressure is proportional to the square of the density, but observation yields that is scales linearly with . Laplace argued that the amount of caloric c must depend on density because each molecule is continually sending out and receiving rays of caloric. But the radiation of heat (caloric) by a molecule is regarded as being caused by the action of the caloric of the surrounding molecules on its own caloric , thus the amount of radiation is proportional to the density and the caloric of the surrounding gas, hence c, and to the caloric of the molecule considered, c. This quantity, proportional to c2, will have to be equal to the extinction at that temperature, since the system as a whole is supposed to be in thermal equilibrium. Combining these thoughts, we find that P ~  at constant temperature (Boyle’s law), and the ideal gas law follows immediately; if the temperature changes, the density changes in a ratio regardless of the nature of the gas (Gay-Lussac’s law).

The outstanding accomplishment of Laplace’s caloric theory is its explanation of adiabatic compression and of the velocity of sound: Laplace was able to show that PV stays constant in adiabatic compressions or expansions, where  is the ratio of specific heat at constant pressure to that at constant volume. By assuming that the propagation of sound involves adiabatic rather than isothermal compressions and rarefactions, Laplace derived a correction factor for the classical speed of sound ($\sqrt{γ}$) that held up to experiment. On the other hand, his theory predicts that specific heat should increase with decreasing pressure or density, which is not true. But experimental techniques did not allow for testing this at the time.

Petit and Dulong directed their attacks on the caloric theory on two accounts: the nature of heat and the atomic theory. Their experiments showed that the heats of reaction and changes in specific heat with temperature were not related and that in most cases the release of heat in a chemical reaction was not accompanied by an overall decrease in heat capacity. Another blow dealt to the caloric theory came by the growth of electrochemical theory. It took away the sole standing of caloric theory to explain chemical heat conceptually.

It took to wait for the decline of the influence of the Laplacian School before caloric theory could be put ad acta. Ampere, Dulong, and Fourier were eventually able to gain enough influence over Laplace’s and Poisson’s position.

In 1842 JR Mayer deduced that the heat produced by mechanical work is directly related to the amount of work performed; i.e. he treated heat like other energy terms. James Joule determined the relation between Joules of energy and calories of heat via friction of water, of mercury, and of cast iron to within 0.33% of the today accepted value. From that time on, the concept of caloric was mainly of historic value. The mechanical concept of heat is, of course, equivalent to heat being motion of particles (atoms).

Joule's experiment used a double mass Atwood machine to turn a spindle. The bottom of the spindle led through a water bath that was heated by multiple paddles that turned with the spindle. A ratchet was used to reset the masses without stirring the water. The amount of work performed is the loss of gravitational potential energy of the two falling masses. For the exact determination of Joules in terms of calories, Joule needed to apply corrections for the cooling of the calorimeter (water) by convection and radiation. With 20 repeated falls through 160.5 cm a temperature change of 0.3129 degrees was measured in some 26 kg of water by the use of a thermometer with an accuracy of 1:360 parts of a degree centigrade. He found 4.19 Joule per calorie.