Concept: Thermodynamics

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Keywords: First law, Second law, Entropy, Work, Energy, Heat

1. Definition

Thermodynamics relates heat to work and energy. In some ways it is a philosophical subject. It sets out three basic laws, none of which have closed-form proofs: they are all derived empirically, i.e., from experience.

1.1. Zeroth Law

The zeroth law of thermodynamics defines temperature as the degree of hotness, and the concept of thermal equilibrium. Objects are said to be at thermal equilibrium if they have the same degree of hotness, or temperature.

1.2. First Law

The first law of thermodynamics relates heat, internal energy and work. It sets out a book-keeping exercise, and specifies limits on the total internal energy of a system, and the amount of work that can be done by a system. It says that when heat is added to a system, or when work is done by the system, its internal energy rises or drops commensurately. This is used to define the limiting ideal efficiency of a heat engine. It shows that there is a limit to how much heat can be usefully converted to heat, because some is invariably left over as the internal energy of the system. Thus in the ideal Carnot Cycle, the efficiency is defined as the work output divided by the heat input, which in turn becomes the amount of heat that can be converted to work, divided by the total heat input. Again that translates to the ratio between two temperature differences. The numerator is the difference between the highest temperature in the engine (where work addition begins) and the temperature at the end of work output. The denominator is the highest temperature itself, denoting the absolute maximum heat of the system. This can be rewritten in a simple, approximate form:

$$\eta_t = \frac{T_3 - T_2}{T_3} \tag{1}$$

where η_t is the thermal efficiency, 3 and 2 refer to the beginning of work extraction, and the end of work extraction.

1.3. Second Law

The second law defines the concept of entropy, a measure of disorder. It defines a reversible process as one where the entropy does not rise, in other words, no losses have been incurred. The compression and extension of a spring is an example, although if done rapidly enough, the heat generated during the compression may be lost and not regained during the expansion. This leads to another idea: very rapid changes are generally irreversible. In general, reversible processes are gradual, whereas sudden, discontinuous changes generate losses, or entropy. The flow of heat from an object at higher temperature to one at a lower temperature, or through a temperature gradient, is irreversible, since it generates entropy. Natural or spontaneous processes are generally irreversible, and involve an increase of entropy. Thus the entropy of the Universe is predicted to increase continuously. Using the first and second laws, we can predict the limiting efficiency of a heat engine. The limiting efficiency of heat addition is when it is done with the minimum entropy rise possible, which is for a gradual heat transfer without a sharp gradient. All other losses in the process of generating useful work, such as friction, loss of heat through boundaries and any other departure from the ideal, are in addition to this minimum entropy rise. Thus the Second Law is often stated as an inequality rather than an equation:

$$ds \geq \frac{dq}{T} \tag{2}$$

where ds is the very small, or differential, rise in entropy caused by transfer of heat dq, at a temperature T. Why do we refer to only one temperature T, rather than the high and low temperature across which heat flows? The answer is that the heat transfer, to be ideal, must occur across essentially zero temperature difference.

The Second Law thus allows us to calculate ideal heat engine efficiency with the added reality that the entropy must increase during heat addition, no matter how slowly or carefully done. We can thus see that the optimistic prediction from the Carnot cycle above, is far above what can really be achieved, because one cannot hope to bring T_2 down to absolute zero, nor can we bring it down to the ambient temperature. Usually the limit is the outside ambient temperature. In this case the highest ideal efficiency becomes

$$\eta_t = \frac{T_3 - T_2}{T_3 - T_1} \tag{3}$$

where T_1 is the outside ambient temperature. Generally, T_2 cannot be higher than T_1, and is quite hot compared to T_1, with the rest of the heat wasted in dissipating to the outside. The implication is that the temperature at the end of useful work output is still higher than the outside ambient, but this remaining temperature difference is hard to exploit.

1.4. Enthalpy and Specific Heats

In aerospace applications especially, we usually deal with machines that work with fluids, mostly gases such as air. The temperature of a gas changes when its pressure and density change, even though the total heat contained inside is not different. Thus a better handle is needed, to describe the amount of heat contained in fluid. This is achieved using the idea of enthalpy (the letter h denotes the enthalpy per unit mass of the substance), which includes the internal energy (e is the internal energy per unit mass) of the molecules, the pressure p and the density ρ (or volume which is inversely proportional to density). In other words,

$$h = e + \frac{p}{\rho} \tag{4}$$

Enthalpy is convenient when we deal with chemical reactions, where we use the term "sensible enthalpy" to denote the part that can be sensed by its temperature, and the heat of formation, denoting the heat tied inside when the substance was formed from (or relative to) its basic elements, and the heat of reaction, denoting the heat released or absorbed when a reaction occurs.

Enthalpy is also convenient to express the idea that flowing fluids have a lot of their energy present as the kinetic energy of motion. Thus the stagnation enthalpy is defined as the value that enthalpy would reach when the flow is stopped, i.e., the speed U is brought to zero:

$$h_0 = h + \frac{U^2}{2} \tag{5}$$

From high school physics, we recognize the second term as the kinetic energy divided by mass, or the kinetic energy per unit pass. So in a sense, the above equation says that the total energy (described as heat) is the sum of the potential energy and the kinetic energy. In other words, the above equation is a statement of the physical law of Conservation of Energy, where there is no work being done or heat being transferred. It is also a statement of the first law of thermodynamics, because the kinetic energy is a form of work, and enthalpy denotes the total amount of energy in the system.

When heat is added to a system, its temperature rises. The amount of heat needed per unit rise in temperature, per unit mass of the system, is defined as the specific heat (as in high school science). In gases, the specific heat depends on how the heat is added: for a process occurring at constant volume, the specific heat c_v is lower than the value c_p is for a process occurring at constant pressure. The ratio of these two specific heats, usually denoted by the Greek letter γ, is 1.4 for the oxygen and nitrogen of air and other diatomic gases at usual temperatures, changing to 1.3 at the highest temperatures in a jet engine. For a monatomic gas, the value is 1.667.

2. Microscopic versus macroscopic thermodynamics

Thermodynamics was probably first developed to describe systems with substantial mass, such as heat engines. However, its roots can be examined starting from microscopic particles, at least from atoms. The sensible energy (outside of nuclear energy and forces) of a molecule is present in the kinetic energy of its movement (or translational kinetic energy), its rotation about axes passing through its center of mass, vibration of the atoms, electronic excitation above the ground level. In addition to these, energy is absorbed when a molecule dissociates into atoms (dissociation), or when an electron leaves an atom (ionization). Quantum theory tells us that the energy is quantized, that is, there are only a discrete number of different levels of energy, and discrete states that have the same energy level, that a particle can assume (think of a bus that can only travel at 5, 25 or 65 miles per hour, and turn corners at 3, 10, 30, 60 or 90 degrees per second!) Stepping up to the level of a packet of gas, which contains trillions of molecules, we can say that the energy of the gas is *partitioned* into translational, rotational, vibrational and electronic energy levels and states. This leads to the definition of Partition Functions for a gas at a given state of temperature and density. At any instant, if one were to take a 3-D photo of the whole gas packet, and could tell what every particle was doing (imagine a kindergarten class with the teacher out) we would be defining a micro-state of the gas. At the next instant at least one particle would have changed something, so we would see a different microstate. The total number of different micro-states in which a gas packet, or the contents of a given volume of gas, could find itself, is obviously a huge number. It can be found by multiplying all the Partition Functions together. This then is related to the total entropy (since entropy is a measure of disorder) of the gas system. Professor Boltzmann is credited with developing this relationship:

$$S = (k)(ln\Omega) \tag{6}$$

where S is the total entropy, a macroscopic quantity for the whole gas packet or system, k is appropriately called Boltzmann's constant, the ln denotes a natural logaritm (logarithm to base e) and Ω is the total number of possible microstates of the system. Apparently this equation is engraved on the tombstone of Professor Boltzmann. It represents the connection between the statistical descriptions of the microscopic properties of matter, to macroscopic thermodynamics.

3. Applications of Thermodynamics

Although the laws of thermodynamics appear to be observations of nature (and of human behavior), they are used in rigorous logical derivations that lead to quantitative analysis of gas dynamics, engine cycles, and chemical processes at all levels. The ideal thermal efficiency of a heat engine, and guidance for improving that efficiency, come from the first law.

In modern power plants, the work needed to generate electric power is extracted in several stages. A primary turbine operates on the Brayton Cycle, where hot, high pressure air or steam drives a turbine. This stage will recover the highest possible percentage of the heat given the pressure ratio and temperature, leaving the gas still quite hot. This is used to heat a secondary engine that generates some fraction of the heat, and then a tertiary stage. The remaining warm fluid is used to heat air for commercial or residential heating. Considering the monetary value of all these, power plants today can claim up to 90 percent efficiency, which is far above the ideal thermal efficiency of the primary turbine converter alone.

Power generators operated in Space can be quite efficient by the above considerations, since the side facing to deep Space sees a temperature of approximately 6 Kelvin. The side seeing the Sun experiences a great deal more heat, and even the side facing Earth, if in low Earth orbit, experiences around 193 Kelvins. However, systems in Space face the great difficulty that there is no air or other working fluid to just take in and throw out. A closed-cycle system must return the fluid to a fixed starting temperature which must be as low as possible. This requires dissipating the waste heat to the outside, and this can only be done by radiant heat transfer, since there is no large solid object (such as the ground) to conduct the heat away, nor flowing fluid (such as air or water) to convect the heat away. Radiator mass, and the mass of the active heat removal system, is thus a major concern, for spacecraft designers. Still, Space-based converters can be quite efficient.

The first law is also a statement of the conservation of energy. Where a process occurs with no increase in entropy, it is said to be *isentropic*. The relations between the properties of a gas undergoing an isentropic process are used extensively in aerodynamics and gas dynamics.

Obviously, the applications of thermodynamics are as numerous and endless as the number of microstates in a gas, and so could this discussion be endless. The curious learner is encouraged to venture into the many subject areas that use thermodynamics, armed with the above perspective.

4. References

(All errors in the above should be blamed on N. Komerath). 1. Vincenti, W.G. and Kruger, C.H., Introduction to Physical Gas Dynamics. Krieger Publishing Company, June 1975. 556p.

2. Hill, P. and Peterson, C., Mechanics and Thermodynamics of Propulsion. 2nd Edition, McGraw-Hill, 1991. 760p.

3. Denbigh, K., The Principles of Chemical Thermodynamics - Third Edition. Cambridge University Press, (1981) Cambridge, U.K. 520p.

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