

INTRODUCTION

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THERMODYNAMICS

WHAT IS IT

The aim of a course on Thermodynamics is to learn (for profit or pleasure) about natural and artificial thermal effects, from stone-age fire-care to present-day global-warming (in some 80 hours of a typical course teaching!).

Thermodynamics can be viewed as the science of heat and temperature, or the science of energy and entropy, or the science of energy assets (nothing disappears) and energy spreading (everything disperses). From another point of view, Thermodynamics is the science of how the myriads of microscopic degrees of freedom in a physical system can best be represented by a few macroscopic variables, and the relations it imposed amongst them, i.e. how one may describe infinitely-complex quantum-mechanical discrete systems, as simple-few-variables continuous-systems; as H.B. Callen said "Thermodynamics is the study of restrictions on the possible properties of matter that follows from the symmetry properties of the fundamental laws of physics".

Origins and relation to other subjects

The discipline of Thermodynamics originated in the 19th century from the study of heat engines and calorimetry. The first book on Thermodynamics was published in 1859 by William Rankine; the name Thermodynamics was introduced in 1850 by William Thomson (named Lord Kelvin in 1892), as the branch of Physics (together with Mechanics and Electromagnetism) dealing with the conservation of energy (established in 1842 by Mayer and Joule) and the theory of heat engines (initiated by Sadi Carnot in 1824); J. Willard Gibbs in 1883 completed the classical formulation of Thermodynamics with the analysis of general heterogeneous systems. <u>A historical review can be found aside</u>.

Physics is the science that models the behaviour of Nature by means of objective observation (measure), generalisation (theory) and experimentation (on purpose trials), with the goal of prediction, and not only description as in other natural sciences. Physics tries to find the mechanism of how bodies behave, whereas Chemistry tries to find the changes in the internal structure of matter when subjected to physical, chemical or nuclear processes (e.g. distillation, oxidation or disintegration, respectively). Biology may be viewed as the physical-chemistry of self-organised complex systems (living matter). Thermodynamics is key to all these sciences, but many disciplines are usually involved even in practical thermal problems: Mechanics, Electromagnetism, Fluid-dynamics, Kinetics and so on; there are not clear cuts in subject matter in practice (neither in theory): division by scientific discipline is a human problem-solving-approach to simplify and render tractable its study. The success of this scientific method is that, in spite of the crude simplifications introduced, the predictions it yields are impressively rewarding.

Thermodynamics should be <u>learnt</u> (in spite of the effort implied) because it is useful, challenging and appealing, providing insight into our world (science) and practical tools to modify it (engineering). Is it not defying to know that a CO_2 fire-extinguisher holds liquid- CO_2 , in spite of carbon-dioxide being a familiar gas (part of our normal exhalation, and of our common drinks), which exits as a solid mist when the extinguisher is used?

Thermodynamics may be viewed either as a science or as a technology, as most other applied-physics subjects, what might be stressed by using compound descriptors as 'Thermal Science and Technology' (in analogy to 'electrical science and technology', or 'materials science and technology'), or 'Thermal Engineering' (in analogy to 'electrical engineering', or 'materials engineering'), or simply 'Basic and Applied Thermodynamics', or 'Thermodynamics: fundamentals and applications'.

Applications

In the past, for the historical reasons mentioned above, Thermodynamics was restricted to the study of heat engines (the motive power of fire, literally following the seminal work of Carnot in 1824), to the extent of defining temperature based on heat-engine performance. Other well-known applications of fire (e.g. lighting, cooking, pottery, metallurgy) were not even mentioned (one might think because they are old applications, and that it is better to focus on present-day problems, but then, one should realise that present-day problems include global warming, combustion pollution, generation of synthetic fuels, industrial and domestic waste recovery and recycling, weather forecast, bioenergetics, and so on). A broad view of thermal applications is presented aside under <u>Thermal Systems</u>.

Thermodynamic applications are valuable services (heating, cooling, moving, demixing...), but not exempt of side problems and risks like any other technology. Leaving aside local safety risks like burns, frostbites, boiler explosions, toxic emissions, and so on, there are the global problems of global warming, and ozone depletion. Most thermal machines make use of harmful working fluids, not just air and water (e.g. think on the many pollutants contributed by cars, not only exhaust emissions, but fuel, oil, and refrigerant leakages; some 9% of the fluid charge in the air-conditioning system of a car is lost every year).

THERMAL EFFECTS

Greek prefix *therm* means heat (its causes and effects, its generation and usage), and Latin prefix *temper* means mixed (originally used for *'temperatura caeli'*, the sky combination).

Thermodynamics studies natural and artificial thermal effects. Some times, the word science is narrowly applied only to natural effects, and the word technology or engineering is narrowly applied only to artificial effects, but we here consider both types of effects as pertaining to science and to engineering, the difference being just on approach and not on scope.

Natural thermal effects may be briefly stated as "Every <u>isolated</u> system naturally evolves decreasing its ability to produce work". In particular, in an isolated system:

- Temperature differences tend to die out (by heat transfer).
- Velocity fields tend to rigid-body motion (by friction) at the macroscopic scale (with a well-defined everlasting molecular motion).
- Concentration and pressure fields tend to be piecewise uniform in absence of force fields.
- Energy tends to degrade so that work-inputs tend to become heat-outputs.

Artificial thermal effects may be briefly stated as "Every <u>isolated</u> system may be artificially forced to evolve against the natural tendency quoted above <u>if</u> an external source of energy (unbalanced universe) exists". In particular, in an isolated system (isolated except for the external forcing!):

- Temperature differences can be created (e.g. by friction, chemical reaction, or a heat pump).
- Velocity differences can be created (propulsion).
- Concentration and pressure differences can be created (e.g. mixture separation).
- Disordered energy, heat, can be converted to ordered energy, work, (e.g. heat engine).

Notice the extended usage here made of 'thermal effects' above, where it is not limited to 'temperature effects' or 'heat effects' but includes energies other than thermal energy and other equilibrium effects (e.g. the voltage from an electric battery is limited by thermodynamic laws, as well as osmotic pressure, mixture stratification in a gravity field, etc., to name a few). For instance, many people would say (including some learned persons), that the fact that moving bodies finally stop, and that fluids show the non-slip condition at walls, is because friction always works against motion, another fact of Nature (unrelated to Thermodynamics, they say); on the contrary, we include that fact here as another thermal effect (velocity fields tend to rigid-body motion). What is the final state after mixing some heavy water with the same amount of normal water? The answer is that a pure system of HDO molecules is formed, not a homogeneous mixture of H₂O and D₂O molecules, as can be checked by mass spectroscopy (this is an isotope-exchange chemical reaction taking place at room conditions).

Although only macroscopic variables will be used in what follows, it is of utmost importance to always remind ourselves of the microscopic nature of matter, evidenced by electron microscopy, X-ray diffraction, definite proportions in chemical reaction, Brownian motion, etc. Feynman said that the richest information-providing sentence in science is "matter is made of molecules that are made of atoms". For instance, if some tap water is dropped into a test-tube and closed, it is important to keep in mind that

water can be separated from air, salts from tap-water, oxygen from air, sodium from salt, electrons from sodium, and so on, and molecules from water and air are being exchanged continuously (macroscopic equilibrium corresponds to microscopic-balanced motion). Most material properties (thermal, mechanical, electrical and chemical) depend basically on the outer structure of the electron-cloud surrounding the nucleus. We are still far from understanding the behaviour of macroscopic systems (solid, liquid or gaseous) from simple microscopic models, but classical Thermodynamics skips through that by taking the macroscopic properties of matter as a given input, and restraining its objective to studying the relations between these properties, predicting the final state of a system when some internal or external restrictions are released, and computing the effect on the environment (input/output involved).

Natural and artificial thermal effects may be of interest to deal with heating/cooling loads, thermal expansion/contraction loads in mechanical systems, energy use/recovery, contamination/recycling, etc.

LEARNING THERMODYNAMICS

Should you embark in learning Thermodynamics? There is not such a thing as 'learning without effort', so that one should better pause at some point to consider if it is worth the effort (a general digression about why and how we learn, can be found aside).

If you feel you are not proficient in giving answers to the following questions (and if they are relevant to you, for business or for pleasure), you should get involved (offers are abundant, but none is free of effort).

- What is the difference between energy, heat, and temperature?
- Why air conditioners need some kind of hose to the outside environment?
- Why it is safer to pressurize a tank with water than with air?
- How can butane-gas be stored as a liquid in a bottle? How the liquid level changes with ambient temperature in a closed bottle?
- Does a fan heat or cool the environment. What is the purpose of a fan inside a refrigerator?
- Can air be liquefied? And stored as a solid?
- When two different liquids are mixed quickly, e.g. water and alcohol, what is conserved: mass, volume, temperature, or energy?
- At what temperature would water-vapour in the air get frozen?
- Could a fuel produce more work than its higher heating value?
- Why metals usually feel colder than wood?

TEACHING THERMODYNAMICS

Theoretical concepts and empirical laws

A science is identified by a set of own concepts and their relations. A Chinese proverb says 'The beginning of wisdom is to call things by their right names'. Of course, names are not the essence of things but just accepted labels we use to pack information; nevertheless, to avoid long descriptions like 'an alcoholic beverage made from the fermentation of grape juice", a 'wine' label is of great help, although not enough for an oenologist or a sommelier. The language of Thermodynamics has been developed as a need for a precise formal structure (the thermodynamic equations), by assigning a precise meaning to every concept, quite aside of the ambiguous colloquial language (e.g. hotness is related to temperature

and not to heat, heat is related to flow and not to content, clear distinction is made between energy, power and force, etc.). There are two caveats, however, that should not be forgotten when trying to be rigorous: 1) not even a science can be created from scratch and a previous 'common' meaning is assumed so that concepts like work, heat, energy, friction, equilibrium, temperature and so on, can be used before being formally defined; absolute precision in the language cannot exits (all dictionaries are tautological); and 2) not even an axiomatic science can elucidate every of its possible proposition (Gödel's Incompleteness Theorem, of 1931).

When teaching a science, care must be taken to remind the student of the empirical nature of all scientific theories; no Law of Nature is immutable. We, humans, construct these laws for our convenience in applying and transmitting what we know so far, but future research will surely make further progress and establish better theories, as we can see by looking back to the history of science. Of course, it does not mean that perpetual motion machines should be considered; as in the case of extraterrestrial beings, present evidence is against. Thermodynamics seems to be the sole science which has the last word on physical artefacts: any mechanical, electrical, optical, chemical or nuclear construction may seem plausible if it does not violate the First and Second Laws of Thermodynamics (the Zeroth and the Third Laws seem no so important; as in a typical meal, the second course is the main one, the first course follows in importance, and other minor dishes may be added as a dessert or starter).

Sometimes, new theories do not come from new findings but from a new look on the subject. An illustrative example may be borrowed from Mechanics: the Aristotelian theory that 'all motions tend to decay' (because there are forces opposing it), was superseded by the Newtonian theory that 'all motions tend to go on, if there is no force applied'; both theories seem identical, and the former may appear closer to common experience and simpler to teach, but the drag force is implicit in the former and explicit in the latter. Similarly, a child may grow with the belief that energy is created and lost (e.g. in a toy battery), but the theory that energy can be neither created not destroyed, better explains our present knowledge of the world. And there are other thermodynamic findings that may seem paradoxical to the non-initiated, and that require special attention, as why wood and iron in contact seem to be at different temperatures, why a negative thermal expansion coefficient does not violate any law of nature, why a liquid may be fully converted to its vapour without bubbling, why oxygen and nitrogen in the air are not segregated if they have different densities, etc.

Common symbols, universally accepted, are introduced for efficiency in communication: e.g. W is used for the work a system gets, not coming from the English 'work' but from the German 'werken', as imposed by tradition against other trials: L for the Latin 'labor' or T from the Latin 'tripaliare' and the French 'travail' and the Spanish 'trabajo'. Although a science should not be taught according to its chronological development but according to the present view of the subject, some obsolete language still permeates today, as when some authors use W for the work a system does, instead of the work it gets, or when talking about calories, frigoríes, therms, degrees centigrades, etc.

Besides this common language on the subject, some common physical and mathematical tools are also assumed (by the teacher) to be known (for the student), in order to follow the explanations, to solve thermodynamic problems and to carry out experimental work. We assume here an intermediate undergraduate level (i.e. at least a previous course on Physics, Chemistry and Mathematics, up to Differential Equations in some topics); in particular, the student is assumed to be fluent with the international system of units (SI), scientific notation, simple chemical formulation, differential calculus with several variables, and simple numerical methods (e.g. being able to solve $x^x=2$).

But <u>teaching</u> a science should not just aim at providing factual information on its own content: its vocabulary (e.g. difference between heat and temperature), and its equations (e.g. dU=TdS-pdV or $Q=W|_{Q=0}-W$). Teaching a physical science should not be superficial and descriptive; it must aim at providing reliable prediction skills, based on a core of unifying theory, with formal instruction to create and extrapolate rational models, not much dependent on particular contexts but in generic reasoning, i.e. developing a relational structure of the mind, memory indexing, searching and sorting, analysis and synthesis, <u>modelling</u>, input/output filtering, imagination..., to <u>solve new problems</u>.

The abstract concepts used in science, like here entropy and chemical potentials, may be seen arbitrarily defined, non-measurable and out of contact with reality, particularly to practical students on their first acquaintance, but the teacher should stress the economy of thought they provide, and show examples of their applicability, to progressively master them (it takes time). For instance, the ideal gas model should be presented as a the best substance-model in Thermodynamics: it is simple, it perfectly shows the coupling between mechanical effects and thermal effects, and it can be applied to natural and artificial processes in/with air, in spite of air not being a trivial substance (it is a gas mixture with suspended particles, more difficult to handle than liquids and solids); and it must be stressed that all concepts and equations in science, including all equations of state, are just models we invent to explain reality; none is 'exact'.

To feed-back the learning process, it is important to demonstrate that the invested effort is productive; particularly in engineering sciences (the author devotes some ³/₄ of the allotted lecture time 'to show how to solve problems', i.e. not to solve problems). And, to evaluate the skill-level acquired (not the effort spent), the author possess problems-to-be-solved (not mere exercises or theme compositions), as can be found in <u>Problems</u>. Notice finally that Thermodynamics is a science, and as such pursues generality, meaning that it should emphasise models of real systems (sketches), instead of actual equipment (pictures); e.g., a sketch of a car's engine is invaluable, whereas a factual photo is nearly irrelevant to understand its working (but serves to realise its relative location, size, interactions, and so on).

Thermodynamic systems

We know from infancy that the world is too complicated for us to analyze it all, and consequently we must narrow the spatial scope, the temporal span, and the level of detail pursued. A thermodynamic system is the region of space the observer selects for the analysis, distinguishing the interior (the system itself) from the surroundings or environment through a dividing frontier that can be impermeable to energy and matter (isolated system), or only to matter (closed system), or open to energy and mass (open system). Properties ascribed to a frontier may seem quite manageable, like impermeability, rigidity, or

total isolation, whereas other properties like semi-permeability or adiabaticity may seem more doubtful to realise; all of them, however, are idealizations.

The observer chooses for his convenience the thermodynamic system, as he chooses the coordinate system in mechanical problems. One may be interested in the system of energy levels associated to the electrons in a solid (e.g. to study semiconductors behaviour), in the system of the whole ecosphere of Earth (atmosphere, hydrosphere, lithosphere and biosphere, e.g. to study the global energy balance), etc. In any case, the observer renounces to the ultimate details of the system, not considering individual particles like electrons or atoms but an averaged blurred state of matter (a continuum, perhaps with some well-defined isolated discontinuities). Moreover, the observer in Thermodynamics renounces to consider spatial and temporal gradients in detail, and only deals with time-jumps in homogeneous systems, without regard of time rates of change (e.g. Heat Transfer deals with thermal-energy flow-rates and their associated temperature fields, Fluid Mechanics deals with momentum transfer and their associated velocity fields).

The typical thermodynamic system is a fluid contained within closed or open walls (solid), the two paradigms in engineering thermodynamics being the gas trapped within a cylinder-piston system, and the fluid that is at some time within a piece of flow-equipment: a pump, a pipe, a turbine, a heat exchanger, etc.

Besides the type of frontier, systems may be classified by the type of internal structure (gaseous, condensed, dispersed, multiphase). The study of Thermodynamics is usually divided accordingly in Thermodynamics of monophase-monocomponent systems, multiphase-monocomponent systems, multiphase-monocomponent systems.

The state of a system (at a given time) may be at equilibrium or not, the most important case in the latter instance being the steady state. The equilibrium states are by far the most important to study, because the analysis of non-equilibrium states rest upon the former. Notice, by the way, that thermodynamic equilibrium should only refer to 'static' equilibrium (although any macroscopic 'static' equilibrium corresponds to a dynamic equilibrium of its microscopic particles), and not to macroscopic steady states, as sometimes wrongly made.

The (time) evolution of a system is dictated by its non-equilibrium initial conditions and/or boundary conditions. Thermodynamic analysis usually restricts to the feasibility of a given process, the relation between end-states and input/output exchanges, the limit for these exchanges if the end-states are known, or the allowable states for given exchanges; but not considering the rate of change or the time needed, which is analysed in kinetic subjects as Heat Transfer, Fluid Mechanics and Chemical Kinetics. Time effects are thence coarsely modelled in Thermodynamics, just considering the limit of short times (where kinetic effects have no time to act and can be neglected), and the limit of long times (where kinetic effects have had all the time to conclude).

Besides narrowing the spatial scope of our system of interest, and simplifying so much the time constraints considered, the lack-of-detail modelling is essential to Thermodynamics: the science that studies myriad-degrees-of-freedom systems, with just a few key parameters (better explained in <u>Chapter</u> <u>2: Entropy</u>).

Although only macroscopic systems are here considered, it is of outmost importance to keep in mind that matter is made of atoms and molecules, some $d_0=10^{-10}$ m is size (macromolecules are much larger), separated by a distance $d \approx d_0$ in the solid or liquid state and by some $d \approx 10d_0$ for gases at room conditions, and colliding with other particles every 10^{-10} s (some 10^{-10} s between collisions in a gas like room air, some 10^{-12} s between rotation states, some 10^{-14} s between vibration states). Collisions (interactions in general) redistribute the energy and momentum of the molecules, and, if the interaction is strong enough, they can break molecules and form new molecules by rearranging the atoms and their electron clouds (atom nuclei are some 10^{-14} m in size, constituted by protons and neutrons some 10^{-15} m in size, and those by quarks some 10⁻¹⁹ m in size; electrons may be 10⁻¹⁸ m in size). Molecular interaction gives way to a highly repulsive force when $d < d_0$ (the apparent impenetrability of matter), and slightly attractive force when $d >> d_0$. All these forces are electromagnetic; the strong force only reaches some 10^{-14} m within the nucleus, and the gravitational force is 20 orders of magnitude smaller than the electromagnetic one (but it is accumulative and thus overrides in astronomical systems). Interaction between charged particles q and q' gives a force $\pm qq'/(4\pi\epsilon r^2)$; interaction between a charged q and an uncharged particle create a polarization dipole α and a force $-\alpha q^2/r^5$; interaction between two uncharged particles create a fluctuating and a force proportional to $-1/r^7$ (van der Waals' forces). For typical thermodynamic system there is no point in working to the 10^{-10} m and 10^{-10} s detail, as stated above, and macroscopic magnitudes are only used, with some of their values assumed to be empirical data (e.g. the density and thermal capacity of water are taken from experiments, instead of from the geometry, mass and energy interactions of its atoms).

Thermodynamic magnitudes

A magnitude is any quantifiable property of a system (we use magnitude, property and variable as synonyms). One key thermodynamic magnitude is temperature, *T*, and one key thermodynamic equation is dU=TdS- $pdV+\Sigma\mu idn_i$, which can be compared to a key mechanical magnitude time, *t*, and a key mechanical equation $md\vec{v}/dt = \vec{F}$. Putting it simply, time is chronology, i.e. the ordering of events according to a before and an after, and different interpretations may be ascribed to the magnitude mass, *m* (inertial mass, gravitational mass). Similarly, temperature is thermometry, i.e. the ordering of thermal states according to a cold and a hot, and different interpretations may be ascribed to the magnitude entropy, *S* (information contents, integration factor).

Before entering into details of the thermodynamic variables, the fact that physical magnitudes may span over many scales, depending on the problem, must be kept in mind. Temperature, e.g., may be near 0 K (cryogenics), near room temperature (refrigeration, air conditioning, comfort heating), typical of flames (some thousands of kelvins), typical of atomic plasmas (some millions of kelvins), or typical of nuclear plasmas (some billions of kelvins). A more general detail on <u>scales</u> can be found aside, as well as a review of <u>magnitudes</u>, units and measurement.

A traditionally difficult magnitude for beginners is pressure. Students know that pressure is the force exerted by a fluid per unit area, but quite often have doubts about its scalar or vectorial character, its units (it is not their fault, I am afraid), orders of magnitude (e.g. their local ambient pressure and its variation, the pressure at the two ends of their home taps, the pressure inside their gas lighters, liquid or gas pipelines, etc.), and they tend to forget the effect of ambient pressure. One reason for this state of confusion is that, contrary to temperature or even energy, pressure is not a frequently-used magnitude (except for the weather map, and they use altitude-corrected values and other intricate variations because their interest is on winds and not on pressure).

From the set of properties that may be assigned to a system (e.g. its mass, its density, its temperature, its entropy) only a few can be independently changed (only two, for simple compressible system of a given mass at rest), the others becoming functions of these variables, but because almost any combination in the set may be thought of, we use the term 'variable' to refer to both: variables and functions. Variables associated to a system may be classified in many ways: as extensive or intensive variables, as state or process variables, etc. Sometimes, variables are classified also as directly measurable, and non-directly-measurable (but computable from measurable ones); typical examples given are temperature and pressure for measurable, and energy and entropy for non-measurable. Obviously, there are thermometers and piezometers, and not energymeters or entropymeters; however, when one analyses the metrological problem in more detail (thermometry, piezometry), that distinction blurs.

Extensive variables are additive and would take a value *N*-times that of a system if *N*-replicas of it are considered (e.g. the mass, the volume, the energy, the entropy), whereas intensive variables take the same value when *N*-replicas of the system are considered (e.g. the density, the temperature, the coefficient of thermal expansion). Intensive variables derive from extensive variables by division (e.g. $\rho=m/V$, e=E/m) or differentiation (e.g. 1/T=dS/dU).

Thermodynamic processes

A process is a sequence of steps taking place (by natural or artificial forces) between two states of the system, called initial and final states, that may coincide and then the process is said to be cyclic (or steady if no time variation is apparent between the end states). Steady-state processes are the most common in engineering systems; cyclic processes are also analysed as a sequence of steady states.

A key point in thermodynamic modelling concerns the rate of a process, whose study lies outside Classical Thermodynamics (it is studied under Heat Transfer and Kinetics), and here it is stretched onto one of the two extremes: the assumption of negligible heat transfer in rapid processes, and the assumption of constant temperature in slow process.

State variables refer to a given instantaneous configuration of a system (e.g. its temperature or its relative energy in a given moment), whereas process variables refer to a given process path between two given states (that may coincide in a cyclic process): e.g. the work and heat transferred across the frontier are process variables (not state variables).

Introduction

Thermodynamic laboratory

To really grasp the subject of Thermodynamics, students have to do some key experimental work (to be set up adequately in a faculty lab, or at the home sink), in order to gain hands-on experience in preparation, execution analysis, and documentation, of experimental trials (i.e., the objective and methodology of experimentation), and to learn generic instrumentation and experimental techniques. An experiment is a purposely-executed trial which is set up, measured and compared with expectations.

<u>Laboratory work in Thermodynamics</u> may refer to measuring thermal state and process variables (e.g. temperature, heat, heat-rate, energy and entropy changes) or measuring thermal properties (e.g. thermal capacity, thermal expansion, thermal conductivity), or the temperature effect on other properties or processes (e.g. phase changes), and mainly use water and air as example working fluids.

The typical instruments are the ubiquitous <u>thermometers</u>, the <u>U-tube manometer and other pressure</u> <u>meters</u>, the balance, the test tube (to measure volumes and compute densities), and the clock (all thermodynamic processes are transient, in spite of thermodynamic emphasis on equilibrium).

Thermodynamic data

Thermodynamics may be used to calculate related materials data (as when vapour-pressure values are used to get boiling-enthalpy values), or to measure directly materials properties (boiling point, thermal capacity, thermal conductivity), sometimes with the goal of identifying a substance, but most thermodynamic problems aim at solving process problems, assuming that the materials properties are known. Finding relevant thermodynamic data is one of the toughest steps, when trying to solve a problem, but the answer is very simple: use the simplest appropriate model for the substances involved (although many times you only know if it is appropriate after solving the problem).

The two substance models most used in Thermodynamics are the perfect gas model (pV=mRT and $\Delta U=mc_v\Delta T$) and the perfect liquid or solid model (ρ =constant and $\Delta U=mc\Delta T$), to be studied in proper perspective later, but that may be assumed to be known from the start of this Thermodynamic course, to start with practical applications from the very beginning, which renders the effort more appealing.

Data needed to solve thermal problems may be generically grouped as:

- Statement of the problem. This information, except in academic exercises, always contains some data irrelevant to the thermal problem, and lacks some 'common' data tacitly assumed.
- Tacit data for all problems:
 - Universal physical constants (e.g. $R_u=8.314 \text{ J/(mol}\cdot\text{K})$).
 - Environmental constants to be assumed, unless modified in the statement:
 - Earth gravitation standard: $g_0=9.80665 \text{ m/s}^2 \approx 10 \text{ m/s}^2$.
 - Earth sea-level time-&-space averaged pressure standard: $p_0=100$ kPa (the old traditional value was 101.325 kPa).
 - Earth sea-level time-&-space averaged temperature standard: $T_0=288.15$ K=15 °C.
 - Initial state of the system in equilibrium with the environment.

• Material properties relevant to the problem (e.g. $c_{p,air}=1000 \text{ J/(kg·K)}$, $T_{b,water}=373 \text{ K}$). This information is usually assumed to be available to the user (in tables, charts, or databases), although uncommon problem-specific data may be provided in the statement. It is important, however, to keep in mind that there is no reliable method, in general, to predict the thermophysical properties of materials from first principles, particularly for natural materials like earth, wood, or food. Tabulated basic <u>data on simple gases</u>, liquids, and <u>solids</u>, can be found aside, as well as additional tables of coefficients for thermal capacity and vapour pressure correlations. Those tables, plus a few property diagrams (Mollier diagrams for water and for humid air, plus a couple of *p-h* diagrams for typical refrigerants, is all that is needed.

Besides all these data, solving problems requires some thermodynamic modelling: is the incompressible substance model good enough?; the ideal gas model, the constant thermal capacity model, the constant composition hypothesis, the equilibrium hypothesis, the adiabatic assumption,... are they appropriate? One of the main targets for the student is to learn the art of modelling.

TYPE OF PROBLEMS

<u>Solving problems</u> is a human need and one of the most rewarding human activities. Thermodynamic problems are always related to thermal effects, but can be as varied as its broad spectrum of applications: there are problems dealing with the states of matter and its variation with temperature, pressure and concentrations; with energy exchanges and energy availability (exergy), with processes in single components (pipes, valves, compressors, expanders, heat exchangers...), whole thermal systems (heat engines, refrigerators...), thermal effects on non-thermal systems, etc.

Some simple exercises are here presented; the student is supposed to know how to solve them from previous courses on Physics or Chemistry (detailed explanations are included anyway).

Exercise 1. Weighting the air within a vessel Exercise 2. Preparing a baby bath Exercise 3. Lessons to learn from a simple piston-cylinder configuration Exercise 4. A simple U-tube used to measure temperature and pressure

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