

LECTURE NOTES ON THERMODYNAMICS AND STATISTICAL PHYSICS

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LECTURE NOTES ON THERMODYNAMICS

LECTURE 1: INTRODUCTION

Content of Lecture 1

1.1. Some semantics

1.2. Historical milestones

1.3. Philosophy of science note

1.4. Some practical applications

1.5. Thermodynamics, statistical mechanics and kinetic theory

1.1. Some semantics

We introduce here classical thermodynamics. The word “thermo-dynamic,” used first by W.Thomson (Fig.1.1) has Greek origin and is translated as the combination of

- θερμη ´ , therme: heat, and
- δυναμις ´ , dynamis: power.



Fig 1.1. William Thomson (Lord Kelvin) (1824-1907) is the first man used the word “thermodynamic” in his 1849 work

The modifier “classical” is used to connote a description in which quantum mechanical effects, the molecular nature of matter, and the statistical nature of molecular behavior are not considered in any detail. These effects will not be completely ignored; however, they will be lumped into simple averaged models which are valid on the macroscale. As an example, for ordinary gases, our classical thermodynamics will be valid for systems whose characteristic length scale is larger than the mean free path between molecular collisions. For air at atmospheric density, this about $0.1 \mu\text{m}$ ($1 \mu\text{m} = 10^{-6} \text{m}$).

Additionally, “classical” also connotes a description in which the effects of finite timedependency are ignored. In this sense, thermodynamics resembles the field of statics from Newtonian mechanics. Recall Newton’s second law of motion,

$$m d^2 \vec{x} / dt^2 = \sum \vec{F} \quad (1.1)$$

where m is the mass, \vec{x} is the position vector, t is time, and \vec{F} is the force vector. In the statics limit where $\sum \vec{F} = 0$, inertial effects are ignored, as is time-dependency. Now, a Newtonian would consider dynamics to imply motion, and so would consider

thermodynamics to imply the time-dependent motion of heat. So a Newtonian would be more inclined to call the subject of these notes “thermostatics.” However, if we return to the earlier Greek translation of dynamics as power, we are actually truer to the classical connotation of thermodynamics. For the fundamental interplay of thermodynamics is that between so-called thermal energy (as might be thought of when considering heat) and mechanical energy (as might be thought of when considering power, a work rate).

- Thermodynamics: the science that deals with heat and work and those properties of matter that relate to heat and work.

One of the main goals of these notes will be to formalize the relationship between heat, work, and energy.

Fig 1.2. Greek philosopher Aristotle (384 BC-322 BC) gives the first recorded use of the word “energy” and whose method of logic permeates classical thermodynamics



We close this section by noting that the concept of energy has evolved through time, but has ancient origins. The word itself had its first recorded use by Aristotle (Fig 1.2). In the Greek, the word , ενεργεια , “energeia,” connotes activity or operation. While the word was known to Aristotle, its modern usage was not; it was the English polymath Thomas Young (Fig 1.3) who first used the word “energy,” consistent with any sort of modern usage, in this case kinetic energy. Finally, though she did not use the word “energy,” the notion of what is now known as kinetic energy being related to the square of velocity was first advanced by du Ch^atelet (Fig 1.4),

Fig 1.3. English natural philosopher Thomas Young (1773-1829)



Fig 1.4. French physicist Gabrielle Emilie Le Tonnelier de Breteuil, marquise du Chatelet



1.2. Historical milestones

Thermodynamics has a long history; unfortunately, it was not blessed with the crispness of development that mechanics realized with Newton. In fact, its growth is filled with false steps, errors, and debate which continues to this day. Some of the milestones of its development are given here:

- first century AD: Hero of Alexandria documents many early thermal engines.
- 1593: Galileo develops a water thermometer.
- 1650: Otto von Guericke designs and builds the first vacuum pump.
- 1662: Robert Boyle develops his law for isothermal ideal gases.
- 1679: Denis Papin develops his steam digester, forerunner to the steam engine.
- 1698: Thomas Savery patents an early steam engine.
- 1710: Thomas Newcomen creates a more practical steam engine.
- 1760s: Joseph Black develops calorimetry.
- 1780s: James Watt improves the steam engine.
- 1798: Benjamin Thompson (Count Rumford) considers the mechanical equivalent of heat from cannon boring experiments.
- 1824: Nicolas L'eonard Sadi Carnot discusses idealized heat engines.
- 1840: Germain Henri Hess considers an early version of the first law of thermodynamics for work-free chemical reactions.
- 1840s: Julius Robert von Mayer relates heat and work.

- 1840s: James Prescott Joule relates heat and work.
- 1847: Hermann von Helmholtz publishes his theory of energy conservation.
- 1848: William Thomson (Lord Kelvin) postulates an absolute zero of temperature.
- 1850: Rudolf Julius Emanuel Clausius formalizes the second law of thermodynamics.
- 1865: Clausius introduces the concept of entropy.
- 1871: James Clerk Maxwell develops the Maxwell relations.
- 1870s: Josiah Willard Gibbs further formalizes mathematical thermodynamics.
- 1870s: Maxwell and Ludwig Boltzmann develop statistical thermodynamics.
- 1889: Gibbs develops statistical mechanics, giving underlying foundations for classical and statistical thermodynamics.

Much development continued in the twentieth century, with pioneering work by Nobel laureates:

- Jacobus Henricus van't Hoff (1901),
- Johannes van der Waals (1910),
- Heike Kamerlingh Onnes (1913),
- Max Planck (1918),
- Walther Nernst (1920),
- Albert Einstein (1921),
- Erwin Schrödinger (1933),
- Enrico Fermi (1938),
- Percy Bridgman (1946),
- Lars Onsager (1968),
- Ilya Prigogine (1977), and

- Kenneth Wilson (1982).

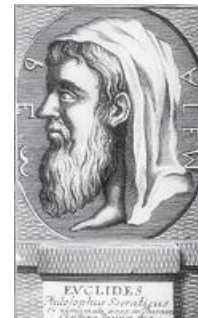
Note that Sir Isaac Newton also considered the subject matter of thermodynamics. Much of his work is concerned with energy; however, his theories are most appropriate only for mechanical energy. The notion that thermal energy existed and that it could be equivalent to mechanical energy was not part of Newtonian mechanics. Note however, that temperature was known to Newton, as was Boyle's law. However, when he tried to apply his theories to problems of thermodynamics, such as calculation of the speed of sound in air, they notably failed. The reason for the failure required consideration of the yet-to-be-developed second law of thermodynamics.

1.3. Philosophy of science note

As with science in general, thermodynamics is based on empirical observation. Moreover, it is important that those observations be repeatable. A few postulates, also known as axioms, will serve as the foundation of our science. Following Occam's razor, we shall seek as few axioms as possible to describe this behavior. We will supplement these axioms with some necessary definitions to describe nature. Then we shall use our reason to deduce from the axioms and definitions certain theorems of engineering relevance.

This approach, which has its foundations in Aristotelian methods, is not unlike the approach taken by Euclid to geometry, Aquinas to theology, or Newton to mechanics. Consider for example that Euclid (Fig 1.5) defined certain entities such as points, lines, and planes, then adopted certain axioms such as parallel lines do not meet at infinity, and went on to prove a variety of theorems. Classical thermodynamics follows the same approach. Concepts such as system and process are defined, and axioms, known as the laws of thermodynamics, are proposed in such a way that the minimum amount of theory is able to explain the maximum amount of data. Now, in some sense science can never be formally proved; it can

Fig 1.5. Greek mathematician Euclid of Alexandria (~325 BC--~265 BC) whose rational exposition of geometry formed a model for how to present classical thermodynamics



only be disproved. We retain our axioms as long as they are useful. When faced with empirical facts that unambiguously contradict our axioms, we are required to throw away our axioms and develop new ones. For example, in physics, the Michelson-Morely

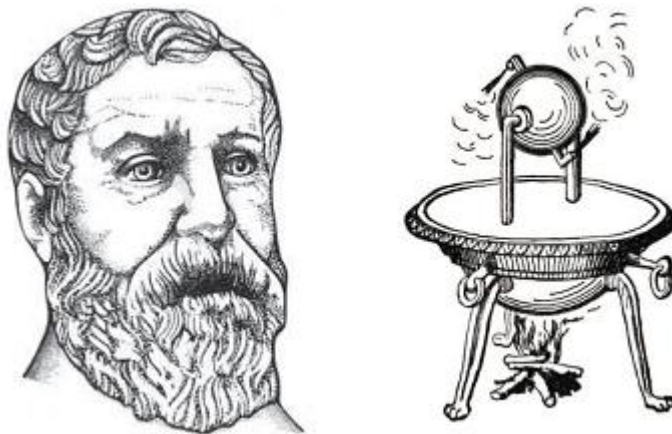
experiment forced Einstein to abandon the axioms of Euclid, Newton, and Clausius for his theory of general relativity. It turns out that we can still use these axioms, as long as we are considering problems in which the speed of our reference frame is far less than the speed of light. In an example from biology that is the topic of a popular science book, it was noted that it was once believed that all swans were white. This working hypothesis was perfectly acceptable until 1697, when a black swan was discovered in Australia. Thus, the “theory” (though it is not a highly profound theory) that all swans were white was unambiguously discredited. It will be briefly seen in this course that non-classical thermodynamics actually has a deep relation to probability and statistics and information, a topic which transcends thermodynamics.

1.4. Some practical applications

It turns out that the classical approach to thermodynamics has had success in guiding the engineering of devices. People have been building mechanical devices based on thermal energy inputs for centuries, without the benefit of a cleanly enunciated theory. Famously, Hero of Alexandria, perhaps the first recognized thermal engineer, documented a variety of devices. These include an early steam engine known as the *æolipile*, pumps, and a device to use fire to open doors. Hero and a nineteenth century rendition of his steam engine are shown in Fig 1.6. While Hero’s contributions are a matter of some speculation inspired by ancient artistry, the much later works of Denis Papin (1647-1712) are more certain. Papin invented the so-called steam digester, which anticipated both the pressure cooker and the steam engine. The device used steam power to lift a weight. Depictions of Papin and his device are found in Fig 1.7. Significant improvements were led by James Watt (1736-1819) of Scotland. An image of Watt and one of his engines is shown in Fig 1.8.

These engines were adopted for transportation. In 1807, the American engineer Robert Fulton (1765-1815) was the first to use steam power in a commercial nautical vessel, the *Clermont*, which was powered by a Boulton and Watt steam

Fig 1.6. Hero of Alexandria (10-70AB), Greek engineer and mathematician who devised some early ways to convert thermal energy into mechanical energy



and his æolipile

Fig 1.7. French-born inventor Denis Papin (1647-1712) and his steam digester

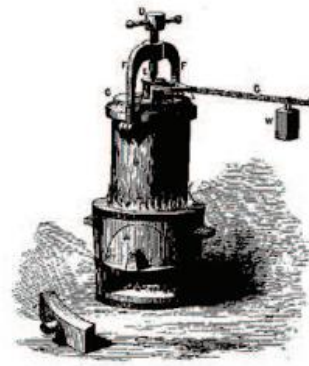
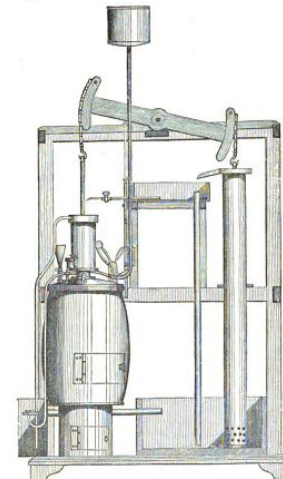


Fig 1.8. a) Scottish engineer James Watt (1736-1819); b) Sketch of one of Watt's steam engines



a)



b)

engine. Soon after, in 1811 in Scotland, the first European commercial steam vessel, the Comet, embarked. We have a sketch of the Comet and its steam power plant in Fig 1.9. On land, steam power soon enabled efficient rail transportation. A famous early steam locomotive was the English engineer Robert Stephenson's (1803-1859) Rocket, sketched in Fig 1.10.

Fig 1.9. Sketch of the Comet and its steam engine

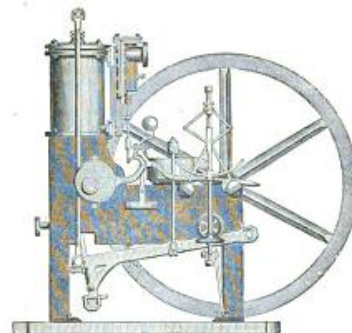
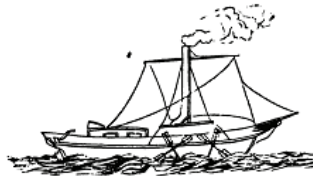
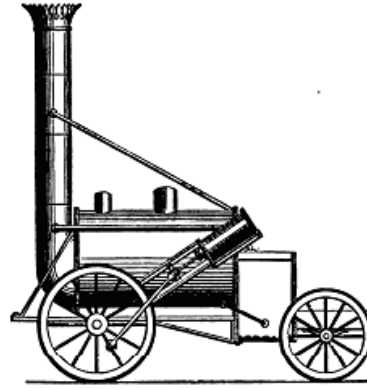


Fig 1.10. Sketch of the Rocket



The effect of steam power, a contribution driven by engineers, on the development of the world remains remarkable. It is what is commonly known as a disruptive technology as its widespread adoption displaced other well-established technologies. While it is difficult to quantify historical pronouncements, it is likely that the effect on the world was even more profound than the introduction of networked computers in the late twentieth century. In short, steam power was the linchpin for the industrial revolution. Steam power replaced animal power as a prime mover throughout much of the world and, where implemented, enabled rapid development of broad economic segments: mining, manufacturing, land and sea transportation, among others. Large scale population movements ensued as opportunities in urban manufacturing centers made industrial work more appealing than agricultural work. Certainly, changes precipitated by the advent of steam power were contributing factors in widespread social unrest in the nineteenth century, ranging from labor strife to war between nation states.

The text of BS has an introduction to some more modern devices, listed here:

- simple steam power plant,
- fuel cells,
- vapor-compression refrigeration cycle,
- air separation plant,
- the gas turbine, and
- the chemical rocket engine

Additionally, one might consider the following topics to have thermodynamic relevance:

- gasoline and Diesel engines,
- the weather,

- cooking,
- heating, ventilation, air conditioning, and refrigeration (HVAC&R), or
- materials processing (metals, polymers, etc.)

We close with an image of Sir Isaac Newton in Fig 1.11, who began to study issues related to thermodynamics and whose scientific methods imbue its development.

Fig 1.11. English genius Sir Isaac Newton (1643-1727) whose classical mechanics broadly influenced the development of thermodynamics



1.5. Thermodynamics, statistical mechanics and kinetic theory

From experience, we know that a macroscopic body generally settles down, or “relaxes” to a stationary state after a short time. We call this a state of thermal equilibrium. When the external condition is changed, the existing equilibrium state will change, and, after a relatively short relaxation time, settles down to another equilibrium state. Thus, a macroscopic body spends most of the time in some state of equilibrium, punctuated by almost sudden transitions. In our study of macroscopic phenomena, we divide the subject roughly under the following headings:

- Thermodynamics is a phenomenological theory of equilibrium states and transitions among them.
- Statistical mechanics is concerned with deducing the thermodynamic properties of a macroscopic system from its microscopic structure.
- Kinetic theory aims at a microscopic description of the transition process between equilibrium states.

The theoretical description of systems consisting of very many particles is the center of interest in this volume of the series of lessons in *Theoretical Physics*. Such many-particle systems can be found everywhere in nature: on the one hand, e.g., the atoms and molecules in gases, fluids, solids or plasmas (with most of which one has daily experience) or on the other hand, the quantum gas of electrons in semiconductors or metals.

In burnt-out suns (white dwarfs) one finds the electron gas and nuclear matter (in the center of neutron stars and in supernova explosions), which consists of many neutrons and protons. Our universe was created in the “big bang” from a many-particle system of leptons, quarks and gluons.

In the following we will see that all these completely different systems obey common and very general physical laws. In particular, we will discuss the properties of such many-particle systems in thermodynamic equilibrium. Special emphasis will be laid on the microscopic point of view of statistical mechanics. Nevertheless, classical macroscopic thermodynamics shall not fall short, since it is of great importance: the concepts of thermodynamics are very general and to a great extent independent of special physical models, so that they are applicable in many fields of physics and the technical sciences.

The task of thermodynamics is to define appropriate physical quantities (the *state quantities*), which characterize macroscopic properties of matter, the so-called *macrostate*, in a way which is as unambiguous as possible, and to relate these quantities by means of universally valid equations (the *equations of state* and the *laws of thermodynamics*).

Thermodynamics:

- Describes macroscopic properties of equilibrium systems
- Entirely Empirical
- Built on 4 Laws and "simple" mathematics

0th Law ⇒ Defines Temperature (T)

1st Law ⇒ Defines Energy (U)

2nd Law ⇒ Defines Entropy (S)

3rd Law ⇒ Gives Numerical Value to Entropy

These laws are UNIVERSALLY VALID, they cannot be circumvented.

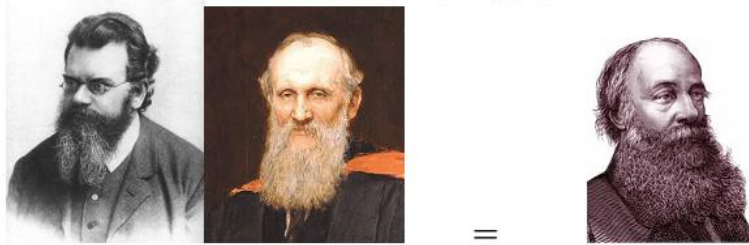
Thermo : heat
dynamics : motion

Thermodynamics is the study of motion of heat.

- Thermodynamics is about MACROSCOPIC properties.

A beardy equation

For each degree of freedom
Boltzmann's * Kelvins = Joules



Thermodynamic equilibrium, ideal gas and kinetic energy "Temperatures" are *the same thing*

Fig 1.12.

Thermodynamics allows you to learn

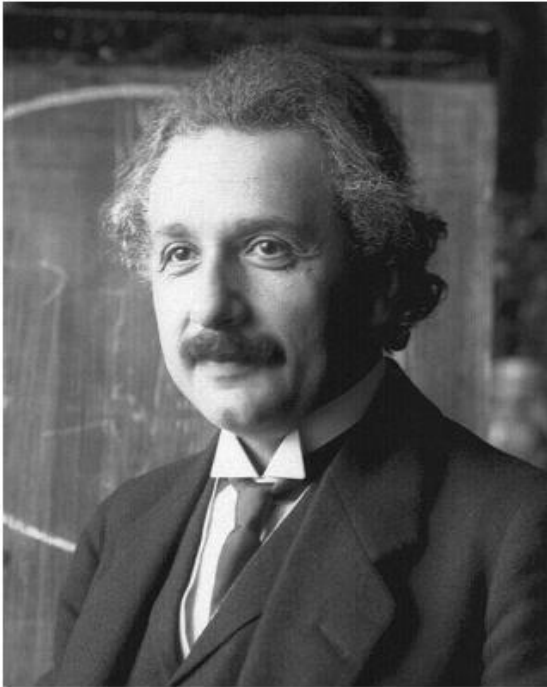


Only thermodynamics breaks time-reversal symmetry.
(strictly CPT(i))



Thermodynamics
drove the modern
world

Einstein's Opinion



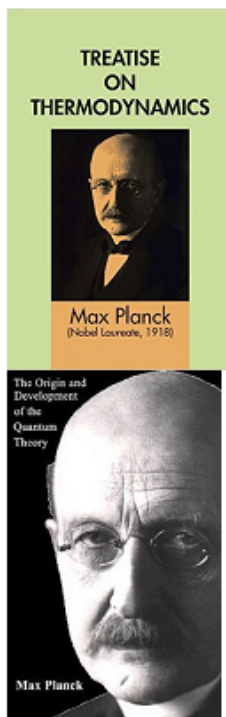
Thermodynamics is the only physical theory of universal content which I am convinced, within the areas of applicability of its basic concepts, will never be overthrown.

A. Einstein 1949



Fig 1.13

How Planck discovered his law of black-body radiation



I had no alternative but to tackle the problem again ... from the side of thermodynamics. In fact, my previous studies of the Second Law of Thermodynamics came to stand me in good stead now, for at the very outset I hit upon the idea of correlating not the temperature of the oscillator but its entropy with the energy... While a host of outstanding physicists worked on the problem of the spectral energy distribution both from the experimental and theoretical aspect, every one of them directed his efforts solely towards exhibiting the dependence of the intensity of radiation on the temperature. On the other hand, I suspected that the fundamental connection lies in the dependence of entropy with the energy ... Nobody paid any attention to the method which I adopted and I could work out by calculations completely at my leisure, with absolute thoroughness, without fear of interference or competition.

Fig 1.14

LECTURE 2: SOME CONCEPTS AND DEFINITIONS

Content of Lecture 2

2.1. Thermodynamic system and control volume

2.2. Macroscopic versus microscopic

2.3. Properties and state of a substance

2.4. Processes and cycles

2.5. Fundamental variables and units

2.6. Zeroth law of thermodynamics

2.7. Secondary variables and units

2.1. Thermodynamic system and control volume

We take the following definitions:

- **THERMODYNAMIC SYSTEM:** a quantity of fixed mass under investigation,
- **SURROUNDINGS:** everything external to the system,
- **SYSTEM BOUNDARY:** interface separating system and surroundings, and
- **UNIVERSE:** combination of system and surroundings.

The system, surroundings, system-boundary for a universe are shown for a potato-shaped system in Fig. [2.1](#). We allow two important interactions between the system and its surroundings:

- heat can cross into the system (our potato can get hot), and
- work can cross out of the system (our potato can expand).

Now, the system boundaries can change, for example the potato might expand on heating, but we can still distinguish the system and the surroundings. We now define an

- **ISOLATED SYSTEM:** a system which is not influenced by its surroundings.

Note that a potato with thick and inelastic skin will be isolated. We distinguish the system, which has constant mass, but possible variable volume, from the

- **CONTROL VOLUME:** fixed volume over which mass can pass in and out of its boundary.

The control volume is bounded by the

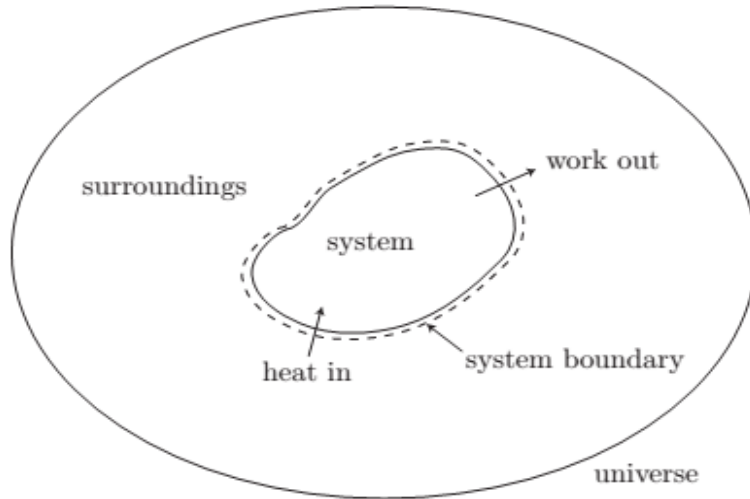


Figure 2.1: Sketch of a universe composed of a system, its surroundings, and the system boundary.

- **CONTROL SURFACE:** boundary of the control volume.

The mass within a control volume may or may not be constant. If there is fluid flow in and out there may or may not be accumulation of mass within the control volume. We will mainly study cases in which there is no accumulation, but this need not be the case. A sketch contrasting scenarios in which a fluid is compressed in which the system approach would be used against those where the control volume approach would be used is shown in Fig. 2.2 In summary,

- system \rightarrow fixed mass, closed, and
- control volume \rightarrow potentially variable mass, open.

2.2. Macroscopic versus microscopic

In principle, we could solve for the forces acting on every molecule and use Newton's laws to determine the behavior of systems. This is difficult for even modestly sized systems.

- If we had a volume of 1 m^3 of gas at atmospheric pressure and temperature, we would find that it was composed of 2.4×10^{25} molecules.
- We would need six equations of motion for each molecule, three for x, y, z , position, and three for u, v, w velocity. This would require then a total of 1.4×10^{26} differential equations to solve simultaneously.

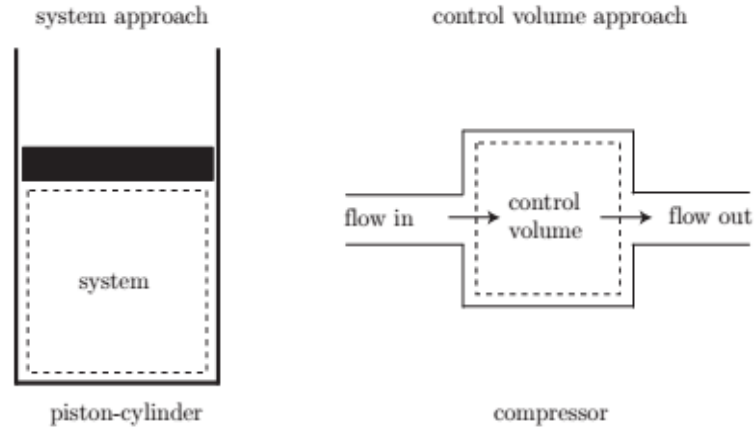


Figure 2.2: Comparison of system (fixed mass) and control volume (fixed volume) approaches in thermodynamics for two common scenarios: piston-cylinder compression (left) and compression in a flow device whose details are not shown (right).

- Even with our largest computers, this is impossible today. Note most desktop computers only can store roughly 10^9 bytes of data in Random Access Memory (RAM).
- We can however model the average behavior of the molecules statistically.
- We can also use simple empirical relations which can be formally proved to capture the statistical nature of the flow. This will be our approach.
- classical thermodynamics will treat macroscopic effects only and ignore individual molecular effects. For example molecules bouncing off a wall exchange momentum with the wall and induce pressure. We could use Newtonian mechanics for each particle collision to calculate the net force on the wall. Instead our approach amounts to considering the *average* over space and time of the net effect of millions of collisions on a wall.

We will in fact assume that matter can be modelled as a

- **CONTINUUM:** the limit in which discrete changes from molecule to molecule can be ignored and distances and times over which we are concerned are much larger than those of the molecular scale. This will enable the use of calculus in our continuum thermodynamics.

The continuum theory can break down in important applications where the length and time scales are of comparable magnitude to molecular time scales. Important applications where the continuum assumption breaks down include

- rarefied gas dynamics of the outer atmosphere (relevant for low orbit space vehicles), and

- nano-scale heat transfer (relevant in cooling of computer chips).

To get some idea of the scales involved, we note that for air at atmospheric pressure and temperature that the time and distance between molecular collisions provide the limits of the continuum. Under these conditions, we find for air

- length $> 0.1 \mu m$, and
- time $> 0.1 ns$,

will be sufficient to use the continuum assumption. For denser gases, these cutoff scales are smaller. For lighter gases, these cutoff scales are larger. Details of collision theory can be found in advanced texts such as that of Vincenti and Kruger¹. They show for air that the mean free path λ is well modeled by the following equation:

$$\lambda = \frac{M}{\sqrt{2}\pi N \rho d^2}. \quad (2.1)$$

Here, M is the molecular mass, N is Avogadro's number, and d is the molecular diameter.

2.3. Properties and state of a substance

We define

- **PHASE:** a quantity of matter that is homogeneous throughout, and
- **PHASE BOUNDARIES:** interfaces between different phases.

An example of a single phase is ice. Another single phase is liquid water. A glass of ice water is a two-phase mixture with the phase boundaries at the edge of each ice cube.

We next define (circularly)

- **STATE:** condition described by observable macroscopic properties, and
- **PROPERTY:** quantity which only depends on the state of the system and is independent of the history of the system.

Examples of properties include temperature and pressure. Two states are equivalent if they have the same properties. So if state 1 is defined by temperature T_1 and pressure P_1 , and state 2 is defined is by temperature T_2 and P_2 , state 1 is equivalent to state 2 iff (that is, *if and only if*) $T_1 = T_2$ and $P_1 = P_2$.

There are two important classes of properties we consider in thermodynamics:

- **EXTENSIVE PROPERTY:** a property which depends on the mass (or the *extent*) of the system, example extensive properties include mass, total volume, total energy, and
- **INTENSIVE PROPERTY:** a property which is independent of the mass of the system. Example intensive properties include temperature and pressure.

In general, if you cut a system in half and re-measure its properties, intensive properties remain unchanged, while extensive properties are cut in half. Properties are defined for systems which are in

- **EQUILIBRIUM:** state in which no spontaneous changes are observed with respect to time.

We actually never totally achieve equilibrium, we only approximate it. It takes infinite time to achieve final equilibrium. In this class we will mainly be concerned with two types of equilibrium:

- **MECHANICAL EQUILIBRIUM:** characterized by equal pressure, and
- **THERMAL EQUILIBRIUM:** characterized by equal temperature.

A third type of equilibrium is chemical equilibrium, which we will not consider here, and is characterized by equal chemical potentials.

A difficult conceptual challenge of thermodynamics is to reckon with two systems initially at their own equilibria, to bring them into contact so that they find a new equilibria. How to do this without consideration of time can be difficult. Another branch of thermodynamics, which we will consider only briefly in this course is

- **NON-EQUILIBRIUM THERMODYNAMICS:** branch of thermodynamics which considers systems often far from equilibrium and the time-dynamics of their path to equilibrium.

We will go to great effort to construct a thermodynamics which is generally not burdened with time. Occasionally we will bring time into our problems. Unfortunately, ignoring time occasionally requires some mental contortions, as seen in the next section.

2.4. Processes and cycles

Often systems undergo a

- **CHANGE OF STATE:** implies one or more properties of the system has changed.

How these properties would change outside of time is curiously outside the framework of equilibrium thermodynamics! The best way to think of them is that the changes are slow relative to the underlying molecular time scales. Fortunately, this will allow us to do a wide variety of problems of engineering relevance.

We also define a

- PROCESS: a succession of changes of state.

We assume our processes are all sufficiently slow such that each stage of the process is near equilibrium. Certain common processes are given special names, based on the Greek *ἴσος*, *isos*, meaning “equal”:

- ISOTHERMAL: constant temperature,
- ISOBARIC: constant pressure, and
- ISOCHORIC: constant volume.

An important notion in thermodynamics is that of a

- CYCLE: series of processes which returns to the original state.

The cycle is a thermodynamic “round trip.”

2.5. Fundamental variables and units

We will mainly use the *Système International* (SI) units in this course. Occasionally, we will use the English Engineering system of units. As found in US National Institute of Standards and Technology (NIST) documents, the important fundamental base SI units, and corresponding English units are

- MASS:
 - KILOGRAM (*kg*): a mass equal to the mass of the international prototype of the kilogram (a platinum-iridium bar stored in Paris), roughly equal to the mass of one liter of water at standard temperature and pressure, and
 - POUND MASS: (*lbm*),
- LENGTH:
 - METER (*m*): the length of the path traveled by light in vacuum during a time interval of $1/299792458$ of a second, and
 - FOOT (*ft*),
- TIME:
 - SECOND: (*s*) the duration of 9192631770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom, and
 - SECOND: (*s*) English time units are identical to those of SI,

- **TEMPERATURE:** an equilibrium property which roughly measures how hot or cold an object is. Note our senses are poor judges of temperature. Consider snow and air in thermal equilibrium at $20\text{ }^{\circ}F$. Usually, it is possible to keep your bare hands warm for many hours at $20\text{ }^{\circ}F$ if you are otherwise dressed warmly. However, if you place your bare hand in a snow bank you for a few minutes, you have a danger of frostbite. Yet both are at the same temperature. Why the difference in sense? Our bodies actually have more sensitivity to heat fluxes instead of temperature; heat leaves our body more rapidly when in contact with high density objects like snow relative to that of low density objects like air. More fundamental than common units such as $^{\circ}F$ are so-called absolute temperature units:
 - **KELVIN:** (K) the fraction $1/273.16$ of the thermodynamic temperature of the triple point of water, and
 - **RANKINE:** ($^{\circ}R$).

2.6. Zeroth law of thermodynamics

In this class we are taking the axiomatic approach. Recall that an axiom cannot be proven. It is a statement whose truth can be ascertained only by comparison with experiment. The axiom can be disproved by a single negative experiment. The so-called zeroth law of thermodynamics is the axiom which is probably most fundamental. It was formalized after the so-called first and second laws, and so it is called the zeroth law. Perhaps if a more fundamental axiom were discovered, it would be called the -1^{st} law of thermodynamics?

- **ZEROTH LAW OF THERMODYNAMICS:** When two bodies have equality of temperature with a third body, then they have equality of temperature.

The origins of the zeroth law are murky. Sommerfeld² attributes the notion to R. H. Fowler in a 1931 review of a thermodynamics book. Fowler and Guggenheim explicitly introduce the term “zeroth law of thermodynamics” later³. The equivalent statement in mathematical logic is that if $x = y$ and $x = z$, then $y = z$; this is in fact equivalent to the first of Euclid’s common notions: things that are equal to the same thing are also equal to each other.

Definition of the zeroth law enables the use of a thermometer as a measurement device. A scale however needs to be defined. The old metric temperature scale, Celsius ($^{\circ}C$), was defined so that

- $0\text{ }^{\circ}C$ is the freezing point of water, and
- $100\text{ }^{\circ}C$ is the boiling point of water.

These quantities varied with pressure however, so that different values would be obtained on top of a mountain versus down in the valley, and so this is not a good standard. The modern Celsius scale is defined to be nearly the same, but has

- $0.01\text{ }^{\circ}\text{C}$ as the so-called triple point of water, and
- $-273.15\text{ }^{\circ}\text{C}$ as absolute zero in K .

The triple point of water is defined at the state where three phase of water (solid, liquid, and gas) are observed to co-exist. The transformation between the absolute Kelvin scale and the Celsius scale is given by

$$K = \text{ }^{\circ}\text{C} + 273.15. \quad (2.9)$$

The English equivalents are degrees Fahrenheit ($^{\circ}\text{F}$) for relative temperature and degrees Rankine ($^{\circ}\text{R}$) for absolute temperature. The conversions are

$$T(^{\circ}\text{R}) = 1.8T(K), \quad T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32, \quad T(^{\circ}\text{F}) = T(^{\circ}\text{R}) - 459.67. \quad (2.10)$$

2.7. Secondary variables and units

Many units can be derived from the base units. Some important units for thermodynamics include

- **FORCE:** This unit is defined from Newton's second law, $m\,d^2y/dt^2 = \sum F$.
 - **NEWTON:** (N), $1\,N = 1\,\frac{kg\,m}{s^2}$, and
 - **POUND FORCE:** (lbf).

Force is straightforward in SI units. It is more confusing in English units, where the so-called gravitational constant g_c is often introduced. In SI units, $g_c = 1$. However in English units, the law for force is better stated as

$$\frac{1}{g_c}m\frac{d^2y}{dt^2} = \sum F. \quad (2.11)$$

Moreover, a gravitational body force is better stated as mg/g_c in English units. Now, $1\,lbf$ is induced by a mass of $1\,lbm$ in places where local gravitational acceleration is $g = 32.1740\,ft/s^2$. Let us consider two important types of problems

- *acceleration of a particle in a uniform gravitational field*: Here the only force acting on the particle is the body force, $-mg/g_c$, and Eq. (2.11) reduces to

$$\frac{1}{g_c} m \frac{d^2 y}{dt^2} = -\frac{mg}{g_c}, \quad (2.12)$$

$$\frac{d^2 y}{dt^2} = -g, \quad (2.13)$$

$$\frac{dy}{dt} = -gt + C_1, \quad (2.14)$$

$$y = -\frac{1}{2}gt^2 + C_1t + C_2. \quad (2.15)$$

Note that g_c plays no role whatsoever in determining the position of the particle.

- *static force balance*: Here one wants to determine the force necessary to hold a particle stationary in a uniform gravitational field. In such a problem the acceleration is zero, but there are two forces, the gravitational force $-mg/g_c$, and the counter-balancing force which we will call F . Eq. (2.11) reduces to

$$\frac{1}{g_c} m \underbrace{\frac{d^2 y}{dt^2}}_{=0} = F - \frac{mg}{g_c}, \quad (2.16)$$

$$0 = F - \frac{mg}{g_c}, \quad (2.17)$$

$$F = \frac{mg}{g_c}. \quad (2.18)$$

If we are at a location where $g = 32.1740 \text{ ft/s}^2$, we can consider the counter-balancing force necessary to hold 1 *lbm* stationary, via Eq. (2.18):

$$F = 1 \text{ lbf} = \frac{(1 \text{ lbm}) (32.1740 \frac{\text{ft}}{\text{s}^2})}{g_c}. \quad (2.19)$$

Thus,

$$g_c = 32.1740 \frac{\text{lbm ft}}{\text{lbf s}^2}. \quad (2.20)$$

- **ENERGY**: roughly speaking, the ability to do work, found from the product of force and distance.
 - **JOULE**: (J), $1 J = 1 (N m)$, and
 - **FOOT-POUND FORCE**: (ft lbf).

- **SPECIFIC VOLUME:** the volume per unit mass, known as $v = V/m$.
 - $\left(\frac{m^3}{kg}\right)$, and
 - $\left(\frac{ft^3}{lbm}\right)$.
- **DENSITY:** the mass per unit volume, the inverse of specific volume $\rho = m/V$.
 - $\left(\frac{kg}{m^3}\right)$, and
 - $\left(\frac{lbm}{ft^3}\right)$.

Note also that

$$v = \frac{1}{\rho}, \quad \rho = \frac{1}{v}. \quad (2.22)$$

- **PRESSURE:** the $\lim_{A \rightarrow 0} F/A$ where A is the cross-sectional area and F is the component of force acting normal to that area. In thermodynamics, we are almost always concerned with the *absolute pressure* as opposed to the *gauge pressure*. Most common pressure gauges do not measure the absolute pressure; instead they measure the difference between the absolute pressure and the atmospheric pressure. The two are related via the formula

$$P_{gauge} = P_{absolute} - P_{atm}. \quad (2.23)$$

We nearly always interpret P as an absolute pressure, so we could also say

$$P_{gauge} = P - P_{atm}. \quad (2.24)$$

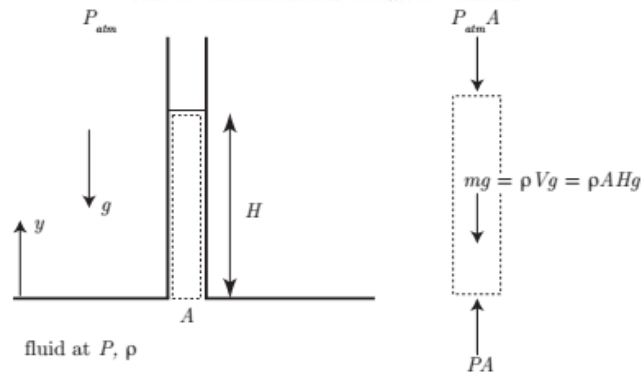
- **PASCAL:** (Pa), $1 Pa = 1 N/m^2$; note other common units are $1 bar = 10^5 Pa$, $1 atm = 1.01325 \times 10^5 Pa = 101.325 kPa = 0.101325 MPa$, and
- ($psia$): $1 psia = 1 lbf/in^2$. $1 atm = 14.696 psia$. The a denotes the “absolute” pressure as opposed to the “gauge” pressure. The units $psig$ refer to a gauge pressure.

The SI unit is named after Blaise Pascal, see Fig. [2.4](#) the French polymath who conducted early scientific experiments with manometers, a common measuring device for pressure, see Fig. [2.5](#). There are a variety of styles of manometers. Here, a pipe containing fluid at pressure P and density ρ has a small tube with cross sectional area A connecting it to the outside atmosphere at a different pressure P_{atm} . The length H is easily measured. The gravitational acceleration is g and is in the negative y direction. Because $P > P_{atm}$, the manometer fluid is pushed up. However, it finds a mechanical equilibrium where the weight of the manometer fluid balances the net force induced by the pressure differential.

Fig 2.4. Blaise Pascal (1623-1662) French scientist and philosopher who considered manometry



Fig 2.5. Manometer sketch



The figure includes a cutaway with a free body diagram. The interior fluid exerts a positive force of PA on the manometer fluid in the cutaway. The atmosphere exerts another force of $P_{atm}A$ in the negative direction. The third force is the weight of the fluid: mg . Thus, Newton's second law tells us

$$m \underbrace{\frac{d^2 y}{dt^2}}_{=0} = PA - P_{atm}A - mg. \quad (2.25)$$

Now, we are concerned with cases which are static, in which case the acceleration $d^2 y/dt^2 = 0$. Thus, we require a force balance, i.e. mechanical equilibrium, which is achieved when

$$0 = PA - P_{atm}A - mg, \quad (2.26)$$

$$PA = P_{atm}A + mg. \quad (2.27)$$

Now, $mg = \rho V g$, where V is the volume of the fluid in the cutaway. Obviously from the geometry, we have $V = AH$, so $mg = \rho AH g$. Thus,

$$PA = P_{atm}A + \rho AH g, \quad (2.28)$$

$$P = P_{atm} + \rho g H. \quad (2.29)$$

Or

$$\Delta P = P - P_{atm} = P_{gauge} = \rho g H. \quad (2.30)$$

NOTES

A *thermodynamic system* is any macroscopic system.

Thermodynamic parameters are measurable macroscopic quantities associated with the system, such as the pressure P , the volume V , the temperature T , and the magnetic field H . They are defined experimentally.

A *thermodynamic state* is specified by a set of values of all the thermodynamic parameters necessary for the description of the system.

Thermodynamic equilibrium prevails when the thermodynamic state of the system does not change with time.

The *equation of state* is a functional relationship among the thermodynamic parameters for a system in equilibrium. If P , V , and T are the thermodynamic parameters of the system, the equation of state takes the form

$$f(P, V, T) = 0$$

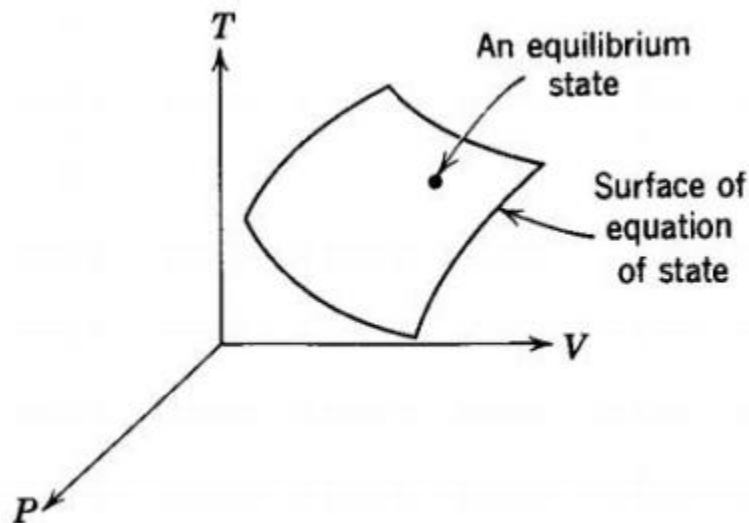


Fig 2.6. Geometrical representation of the equation of state

A *thermodynamic transformation* is a change of state. If the initial state is an equilibrium state, the transformation can be brought about only by changes in the external condition of the system. The transformation is *quasi-static* if the external condition changes so slowly that at any moment the system is approximately in equilibrium. It is *reversible* if

the transformation retraces its history in time when the external condition retraces its history in time. A reversible transformation is quasi-static, but the converse is not necessarily true. For example, a gas that freely expands into successive infinitesimal volume elements undergoes a quasi-static transformation but not a reversible one.

The P - V diagram of a system is the projection of the surface of the equation of state onto the P - V plane. Every point on the P - V diagram therefore represents an equilibrium state. A reversible transformation is a continuous path on the P - V diagram. Reversible transformations of specific types give rise to paths with specific names, such as *isotherms*, *adiabatics*, etc. A transformation that is not reversible cannot be so represented.

The concept of *work* is taken over from mechanics. For example, for a system whose parameters are P , V , and T , the work dW done by a system in an infinitesimal transformation in which the volume increases by dV is given by

$$dW = P dV$$

Heat is what is absorbed by a homogeneous system if its temperature increases while no work is done. If ΔQ is a small amount of the heat absorbed, and ΔT is the small change in temperature accompanying the absorption of heat, the *heat capacity* C is defined by

$$\Delta Q = C \Delta T$$

The heat capacity depends on the detailed nature of the system and is given as a part of the specification of the system. It is an experimental fact that, for the same ΔT , ΔQ is different for different ways of heating

up the system. Correspondingly, the heat capacity depends on the manner of heating. Commonly considered heat capacities are C_V and C_P , which respectively correspond to heating at constants V and P . Heat capacities per unit mass or per mole of a substance are called *specific heats*.

A *heat reservoir*, or simply *reservoir*, is a system so large that the gain or loss of any finite amount of heat does not change its temperature.

A system is *thermally isolated* if no heat exchange can take place between it and the external world. Thermal isolation may be achieved by surrounding a system with an *adiabatic wall*. Any transformation the system can undergo in thermal isolation is said to take place *adiabatically*.

A thermodynamic quantity is said to be *extensive* if it is proportional to the amount of substance in the system under consideration and is said to be *intensive* if it is independent of the amount of substance in the system under consideration. It is an important empirical fact that to a good approximation thermodynamic quantities are either extensive or intensive.

The *ideal gas* is an important idealized thermodynamic system. Experimentally all gases behave in a universal way when they are sufficiently dilute. The ideal gas is an idealization of this limiting behavior. The parameters for an ideal gas are pressure P , volume V , temperature T , and number of molecules N . The equation of state is given by Boyle's law:

$$\frac{PV}{N} = \text{constant} \quad (\text{for constant temperature})$$

Isolated systems do not interact in any way with the surroundings. *Closed systems* only exchange energy but not exchange matter with their surroundings. *Open systems* can exchange energy and matter with their surroundings.

In general one distinguishes two classes of **state quantities**:

Extensive (additive) state quantities

These quantities are proportional to the amount of matter in a system, e.g., to the particle number or mass. Characteristic examples of extensive properties are the volume and the energy. In particular, an extensive state quantity of a heterogeneous system is *additively* composed of the corresponding extensive properties of the single phases. Thus, the volume of a pot containing water, steam and air is the sum of the volumes of the fluid and gaseous phases. The most characteristic extensive state quantity for thermodynamics (and statistical mechanics) is the entropy, which is closely related to the microscopic probability of a state.

Intensive state quantities

These quantities are independent of the amount of matter and are not additive for the particular phases of a system. They might assume different values in different phases, but this is not necessarily the case. Examples are: refractive index, density, pressure, temperature, etc. Typically, intensive state quantities can be defined locally; i.e., they may vary spatially. Consider, for instance, the density of the atmosphere, which is largest at the surface of the earth and continuously decreases with height, or the water pressure in an ocean, which increases with increasing depth.

We consider a material body consisting of N atoms in volume V , in the absence of a nonuniform external potential, to be the idealized limit

$$\begin{aligned}N &\rightarrow \infty \\V &\rightarrow \infty \\ \frac{N}{V} &= \text{fixed number}\end{aligned}$$

This is called the *thermodynamic limit*, in which the system becomes translationally invariant.

Zeroth Law: If each of two systems is in thermal equilibrium with a third system they are in thermal equilibrium with each other.

The argument can be repeated for fourth, fifth, ... systems (D, E, ...). If each is in thermal equilibrium with all the others, they must have the same value of some property that has a common value.

This property is called thermodynamic temperature T .

The temperature of a system is a property that determines whether or not that system would be in thermal equilibrium with other systems.

LECTURE 3: PROPERTIES OF A PURE SUBSTANCE

Content of Lecture 3

- 3.1. The pure substance
- 3.2. Vapor-liquid-solid phase equilibrium
- 3.3. Independent properties
- 3.4. Thermal equations of state
 - 3.4.1. Ideal gas law
 - 3.4.2. Non-ideal thermal equations of state
 - 3.4.3. Compressibility factor
 - 3.4.4. Tabular thermal equations of state

3.1. The pure substance

We define a

- PURE SUBSTANCE: a material with homogeneous and invariable composition.

To elaborate,

- Pure substances can have multiple phases: an ice-water mixture is still a pure substance.
- An air-steam mixture is not a pure substance.
- Air, being composed of a mixture of N_2 , O_2 , and other gases, is formally not a pure substance. However, experience shows that we can often treat air as a pure substance with little error.

3.2. Vapor-liquid-solid phase equilibrium

Often we find that different phases of pure substances can exist in equilibrium with one another. Let us consider an important *gedankenexperiment* (Latin-German for “thought experiment”) in which we boil water. Ordinary water boiling is shown in Fig. [3.1](#). However, this ordinary experiment has constraints which are too loose. Most importantly, the mass of water leaks into the atmosphere; thus, the water vapor and the air become a mixture and no longer a pure substance.

Let us instead consider a more controlled piston-cylinder arrangement. Inside the cylinder, we begin with pure liquid water at $T = 20\text{ }^\circ\text{C}$. The piston is free to move in the cylinder, but it is tightly sealed, so no water can escape. On the other side of the piston is a constant pressure atmosphere, which we take to be at $P = 100\text{ kPa} = 0.1\text{ MPa} = 10^5\text{ Pa} = 1\text{ bar}$.



Figure 3.1: Water boiling isobarically in an *open* environment.

We slowly add heat to the cylinder, and observe a variety of interesting phenomena. A sketch of what we observe is given in Fig. 3.2. We notice the following behavior:

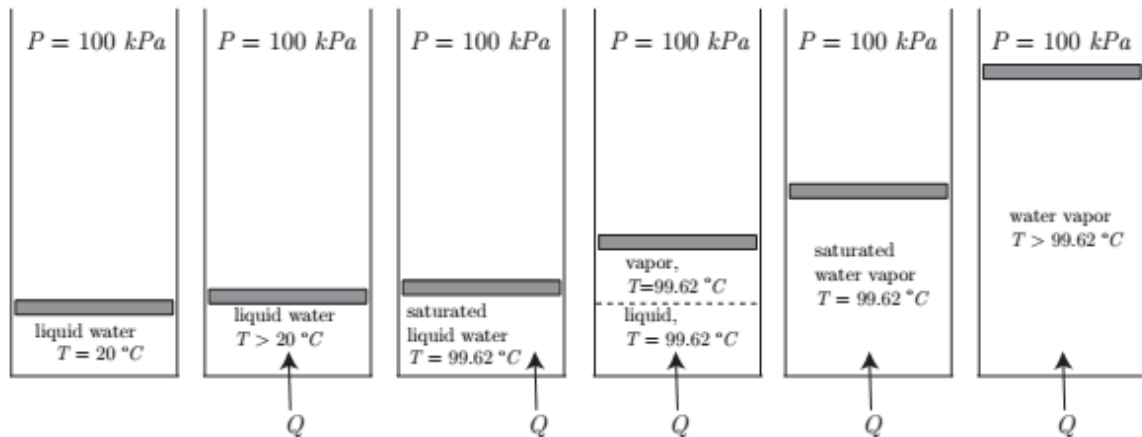


Figure 3.2: Sketch of experiment in which heat is added isobarically to water in a *closed* piston-cylinder arrangement.

- The pressure remains at a constant value of 100 kPa . This is an isobaric process.
- The total volume increases slightly as heat is added to the liquid.
- The temperature of the liquid increases significantly as heat is added to the liquid.
- At a special value of temperature, observed to be $T = 99.62 \text{ }^\circ\text{C}$, we have all liquid, but cannot add any more heat and retain all liquid. We will call this state the *saturated liquid* state. We call $T = 99.62 \text{ }^\circ\text{C}$ the *saturation temperature* at $P = 100 \text{ kPa}$. As we continue to add heat,

- The temperature remains constant (this is *isothermal* now as well as isobaric).
 - The total volume continues to increase.
 - We notice *two* phases present: liquid and vapor, with a distinct phase boundary. The liquid is dense relative to the vapor. That is $\rho_f > \rho_g$, where f denotes fluid or liquid and g denotes gas or vapor. Thus, $v_g > v_f$.
 - As more heat is added, more vapor appears, all while $P = 100 \text{ kPa}$ and $T = 99.62 \text{ }^\circ\text{C}$.
 - At a certain volume, we have all vapor and no liquid, still at $P = 100 \text{ kPa}$, $T = 99.62 \text{ }^\circ\text{C}$. We call this state the *saturated vapor* state.
- As heat is added, we find both the temperature and the volume rise, with the pressure remaining constant. The water remains in the all vapor state.

We have just boiled water! We sketch this process in the temperature-specific volume plane, that is, the $T - v$ plane, in Fig. 3.3. Note that the mass m of the water is constant in this

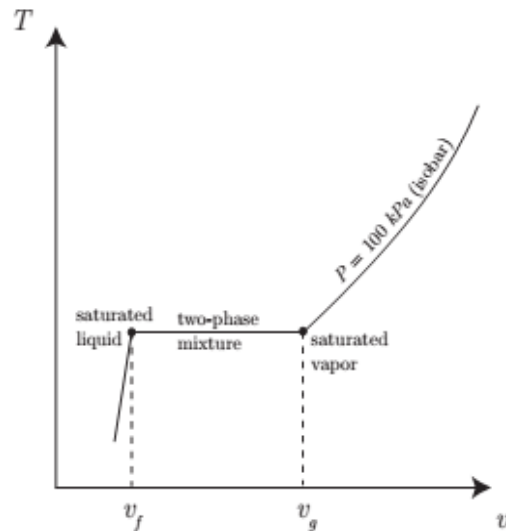


Figure 3.3: Isobar in the $T - v$ plane for our thought experiment in which heat is added isobarically to water in a piston-cylinder arrangement.

problem, so the extensive V is strictly proportional to specific volume, $v = V/m$.

We next repeat this experiment at lower pressure (such as might exist on a mountain top) and at a higher pressure (such as might exist in a valley below sea level). For moderate pressures, we find qualitatively the exact same type of behavior. The liquid gets hotter, turns into vapor isothermally, and then the vapor gets hotter as the heat is added. However, we note the following important facts:

- The saturation temperature (that is the boiling point) increases as pressure increases, as long as the pressure increase is not too high.

- As pressure increases v_f becomes closer to v_g .
- Above a *critical pressure*, $P = P_c = 22.089 \text{ MPa}$, there is no phase change observed¹. At the critical pressure, the temperature takes on a *critical temperature* of $T_c = 374.14 \text{ }^\circ\text{C}$. At the critical pressure and temperature, the specific volume takes the value $v_f = v_g = v_c = 0.003155 \text{ m}^3/\text{kg}$.

We see how the boiling point changes with pressure by plotting the saturation pressure as a function of saturation temperature in the $T - P$ plane in Fig. 3.4. This is the so-called vapor pressure curve. Here, we focus on liquid-vapor mixtures and keep T high enough to

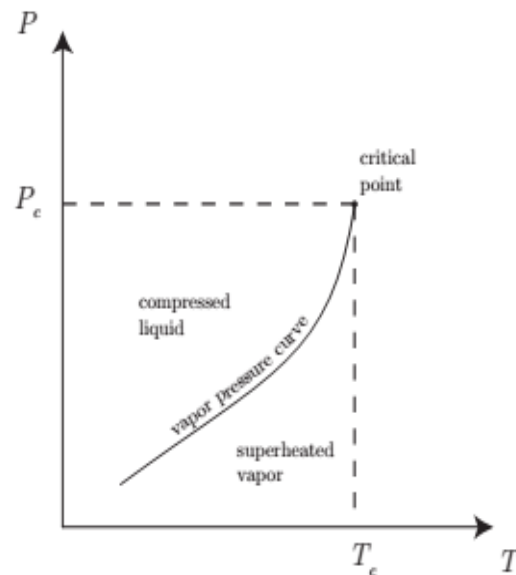


Figure 3.4: Saturation pressure versus saturation temperature sketch.

prevent freezing. Note the curve terminates abruptly at the *critical point*.

We adopt the following nomenclature:

- SATURATED LIQUID: the material is at T_{sat} and is all liquid.
- SATURATED VAPOR: the material is at T_{sat} and is all vapor.
- COMPRESSED (SUBCOOLED) LIQUID: the material is liquid with $T < T_{sat}$.
- SUPERHEATED VAPOR: the material is vapor with $T > T_{sat}$.
- TWO-PHASE MIXTURE: the material is composed of co-existing liquid and vapor with both at T_{sat} .

For two-phase mixtures, we define a new property to characterize the relative concentrations of liquid and vapor. We define the

- QUALITY= x : as the ratio of the mass of the mixture which is vapor (vap) to the total mixture mass:

$$x = \frac{m_{vap}}{m_{total}}. \quad (3.1)$$

We can also take the total mass to be the sum of the liquid and vapor masses:

$$m_{total} = m_{liq} + m_{vap}. \quad (3.2)$$

So

$$x = \frac{m_{vap}}{m_{liq} + m_{vap}}. \quad (3.3)$$

There are two important limits to remember:

- $x = 0$: corresponds to $m_{vap} = 0$. This is the all liquid limit.
- $x = 1$: corresponds to $m_{vap} = m_{total}$. This is the all gas limit.

We must have

$$0 \leq x \leq 1. \quad (3.4)$$

We sketch water's $T - v$ plane again for a wide variety of isobars in Fig. 3.5. We sketch

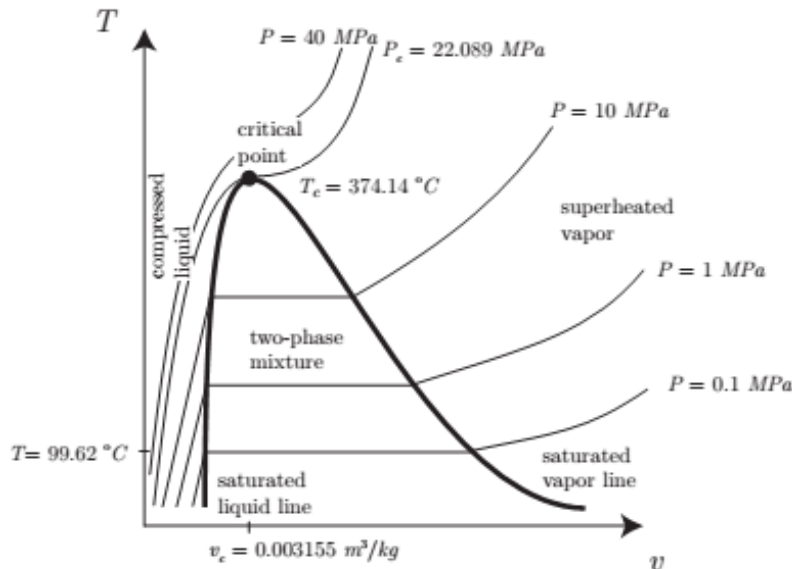


Figure 3.5: Sketch of $T - v$ plane for water for a variety of isobars.

water's $P - v$ plane for a wide variety of isotherms in Fig. 3.6. We can perform a similar thought experiment for ice. We can start with ice at $P = 100 \text{ kPa}$ and add heat to it. We

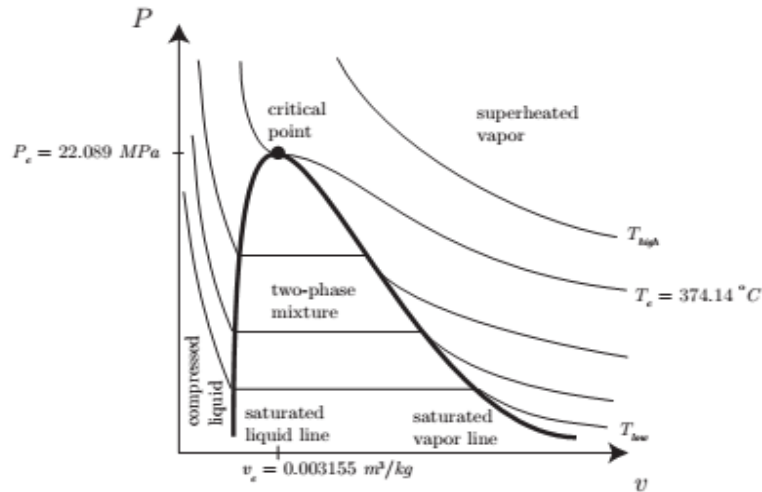


Figure 3.6: Sketch of $P - v$ plane for water for a variety of isotherms.

observe the ice's temperature rise until $T = T_{sat} \sim 0^\circ C$. At that temperature, the ice begins to melt and the temperature remains constant until all the ice is melted. At this point the liquid temperature begins to rise. If we continued to add heat, we would boil the water.

We note if we perform this experiment for $P < 0.6113 \text{ kPa}$ the ice in fact goes directly to vapor. It is said to have undergone *sublimation*. There exists a second important point where ice being heated isobarically can transform into either liquid or gas. This is the so-called *triple point*. At the triple point we find the saturation pressure and temperature are $P_{tp} = 0.6113 \text{ kPa}$ and $T_{tp} = 0.01^\circ C$, respectively. It is better described as a triple line, because in the $P - v - T$ space we will study, it appears as a line with constant P and T , but variable v . In the $P - T$ projected plane of the $P - v - T$ volume, it projects as a point. We sketch water's $P - T$ plane again for a wider range to include the vapor-liquid-solid phase behavior in Fig. [3.7](#)

These characteristics apply to all pure substances. For example, nitrogen has a triple point and a critical point. Table A.2 in BS lists critical constants for many materials. Note also that phase transitions can occur within solid phases. This involves a re-arrangement of the crystal structure. This has important implications for material science, but will not be considered in detail in this course.

3.3. Independent properties

Let us define a

- **SIMPLE COMPRESSIBLE SUBSTANCE:** a material that can be worked upon by pressure forces.

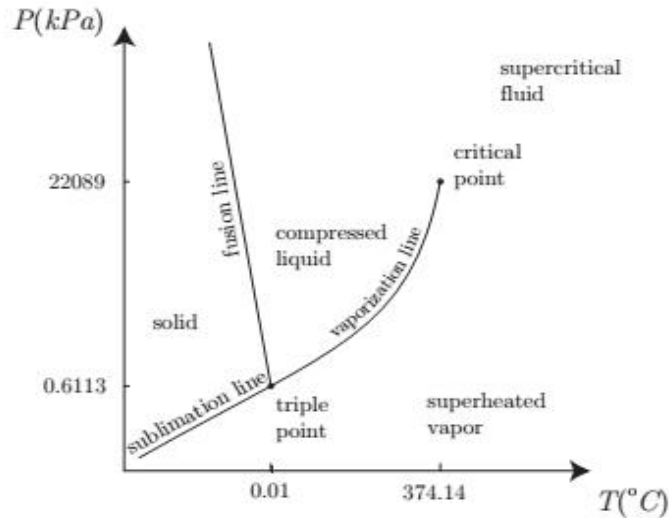


Figure 3.7: Sketch of $P - T$ plane for water.

Note we neglect electric, magnetic, and chemical work modes. While this is indeed restrictive, it will be important for many mechanical engineering applications. The following important statement can be proved (but will not be so here):

- *For a simple compressible substance, two independent intensive thermodynamic properties define the state of the system.*

Consider the implications for

- *superheated vapor:* If we consider P , T , and v , this states that we must allow one of the variables to be functions of the other two. We could have $P = P(T, v)$, $v = v(T, P)$, or $T = T(P, v)$. All are acceptable.
- *two-phase mixture:* If we have a two-phase mixture, our experiments show that P and T are not independent. In this case, we need another property to characterize the system. That property is the quality, x . So for two-phase mixtures, we might have $v = v(T, x)$, for example.

3.4. Thermal equations of state

Here, we will describe some of the many different ways to capture the relation between two independent properties and a third dependent property for a simple compressible substance. We will focus on a so-called

- **THERMAL EQUATION OF STATE:** an equation which gives the pressure as a function of two independent state variables. An example is the general form:

$$P = P(T, v). \quad (3.5)$$

We will progress from simple thermal equations of state to more complex.

3.4.1 Ideal gas law

For many gases, especially at low density and far from the critical point, it is possible to write a simple thermal equation of state which accurately describes the relation between pressure, volume, and temperature. Such equations were developed in the 1600s and early 1800s based entirely on macroscopic empirical observation. In the late 1800s, statistical mechanics provided a stronger theoretical foundation for them, but we will not consider that here.

Let us start with the most important equation of state:

- **IDEAL GAS LAW:** This equation, which is a combination of *Boyle's law*^[2], *Charles' law*^[3] and *Avogadro's law*^[4] is most fundamentally stated as

$$PV = n\bar{R}T. \quad (3.6)$$

On the continent, Boyle's law is sometimes known as Mariotte's law after Edme Mariotte (1620-1684), but Boyle published it fourteen years earlier^[5]. A reproduction of Boyle's data is given in Fig. 3.8^[6]. The data in $(V, 1/P)$ space is fit well by a straight line with intercept at the origin; that is $1/P = KV$, where K is a constant. Thus, $PV = C$, where $C = 1/K$ is a constant.

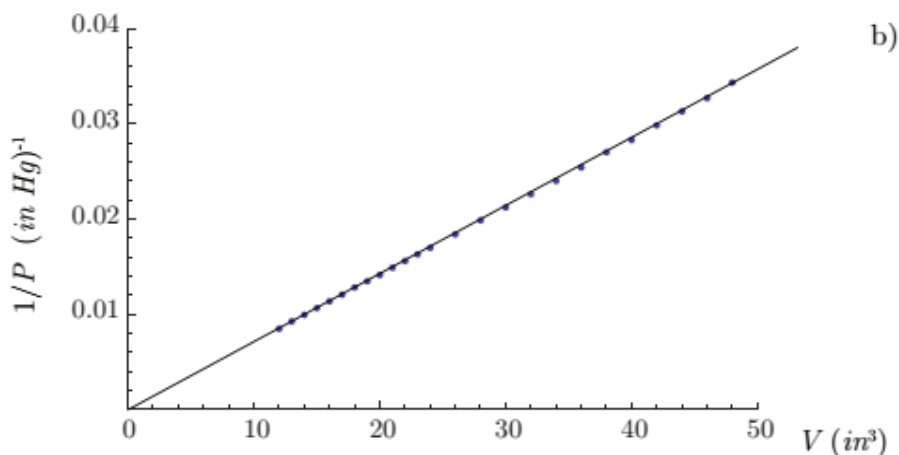


Figure 3.8: a) Boyle's 1662 data to validate his law (PV is constant for an isothermal process), b) plot of Boyle's data: V (column A) versus reciprocal of P (reciprocal of column D), demonstrating its near linearity.

Depictions of Boyle, Charles, and Avogadro are given in Fig. 3.9. The ideal gas law was first stated in the form roughly equivalent to Eq. (3.6) by Clapeyron⁷ depicted in Fig. 3.10.

It is critical that the temperature here be the absolute temperature. For the original argument, see Thomson⁸. Here, n is the number of moles. Recall there are $N = 6.02214179 \times 10^{23}$ molecules in a *mole*, where N is Avogadro's number. Also \bar{R} is the *universal gas constant*, whose history is recounted by Jensen.⁹ From experiment, many performed by by Regnault, depicted in Fig. 3.11, it is determined to be

$$\bar{R} = 8.314472 \frac{kJ}{kmole K}. \quad (3.7)$$

In this class the over bar notation will denote an intensive property on a per mole basis. Intensive properties without over bars will be on a per mass basis. Recall the mass-basis



Fig 3.9. a) Robert Boyle (1627-1691), Irish scientist who developed an important special case of the ideal gas law; b) Jacques Alexandre Cesar Charles (1746-1823), French scientist credited in 1802 by Joseph Louis Gay-Lussac (1778-1850) for developing an important special case of the ideal gas law in the 1780s; c) Lorenzo Romano Amedeo Carlo Avogadro di Quarengha e di Cerreto (1776-1856), Italian physicist, nobleman and revolutionary.

Fig 3.10. Benoit Paul Emile Clapeyron (1799-1824), French engineer and physicist who furthered the development of thermodynamics.



Fig 3.11. Henry Victor Regnault (1810-1878), French chemist and physicist who made careful early measurements of thermodynamic parameters for ideal and non-ideal gases



specific volume is $v = V/m$. Let us define the mole-based specific volume as

$$\bar{v} = \frac{V}{n}. \quad (3.8)$$

Thus, the ideal gas law can be represented in terms of intensive properties as

$$P \underbrace{\frac{V}{n}}_{=\bar{v}} = \bar{R}T, \quad (3.9)$$

$$P\bar{v} = \bar{R}T. \quad (3.10)$$

There are other ways to write the ideal gas law. Recall the molecular mass M is the mass in g of a *mole* of substance. More common in engineering, it is the mass in kg of a *kmole* of substance. These numbers are the same! From chemistry, for example, we know the molecular mass of O_2 is $32 \text{ g/mole} = 32 \text{ kg/kmole}$. Symbolically, we can say that

$$M = \frac{m}{n}. \quad (3.11)$$

Now, take the ideal gas law and divide by m :

$$PV = n\bar{R}T, \quad (3.12)$$

$$P \underbrace{\frac{V}{m}}_{=v} = \underbrace{\frac{n}{m}}_{=1/M} \bar{R}T, \quad (3.13)$$

$$Pv = \underbrace{\frac{\bar{R}}{M}}_{\equiv R} T. \quad (3.14)$$

Now, let us define

$$R \equiv \frac{\bar{R}}{M}. \quad (3.15)$$

Let's check the units:

$$[R] = \frac{kJ}{kmole K} \frac{kmole}{kg} = \frac{kJ}{kg K}. \quad (3.16)$$

We have actually just lost some universality. Recall \bar{R} is independent of material. But since each different gas has a different M , then *each gas will have its own R* . These values for various gases are tabulated in Table A.5 of BS.

With this definition, the ideal gas law becomes

$$\boxed{Pv = RT}. \quad (3.17)$$

This is the form we will use most often in this class. Note the useful fact that

$$\frac{Pv}{T} = R. \quad (3.18)$$

Thus, if an ideal gas undergoes a process going from state 1 to state 2, we can safely say

$$\boxed{\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}}. \quad (3.19)$$

Consider some notions from algebra and geometry. The function $f(x, y) = 0$ describes a curve in the $x - y$ plane. In special cases, we can solve for y to get the form $y = y(x)$. The function $f(x, y, z) = 0$ describes a surface in the $x - y - z$ volume. In special cases, we can solve for z to get $z = z(x, y)$ to describe the surface in the $x - y - z$ volume.

Similarly, the ideal gas equation $P(v, T) = RT/v$ describes a surface in the $P - v - T$ volume. A surface for air is shown in Fig. 3.14. Often, it is easier to understand the behavior

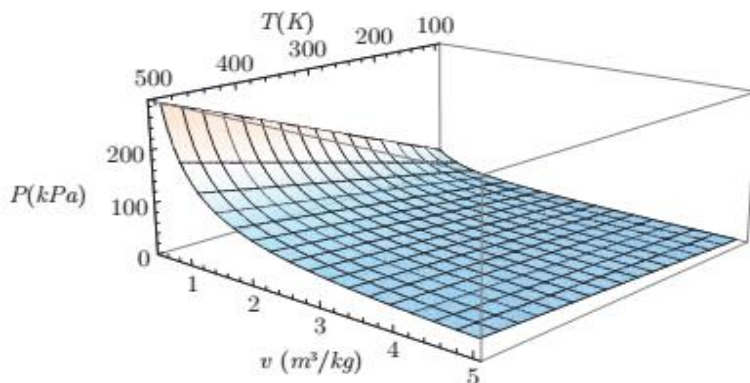


Figure 3.14: Thermodynamic surface for air modeled as an ideal gas.

of the thermodynamic surfaces by projection into various thermodynamic planes and plotting various iso-contours. Let us do this for an ideal gas.

- isobars:

- Consider curves in the $T - v$ plane on which P is constant. Thus, for the ideal gas, we consider

$$T = \underbrace{\left(\frac{P}{R}\right)}_{\text{slope}} v. \quad (3.25)$$

If we insist that P is constant, this gives the equation of an isobar in the $T - v$ plane. Moreover, for the ideal gas, we see that in the $T - v$ plane isobars are *straight lines* with slope P/R . The slope is always positive since $P > 0$ and $R > 0$. So if the pressure is high, the slope is positive and steep. If the pressure is low, the slope is positive and shallow.

- Consider curves in the $P - v$ plane in which P is constant. Thus, we consider

$$P = \text{constant}, \quad (3.26)$$

which are straight horizontal lines in the $P - v$ plane.

- Consider curves in the $P - T$ plane in which P is a constant. Thus, we consider

$$P = \text{constant}, \quad (3.27)$$

which are straight horizontal lines in the $P - v$ plane.

Isobars in various planes are shown in Fig. 3.15.

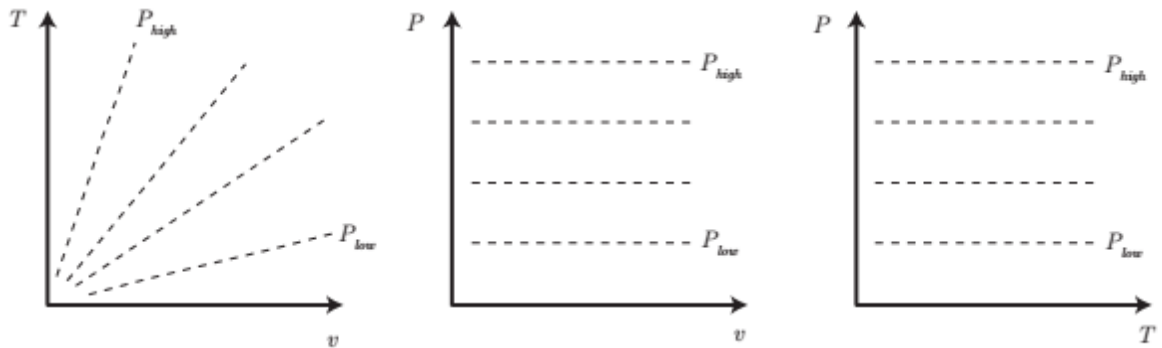


Figure 3.15: Isobars for an ideal gas in $T - v$, $P - v$, and $P - T$ planes.

- isotherms

- Consider curves in the $T - v$ plane on which T is constant. Thus, for the ideal gas, we have

$$T = \text{constant} \quad (3.28)$$

These are straight horizontal lines in the $T - v$ plane.

- Consider curves in the $P - v$ plane on which T is a constant. Thus, for the ideal gas, we have

$$P = (RT) \frac{1}{v}. \quad (3.29)$$

These are *hyperbolas* in the $P - v$ plane.

- Consider curves in the $P - T$ plane on which T is a constant. Thus, for the ideal gas, we have

$$T = \text{constant}. \quad (3.30)$$

These are straight vertical lines in the $P - T$ plane.

Isotherms in various planes are shown in Fig. 3.16

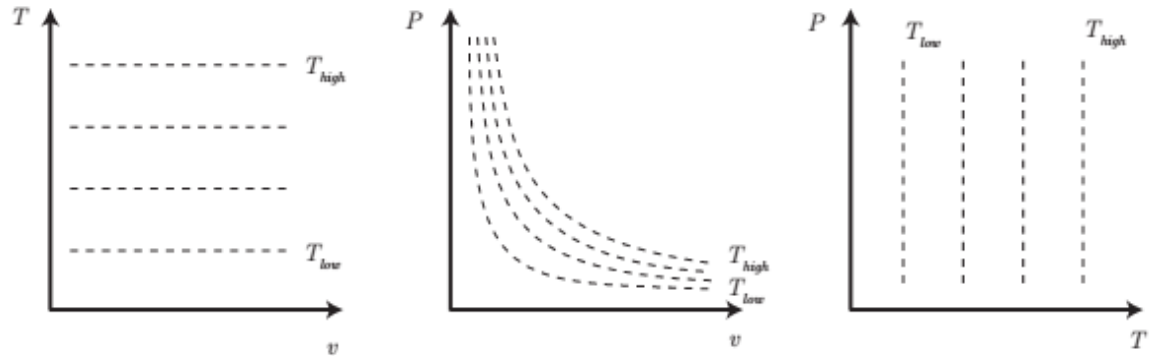


Figure 3.16: Isotherms for an ideal gas in $T - v$, $P - v$, and $P - T$ planes.

- isochores

- Consider curves in the $T - v$ plane on which v is constant. Thus, for the ideal gas, we have

$$v = \text{constant} \quad (3.31)$$

These are straight vertical lines in the $T - v$ plane.

- Consider curves in the $P - v$ plane on which v is a constant. Thus, for the ideal gas, we have

$$v = \text{constant}. \quad (3.32)$$

These are straight vertical lines in the $P - v$ plane.

- Consider curves in the $P - T$ plane on which v is a constant. Thus, for the ideal gas, we have

$$P = \underbrace{\left(\frac{R}{v}\right)}_{\text{constant}} T. \quad (3.33)$$

These are straight lines in the $P - T$ plane with slope R/v . Since $R > 0$ and $v > 0$, the slope is always positive. For large v , the slope is shallow. For small v , the slope is steep.

Isochores in various planes are shown in Fig. 3.17

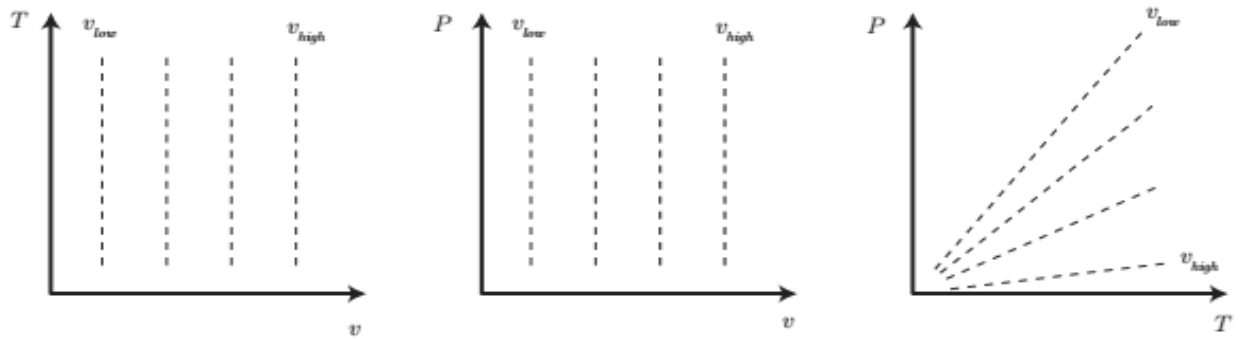


Figure 3.17: Isochores for an ideal gas in $T - v$, $P - v$, and $P - T$ planes.

3.4.2 Non-ideal thermal equations of state

The ideal gas law is not a good predictor of the $P - v - T$ behavior of gases when

- the gas has high enough density that molecular interaction forces become large and the molecules occupy a significant portion of the volume; this happens near the vapor dome typically, or
- the temperature is high enough to induce molecular dissociation (e.g. $N_2 + N_2 \rightleftharpoons 2N + N_2$)

One alternative is a corrected thermal equation of state.

3.4.2.1 van der Waals

For the *van der Waals*¹⁰ equation of state, which will be studied in more detail in Sec. 11.6, one has

$$P = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (3.45)$$

with

$$a = \frac{27}{64} R^2 \frac{T_c^2}{P_c}, \quad b = \frac{1}{8} R \frac{T_c}{P_c}. \quad (3.46)$$

A depiction of van der Waals is given in Fig. 3.20.

Fig 3.20. Johannes Diderik van der Waals (1837-1923), Dutch physicist and Nobel laureate who developed a corrected state equation



3.4.2.2 Redlich-Kwong

For the Redlich-Kwong^[11] equation of state, one has

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)\sqrt{T}}, \quad (3.47)$$

with

$$a = (0.42748) \frac{R^2 T_c^{5/2}}{P_c}, \quad b = (0.08664) \frac{RT_c}{P_c}. \quad (3.48)$$

3.4.3 Compressibility factor

In some cases, more detail is needed to capture the behavior of the gas, especially near the vapor dome. Another commonly used approach to capturing this behavior is to define the

- COMPRESSIBILITY FACTOR: the deviation from ideality of a gas as measured by

$$Z = \frac{Pv}{RT}. \quad (3.49)$$

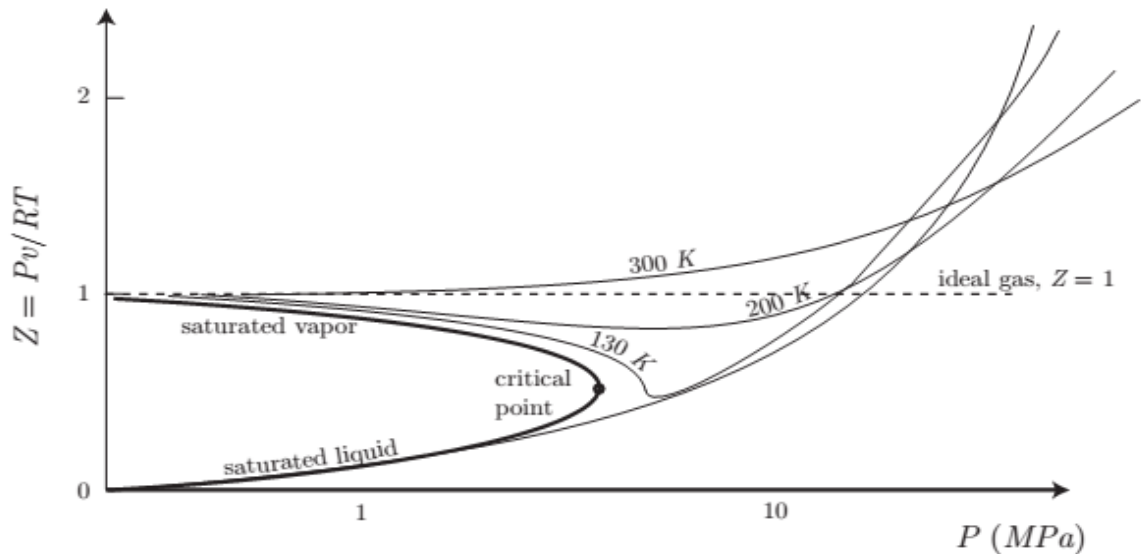


Figure 3.21: Sketch of compressibility chart for N_2 .

For ideal gases, $Pv = RT$, so $Z = 1$. Experiments show the behavior of real gases, and this can be presented in graphical form, as shown for N_2 in Fig. 3.21. Note

- for all T , $Z \rightarrow 1$ as $P \rightarrow 0$. Thus, one has ideal gas behavior at low pressure
- for $T > 300\text{ K}$, $Z \sim 1$ for $P < 10\text{ MPa}$.
- Hold at $P = 4\text{ MPa}$ and decrease temperature from 300 K ; we see Z decrease below unity. Now

$$Z = \frac{Pv}{RT} = \frac{P}{\rho RT}, \quad \rho = \frac{P}{ZRT}. \quad (3.50)$$

Since $Z < 1$, the density ρ is higher than we would find for an ideal gas with $Z = 1$. Thus, in this region, there is an attractive force between molecules.

- For $P > 30\text{ MPa}$, we find $Z > 1$. Thus, a repulsive force exists in this regime. The forces are complicated.

Note that generalized compressibility charts have been developed for general gases. These are based on the so-called reduced pressures and temperatures, P_r and T_r , where

$$P_r = \frac{P}{P_c}, \quad T_r = \frac{T}{T_c}. \quad (3.51)$$

3.4.4 Tabular thermal equations of state

Often equations are too inaccurate for engineering purposes. This is generally because we may be interested in behavior under a vapor dome. Consider that the surface for steam is well represented by that shown in Fig. 3.22



Figure 3.22: $P - v - T$ surface for H_2O , showing solid, liquid, and vapor phases.

In such cases, one should use tables to find a third property, given two independent properties. We can say that the thermal equation of state is actually embodied in the tabular data.

We lay down some rules of thumb for this class:

- If steam, use the tables.
- If air or most other gas, use the ideal gas law, but check if the pressure is high or the properties are near the vapor dome, in which case use compressibility charts or non-ideal state equations.

Let us look at how the tables are organized.

3.4.4.1 Saturated liquid-vapor water, temperature tables

For water, the most important table is the saturated steam table. One should go to such tables first. If the water is a two-phase mixture, tables of this type must be used as the equation of state. Recall, *for two-phase mixtures, pressure and temperature are not independent thermodynamic variables*. Two properties still determine the state, but quality x is now important. So for two-phase mixtures we allow

- $T = T(v, x)$,
- $P = P(v, x)$, or
- $v = v(T, x)$,

for example. But $P \neq P(T, v)$ as for ideal gases.

Consider the structure of saturation tables, as shown in Table 3.2 extracted from BS's Table B.1.1. Data from the steam tables is sketched in Fig. 3.23. We have the notation:

Temp. $^{\circ}C$	Press. kPa	Specific Volume, $\frac{m^3}{kg}$		
		Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g
0.01	0.6113	0.001000	206.131	206.132
5	0.8721	0.001000	147.117	147.118
10	1.2276	0.001000	106.376	106.377
15	1.705	0.001001	77.924	77.925
\vdots	\vdots	\vdots	\vdots	\vdots
35	5.628	0.001006	25.2148	25.2158
40	7.384	0.001008	19.5219	19.5229
\vdots	\vdots	\vdots	\vdots	\vdots
374.1	22089	0.003155	0	0.00315

Table 3.2: Saturated liquid-vapor water tables, temperature entry, from BS, Table B.1.1.

- f : saturated liquid,
- g : saturated vapor,
- v_f : specific volume of saturated liquid, and
- v_g : specific volume of saturated vapor.

Note for liquid-vapor mixtures, this table begins at the triple point temperature $0.01\text{ }^\circ\text{C}$ and ends at the critical temperature $374.1\text{ }^\circ\text{C}$. At $P = P_c$ and $T = T_c$, we have $v_f = v_g$. Note that

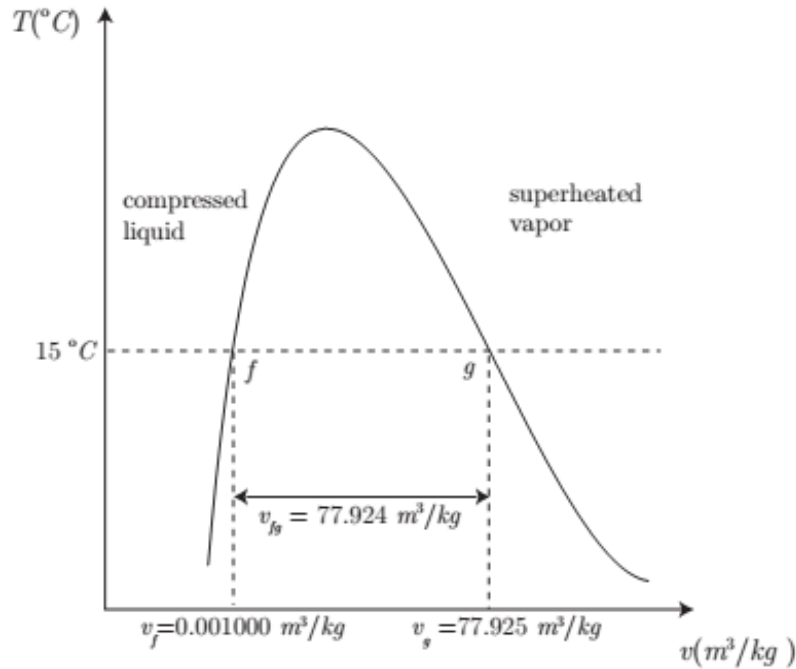


Figure 3.23: Vapor dome for H_2O with data for v_f , v_g , and v_{fg} at $T = 15^\circ\text{C}$.

- $v_f \simeq \text{constant}$
- v_g decreases with increasing T

We define v_{fg} as

$$v_{fg} \equiv v_g - v_f. \quad (3.52)$$

Recall the quality x is

$$x = \frac{m_{\text{vap}}}{m_{\text{total}}}.$$

Consider a mass of fluid m in total volume V . We must have

$$V = V_{\text{liq}} + V_{\text{vap}}, \quad (3.53)$$

$$m = m_{\text{liq}} + m_{\text{vap}}. \quad (3.54)$$

Now, use the definition of specific volume and analyze to get

$$mv = m_{liq}v_f + m_{vap}v_g, \quad (3.55)$$

$$v = \frac{m_{liq}}{m}v_f + \frac{m_{vap}}{m}v_g, \quad (3.56)$$

$$v = \frac{m - m_{vap}}{m}v_f + \frac{m_{vap}}{m}v_g, \quad (3.57)$$

$$v = (1 - x)v_f + xv_g, \quad (3.58)$$

$$v = v_f + x \underbrace{(v_g - v_f)}_{=v_{fg}}. \quad (3.59)$$

We get the final important results:

$$\boxed{v = v_f + xv_{fg}.} \quad (3.60)$$

$$\boxed{x = \frac{v - v_f}{v_{fg}}.} \quad (3.61)$$

3.4.4.2 Saturated liquid-vapor water, pressure tables

Sometimes we are given the pressure of the mixture, and a saturation table based on the pressure is more useful. An example of a portion of such a table is shown in Table [3.3](#).

Press. <i>kPa</i>	Temp. <i>°C</i>	Specific Volume, $\frac{m^3}{kg}$		
		Sat. Liquid <i>v_f</i>	Evap. <i>v_{fg}</i>	Sat. Vapor <i>v_g</i>
0.6113	0.01	0.001000	206.131	206.132
1.0	6.98	0.001000	129.20702	129.20802
1.5	13.03	0.001001	87.97913	87.98013
2.0	17.50	0.001001	67.00285	67.00385
⋮	⋮	⋮	⋮	⋮
22089	374.1	0.003155	0	0.00315

Table 3.3: Saturated water tables, pressure entry from BS, Table B.1.2.

3.4.4.3 Superheated water tables

The superheat regime is topologically similar to an ideal gas. For a superheated vapor, the quality x is meaningless, and we can once again allow pressure and temperature to be independent. Thus, we can have $v = v(T, P)$. And the tables are in fact structured to give $v(T, P)$ most directly. An example of a portion of such a table is shown in Table [3.4](#). This portion of the superheated tables focuses on a single isobar, $P = 10 \text{ kPa}$. At that pressure, the saturation temperature is 45.81 °C , indicated in parentheses. As long as $T > 45.81 \text{ °C}$, we can use this table for $P = 10 \text{ kPa}$ water. And for various values of $T > 45.81 \text{ °C}$, we find other properties, such as specific volume v , and properties we have not yet focused on, internal energy u , enthalpy h , and entropy s .

Temp. °C	v $\frac{m^3}{kg}$	u $\frac{kJ}{kg}$	h $\frac{kJ}{kg}$	s $\frac{kJ}{kg K}$
$P = 10 \text{ kPa} (45.81 \text{ }^\circ\text{C})$				
Sat.	14.67355	2437.89	2584.63	8.1501
50	14.86920	2443.87	2592.56	8.1749
100	17.19561	2515.50	2687.46	8.4479
150	19.51251	2587.86	2782.99	8.6881
⋮	⋮	⋮	⋮	⋮

Table 3.4: Superheated water tables, from BS, Table B.1.3.

3.4.4.4 Compressed liquid water tables

Liquids truly have properties which vary with both T and P . To capture such variation, we can use compressed liquid tables as an equation of state. An example for water is given in Table 3.5. If compressed liquid tables do not exist, it is usually safe enough to assume

Temp. °C	v $\frac{m^3}{kg}$	u $\frac{kJ}{kg}$	h $\frac{kJ}{kg}$	s $\frac{kJ}{kg K}$
$P = 500 \text{ kPa} (151.86 \text{ }^\circ\text{C})$				
Sat.	0.001093	639.66	640.21	1.8606
0.01	0.000999	0.01	0.51	0.0000
20	0.001002	83.91	84.41	0.2965
40	0.001008	167.47	167.98	0.5722
⋮	⋮	⋮	⋮	⋮

Table 3.5: Compressed liquid water tables, from BS, Table B.1.4.

properties are those for $x = 0$ saturated liquid at the appropriate temperature.

3.4.4.5 Saturated water, solid-vapor

Other types of saturation can exist. For example, below the triple point temperature, one can have solid water in equilibrium with water vapor. The process where ice transforms directly to water vapor is known as *sublimation*. Saturation tables for ice-vapor equilibrium exist as well. For example, consider the structure of saturation tables, as shown in Table 3.6, extracted from BS's Table B.1.5.

Temp. $^{\circ}C$	Press. kPa	Specific Volume, $\frac{m^3}{kg}$		
		Sat. Solid v_i	Evap. v_{ig}	Sat. Vapor v_g
0.01	0.6113	0.0010908	206.152	206.153
0	0.6108	0.0010908	206.314	206.315
-2	0.5177	0.0010905	241.662	241.663
-4	0.4376	0.0010901	283.798	283.799
\vdots	\vdots	\vdots	\vdots	\vdots

Table 3.6: Saturated solid-vapor water tables, temperature entry, from BS, Table B.1.5.

3.4.4.6 Tables for other materials

For many materials similar tables exist, e.g., ammonia, NH_3 . Consider the ammonia saturation tables, as shown in Table 3.7, extracted from BS's Table B.2.1. One also has tables for

Temp. $^{\circ}C$	Press. kPa	Specific Volume, $\frac{m^3}{kg}$		
		Sat. Liquid v_f	Evap. v_{fg}	Sat. Vapor v_g
-50	40.9	0.001424	2.62557	2.62700
-45	54.5	0.001437	2.00489	2.00632
-40	71.7	0.001450	1.55111	1.55256
-35	93.2	0.001463	1.21466	1.21613
\vdots	\vdots	\vdots	\vdots	\vdots
132.3	11333.2	0.004255	0	0.004255

Table 3.7: Saturated liquid-vapor ammonia tables, temperature entry, from BS, Table B.2.1.

superheated ammonia vapor. An example of a portion of such a table is shown in Table 3.8. Other tables in BS, include those for carbon dioxide, CO_2 , a modern refrigerant, R-410a¹² another common refrigerant, R-134a¹³ diatomic nitrogen, N_2 , and methane, CH_4 .

Temp. $^{\circ}C$	v $\frac{m^3}{kg}$	u $\frac{kJ}{kg}$	h $\frac{kJ}{kg}$	s $\frac{kJ}{kg K}$
$P = 50 kPa (-46.53 ^{\circ}C)$				
Sat.	2.1752	1269.6	1378.3	6.0839
-30	2.3448	1296.2	1413.4	6.2333
-20	2.4463	1312.3	1434.6	6.3187
-10	2.5471	1328.4	1455.7	6.4006
\vdots	\vdots	\vdots	\vdots	\vdots

Table 3.8: Superheated ammonia tables, from BS, Table B.2.2.

NOTES

Ideal Gases

Boyle's Law and the Kelvin scale

$$\lim_{p \rightarrow 0} (p\bar{V})_T = \left[\frac{\lim_{p \rightarrow 0} (p\bar{V})_{tp}}{273.16} \right] T \equiv RT \quad \text{valid for all gases for } p \rightarrow 0$$

define \uparrow the "gas constant" \uparrow

An ideal gas obeys the expression $p\bar{V} = RT$ at all pressures
(\Rightarrow the gas molecules do not interact)

$$R = \left[\frac{\lim_{p \rightarrow 0} (p\bar{V})_{tp}}{273.16} \right] = 8.31451 \frac{J}{K \cdot mol} \quad (\text{gas constant})$$

The Ideal gas law

$$\boxed{p\bar{V} = RT} \quad \text{or} \quad \boxed{pV = nRT}$$

This is an example of an equation of state

$$V = f(n, p, T)$$

Equations of state

IDEAL GAS LAW: $\boxed{pV = nRT} \rightarrow p\bar{V} = RT$

Mixture of ideal gases comprising n_i moles of each

$$p_i = \frac{n_i RT}{V} \quad \leftarrow \text{Partial pressure of } i^{\text{th}} \text{ gas}$$

$$p = p_{\text{Total}} = \sum_i p_i ; \quad X_i = \frac{n_i}{n} \quad \text{mole fraction of } i^{\text{th}} \text{ gas}$$

$p_i = \frac{n_i}{n} p = X_i p$	Dalton's Law
---------------------------------	--------------

Real Gases -- do not necessarily obey ideal gas law

(a) Compressibility factor

$$p\bar{V} = ZRT \quad Z = \frac{\bar{V}_{\text{real}}}{\bar{V}_{\text{ideal}}}$$

High T \Rightarrow Repulsions dominate $Z > 1$ $\bar{V}_{\text{real}} > \bar{V}_{\text{ideal}}$

Low T \Rightarrow Attractions dominate $Z < 1$ $\bar{V}_{\text{real}} < \bar{V}_{\text{ideal}}$

(b) Virial Expansion

$$\frac{p\bar{V}}{RT} = Z(T) = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \dots$$

generally neglect

As $p \rightarrow 0, \bar{V} \rightarrow \infty, \Rightarrow$ ideal gas $B = 0 \Rightarrow$ ideal gas
 (neglect C and higher order terms)

(c) van der Waals Equation of state

only two parameters, derived from molecular concepts

- First assume "hard sphere" molecules

$$p\bar{V} = RT \quad \text{becomes} \quad p(\bar{V} - b) = RT$$

- Now put in attraction

So $p = \left(\frac{RT}{\bar{V} - b} \right)$ becomes $p = \left(\frac{RT}{\bar{V} - b} \right) - \frac{a}{\bar{V}^2}$

Rearranging $\Rightarrow \boxed{\left(p + \frac{a}{\bar{V}^2} \right) (\bar{V} - b) = RT}$

LECTURE 4: WORK AND HEAT

Content of Lecture 4

4.1. Mathematical preliminaries: exact differentials

4.1.1. Partial derivatives

4.1.2. Total derivative

4.2. Work

4.2.1. Definitions

4.2.2. Work for a simple compressible substance

4.2.3. Other forms of work

4.3. Heat

4.1. Mathematical preliminaries: exact differentials

Here, we review some notions from calculus of many variables. Recall in thermodynamics, we are often concerned with functions of two independent variables, e.g. $P = P(v, T)$, as is found in an equation of state. Here, let us consider $z = z(x, y)$ for a general analysis.

4.1.1 Partial derivatives

Recall if $z = z(x, y)$, then the *partial derivative* of z can be taken if one of the variables is held constant.

4.1.2 Total derivative

If $z = z(x, y)$, for every x and y , we have a z . We also have the *total differential*

$$dz = \left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy. \quad (4.3)$$

On a particular path C in the $x - y$ plane along which we know $y = y(x)$, we also have the total derivative

$$\frac{dz}{dx} = \left. \frac{\partial z}{\partial x} \right|_y + \left. \frac{\partial z}{\partial y} \right|_x \frac{dy}{dx}. \quad (4.4)$$

Now, we can integrate dz along a variety of paths C in the $x - y$ plane. Two paths from z_1 to z_2 are shown in Fig. [4.1](#). Integrating Eq. [\(4.3\)](#), we get

$$\int_1^2 dz = \int_C \left(\left. \frac{\partial z}{\partial x} \right|_y dx + \left. \frac{\partial z}{\partial y} \right|_x dy \right). \quad (4.5)$$

Now, because $z = z(x, y)$, it will not matter which path we choose. The integral is said to be *path-independent*

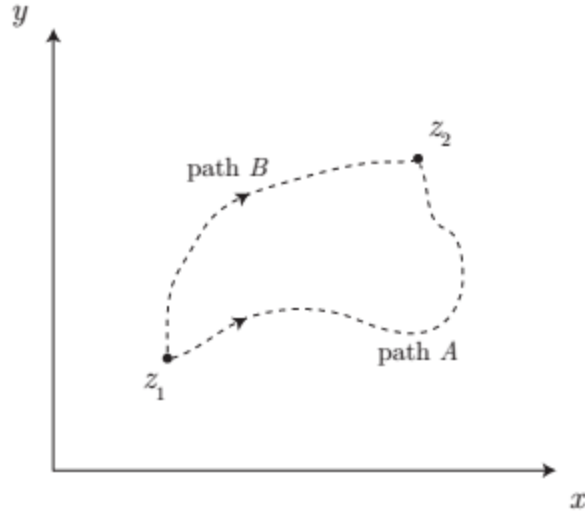


Figure 4.1: Sketch of two paths from z_1 to z_2 in the $x - y$ plane. Conversely, if we were given

$$dz = M(x, y)dx + N(x, y)dy, \quad (4.6)$$

the associated integrals are path-independent iff $z(x, y)$ can be found by solving.

$$M = \left. \frac{\partial z}{\partial x} \right|_y, \quad N = \left. \frac{\partial z}{\partial y} \right|_x. \quad (4.7)$$

One easy way to check this is to form the following two partial derivatives of Eqs. (4.7):

$$\left. \frac{\partial M}{\partial y} \right|_x = \frac{\partial^2 z}{\partial y \partial x}, \quad \left. \frac{\partial N}{\partial x} \right|_y = \frac{\partial^2 z}{\partial x \partial y}. \quad (4.8)$$

Now, if $z(x, y)$ and all its partial derivatives are continuous and differentiable, it is easy to prove the order of differentiation does not matter: $\partial^2 z / \partial x \partial y = \partial^2 z / \partial y \partial x$. Thus, if $z = z(x, y)$, we must insist that

$$\left. \frac{\partial M}{\partial y} \right|_x = \left. \frac{\partial N}{\partial x} \right|_y. \quad (4.9)$$

We define the following:

- EXACT DIFFERENTIAL: a differential which yields a path-independent integral.

4.2. Work

4.2.1 Definitions

From Newtonian mechanics, we know going from state 1 to state 2, that the work ${}_1W_2$ is done by a force moving through a distance. The word “work” was first used in this sense by the French mechanician Gaspard-Gustave Coriolis, depicted in Fig. 4.3. Work is defined as

$${}_1W_2 = \int_1^2 \mathbf{F} \cdot d\mathbf{x}. \quad (4.26)$$

In differential form, we have

$$\delta W = \mathbf{F} \cdot d\mathbf{x}. \quad (4.27)$$

In one-dimensional systems, we have

$${}_1W_2 = \int_1^2 F dx, \quad (4.28)$$

$$\delta W = F dx. \quad (4.29)$$

Note that we have anticipated that the work differential is inexact. This is an important point, as work integrals will be *path-dependent*, and work will not be a state variable for a system. Here, \mathbf{F} is a three-dimensional force vector, \mathbf{x} is a three-dimensional distance vector,

Fig 4.3. Gaspard-Gustave Coriolis (1792-1843), French physicist who used the word “work” to characterize a force acting through a distance



and \cdot is the dot product operator. Recall that the dot product of two vectors yields a scalar. The terms F and x are scalar equivalents valid for one-dimensional systems. The units of force are N , those of distance are m , so the units of work are $N m$, which have been defined as Joules (J).

Work is done by a system if the sole effect on the surroundings (i.e. everything external to the system) could be the raising of a weight. We take the following sign convention:

- + work done by the system,
- – work done on the system.

This sign convention is not universal. Many physicists use precisely the opposite convention. Probably the reason for this convention is that thermodynamics is a science that was invented by engineers in the nineteenth century. And those engineers wanted to produce work from steam engines. Systems doing work were viewed favorably and endowed with a positive sign.

We associate energy with the ability to do work. We define

- POWER: the time rate of doing work $= \delta W/dt$.
- SPECIFIC WORK: the work per unit mass $w = W/m$. Because work is path-dependent, the intensive quantity w is not a thermodynamic state variable.

4.2.2 Work for a simple compressible substance

Consider the scenario sketched in Fig. 4.4. In state 1, we have a material at pressure P confined in a cylinder of cross-sectional area A . The height of the piston in the cylinder is x . The pressure force of the material on the piston is just balanced by weights on top of the piston.

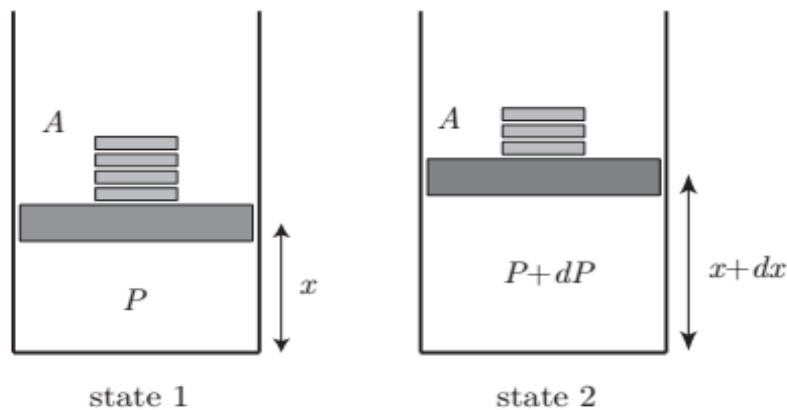


Figure 4.4: Sketch of piston-cylinder arrangement as work is done as the material expands when weights are removed.

Now, remove one of the weights. We notice a motion of the piston to a new height $x + dx$. We let a long time elapse so the system comes to rest at its new equilibrium. We notice there is a new pressure in the chamber, $P + dP$ sufficient to balance the new weight force. Obviously work was done as a force acted through a distance. Let us calculate how much work was done. The differential work is given from Eq. (4.29) as

$$\delta W = F dx. \quad (4.30)$$

Now, F varies during the process. At state 1, we have $F = PA$. At state 2, we have $F = (P + dP)A$. Let us approximate F by its average value:

$$F \sim \frac{1}{2}(PA + (P + dP)A) = PA + \frac{dP}{2}A. \quad (4.31)$$

So

$$\delta W = \left(PA + \frac{dP}{2}A \right) dx = PA dx + \frac{A}{2} \underbrace{dP dx}_{\sim 0}. \quad (4.32)$$

Let us only retain terms which are differential and neglect the square of differential terms, so

$$\delta W = PA dx. \quad (4.33)$$

Now, since $A dx = dV$, the differential volume, we get the important formula:

$$\boxed{\delta W = PdV}. \quad (4.34)$$

We can integrate this and get the equally important

$$\boxed{{}_1W_2 = \int_1^2 P dV.} \quad (4.35)$$

Note we employ the unusual notation ${}_1W_2$ to emphasize that the work depends on the path from state 1 to state 2. We are tempted to write the incorrect form $\int_1^2 \delta W = W_2 - W_1$, but this would imply the work is a state function, which it is not, as shown directly.

We can also see the path-dependence of ${}_1W_2$ by realizing that ${}_1W_2 = \int_1^2 P dV$ represents the area under a curve in a $P - V$ diagram. Consider two paths, A and B from the same points 1 to 2 as depicted in the $P - V$ space of Fig. 4.5. The area under the curve defined by Path A is clearly different from that under the curve defined by Path B . Clearly, the work ${}_1W_2$ depends on the path selected, and not simply the end points. Obviously then, to calculate the work, we will need full information on $P(V)$ for the process under consideration.

Many processes in thermodynamics are well modeled as a

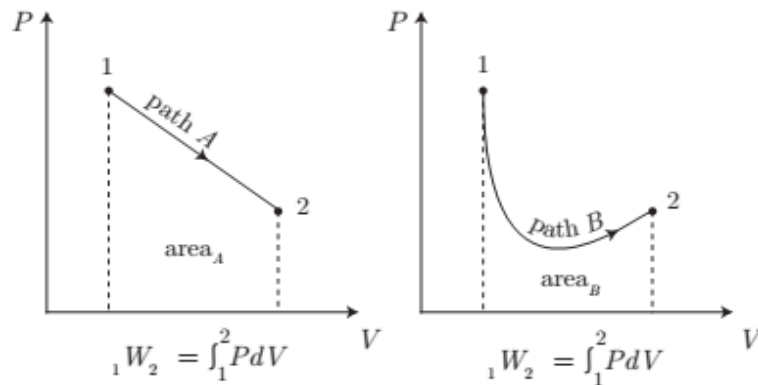


Figure 4.5: $P - V$ diagram for work for two different processes connecting the same states.

- **POLYTROPIC PROCESS:** a process which is described well by an equation of the form $PV^n = \text{constant} = C$.

Here, n is known as the polytropic exponent.

Now, if $n = 1$, we have $PV = C$, which corresponds to an isothermal process if the material is also an ideal gas. Note that non-ideal gases can also have $PV = C$; they just are not isothermal. We need to be able to analyze polytropic processes with $n = 1$.

A family of paths in the $P - V$ plane for a set of polytropic processes of varying n is shown in Fig. 4.6

4.2.3 Other forms of work

We note that there are other forces besides pressure forces, and those forces can also do work. Consider

- a stretching wire stretched by tension force \mathcal{T} through length change dL . The differential work is

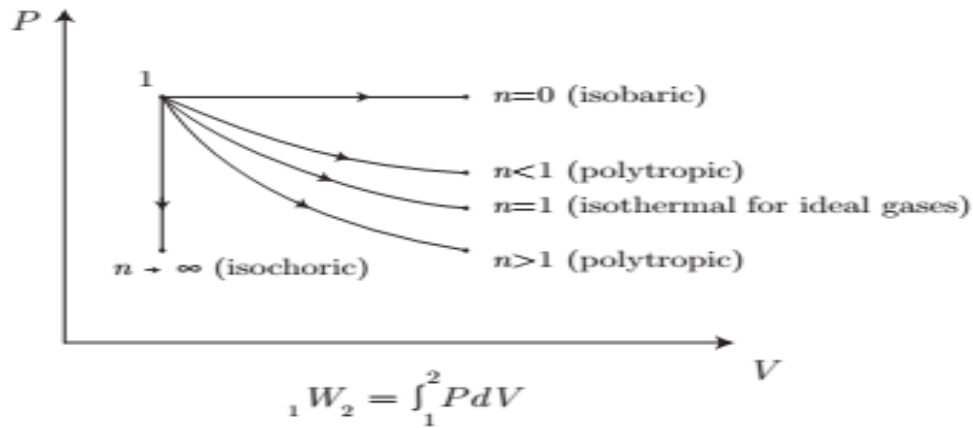


Figure 4.6: $P - V$ diagram for various polytropic processes.

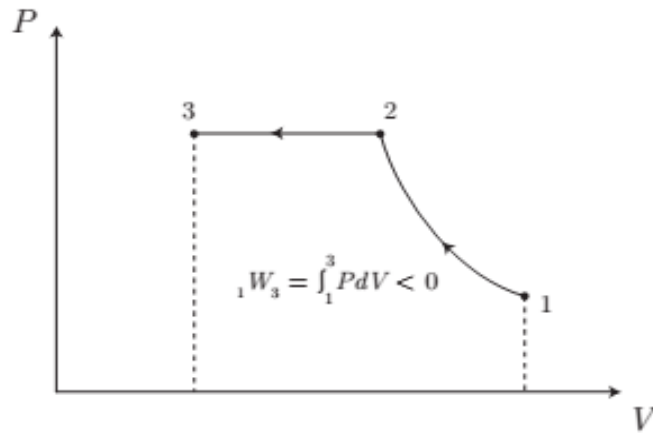


Figure 4.7: Sketch of two-step, isothermal-isobaric, compression of an ideal gas.

$$\delta W = -\mathcal{T}dL. \quad (4.107)$$

- a surface with surface tension \mathcal{S} . The differential work is

$$\delta W = -\mathcal{S}dA. \quad (4.108)$$

- a system with electrical work where \mathcal{E} is the electrical field strength, q is the particle charge, and x is the distance:

$$\delta W = -q\mathcal{E}dx. \quad (4.109)$$

In total, for materials which are more than simple compressible substances, we have

$$\delta W = -PdV - \mathcal{T}dL - \mathcal{S}dA - q\mathcal{E}dx - \dots \quad (4.110)$$

It can be shown that the more work modes we include, the more independent thermodynamic variables are necessary to specify the state of the system.

Lastly we note that a gas expanding into a vacuum has ${}_1W_2 \neq \int_1^2 P dV$ because it is inherently a non-equilibrium process.

4.3. Heat

Let us make the following definition:

- **HEAT:** a form of energy transferred across the boundary of a system at a given temperature to another system (or the surroundings) at a different temperature by virtue of the temperature difference between the two.

We adopt the notion that bodies do not contain heat, but that heat only has relevance as a type of energy that crosses system boundaries. Note that work is in a similar class; it is not contained within a system, but can be identified when it crosses system boundaries. We will make a distinction between heat and work energy transfers.

We also note that when two bodies are at the same temperature, there can be no heat transferred between the two bodies. The subject of *heat transfer* considers the details of the heat transfer process. There are three fundamental classes of heat transfer:

- *heat diffusion, also called conduction.* Physically this is due to local effects. Bacon is fried via conduction effects as a culinary example. This is characterized by Fourier's law¹

$$\mathbf{q} = -\mathbf{k}\nabla T, \quad (4.111)$$

where \mathbf{q} is the *heat flux vector* with units $J/s/m^2 = W/m^2$, \mathbf{k} is the *thermal conductivity* with units $J/s/m/K = W/m/K$, and ∇T is the vector representing the gradient of temperature. Recall that ∇T is a vector pointing in the direction in which T rises most rapidly. Because of the minus sign, we see then that the thermal energy flows in the direction of most rapid temperature decrease. This law was developed by Joseph Fourier, who built an elegant and correct theory of a special case of non-equilibrium thermodynamics before the laws of equilibrium thermodynamics were formulated, let alone fully understood. Fourier is depicted in Fig. 4.16

In one dimension, we get

$$\mathbf{q} = -\mathbf{k}\frac{dT}{dx}. \quad (4.112)$$

If we multiply by the local cross-sectional area, we find $\dot{Q} = \mathbf{q}A$, and

$$\dot{Q} = -\mathbf{k}A\frac{dT}{dx} \sim -\mathbf{k}A\frac{T_{hot} - T_{cold}}{L}. \quad (4.113)$$

Here, \dot{Q} has units J/s or W (Watts).

Fig 4.16. Jean Baptiste Joseph Fourier (1768-1830), French physicist and mathematician who developed a correct theory of heat conduction



- *convection*. This is actually a version of conduction, albeit enhanced by fluid flow. For some systems, convective effects are well modeled by Newton's law of cooling⁴³:

$$q = h(T_{hot} - T_{cold}), \quad (4.114)$$

$$\dot{Q} = qA = hA(T_{hot} - T_{cold}). \quad (4.115)$$

Here, h is a constant with units $W/m^2/K$.

- *thermal radiation*. Physically this is due to remote effects. The earth is heated by the sun via radiation effects, not conductive energy diffusion. For some systems, the radiative heat transfer rate is well modeled by

$$q = \sigma(T_{hot}^4 - T_{cold}^4), \quad (4.116)$$

$$\dot{Q} = qA = \sigma A(T_{hot}^4 - T_{cold}^4). \quad (4.117)$$

Here, σ is the Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8} W/m^2/K^4$.

We adopt the traditional engineering sign convention for heat:

- + heat enters the system,
- - heat leaves the system.

The sign convention again is motivated by nineteenth century steam engines. Heat had to be added into a system to get work out of the system. Since engineers were and are concerned with this problem, this convention is taken.

We define a special kind of process in which $Q = 0$ as

- **ADIABATIC**: a type of process for which there is no heat transfer.

The word "adiabatic" was first used by Rankine⁴⁴. It is from the Greek ἀδιάβατος: not to be passed through; in detail, ἀ (not) + διά (through) + βατός (passable). An image of Rankine's text containing the first use of the word is shown in Fig. 4.17.

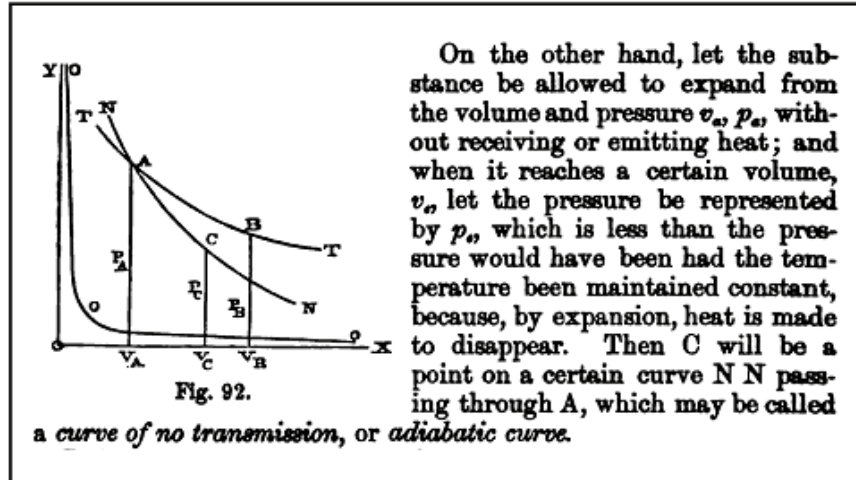


Figure 4.17: Image of the first modern use of the word “adiabatic” from [Rankine's 1859 text](#).

As is work, heat transfer is a path function characterized by inexact differentials. We take

$${}_1Q_2 = \int_1^2 \delta Q, \quad (4.118)$$

$$\dot{Q} = \frac{\delta Q}{dt}, \quad (4.119)$$

$$q = \frac{Q}{m}. \quad (4.120)$$

Here, q is the specific thermal energy transfer. It has units J/kg . Note $q \neq \mathbf{q}$, where \mathbf{q} is the heat flux with units W/m^2 . In this thermodynamics course, we will mainly be concerned with q . In a heat transfer course, \mathbf{q} is more important.

Now, ${}_1W_2 = \int_1^2 P dV$. We will see in future chapters that there is an equivalent for heat in that ${}_1Q_2 = \int_1^2 T dS$, where S is the *entropy*, to be defined later.

We finish with some notes of comparison:

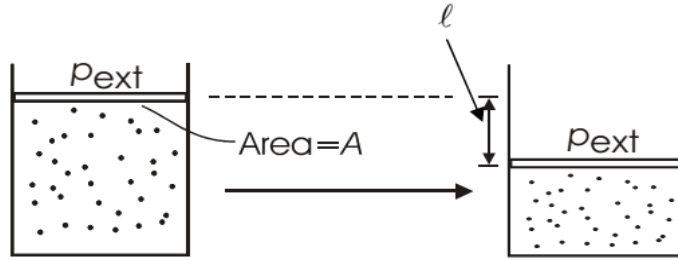
- Q and W as well as q and w are affiliated with transient phenomena; both cross boundaries when the system changes state.
- Q and W as well as q and w only exist at system boundaries.
- Q and W as well as q and w are both path-dependent, have inexact differentials, and are not properties of the system.

NOTES

- Work: $w = F \cdot \ell$
↑ applied force ↑ distance

Expansion work

$$F = p_{ext} A$$



$$w = -(p_{ext} A) l = -p_{ext} \Delta V$$

convention:

Having a "-" sign here implies $w > 0$ if $\Delta V < 0$, that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings ($\Delta V > 0$) then $w < 0$.

If p_{ext} is not constant, then we have to look at infinitesimal changes

$$dw = -p_{ext} dV \quad d \text{ means this is not an exact differential}$$

$$\text{Integral } w = -\int_1^2 p_{ext} dV \quad \text{depends on the path!!!}$$

- Path dependence of w

Example: assume a reversible process so that $p_{ext} = p$

$$\text{Ar} (g, p_1, V_1) = \text{Ar} (g, p_2, V_2)$$

Compression $V_1 > V_2$ and $p_1 < p_2$

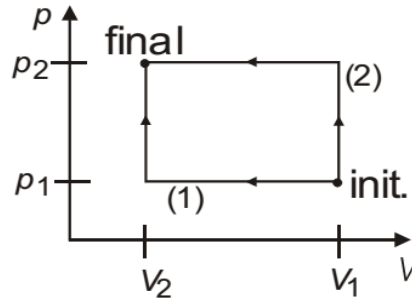


Two paths:

- (1) First $V_1 \rightarrow V_2$ at $p = p_1$ then $p_1 \rightarrow p_2$ at $V = V_2$
- (2) First $p_1 \rightarrow p_2$ at $V = V_1$ then $V_1 \rightarrow V_2$ at $p = p_2$

$$Ar(g, p_1, V_1) = Ar(g, p_1, V_2) = Ar(g, p_2, V_2)$$

$$Ar(g, p_1, V_1) = Ar(g, p_2, V_1) = Ar(g, p_2, V_2)$$



$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext} dV - \int_{V_2}^{V_1} p_{ext} dV$$

$$= -\int_{V_1}^{V_2} p_1 dV = -p_1(V_2 - V_1)$$

$$w_{(2)} = -\int_{V_1}^{V_1} p_{ext} dV - \int_{V_1}^{V_2} p_{ext} dV$$

$$= -\int_{V_1}^{V_2} p_2 dV = -p_2(V_2 - V_1)$$

$$w_{(1)} = p_1(V_1 - V_2)$$

$$w_{(2)} = p_2(V_1 - V_2)$$

(Note $w > 0$, work done to system to compress it)

$$w_{(1)} \neq w_{(2)} !!!$$

Note for the closed cycle [path (1)] - [path (2)], $\oint dw \neq 0$

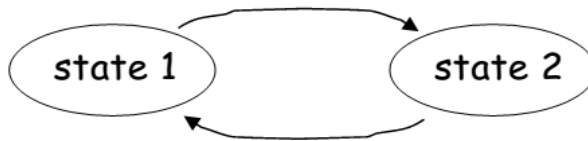
w is not a state function

cannot write $w = f(p, V)$

WORK

Work (w) is not a function of state.

For a cyclic process, it is possible for $\oint dw \neq 0$



HEAT

That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.

Sign convention: If heat enters the system, then it is positive.

Heat (q), like w , is a function of path. Not a state function

It is possible to have a change of state

$$(p_1, V_1, T_1) = (p_2, V_2, T_2)$$

adiabatically (without heat transferred)
or nonadiabatically.

Historically measured in calories

[1 cal = heat needed to raise 1 g H₂O 1°C,
from 14.5°C to 15.5°C]

The modern unit of heat (and work) is the Joule.

$$1 \text{ cal} = 4.184 \text{ J}$$

It is a general property of the energy added to or subtracted from a system that it is the product of an intensive state quantity (pressure) and the change of an extensive state quantity (volume). We can illustrate this with further examples. If the system, for instance, contains an electric charge q , this charge gives rise to an electric potential ϕ . If one wants to add another charge dq with the same sign to the system, one has to perform an amount of work

$$dW = \phi dq$$

The locally defined electric potential is the intensive quantity which describes the resistance of the system against adding another charge, just as the pressure is the resistance against a compression. Here the sign is caused by the fact that adding a positive charge while the potential is positive corresponds to work performed on the system,

If our thermodynamic system has an electric or magnetic dipole moment, adding another dipole to the system requires the work

$$\delta W_{el} = \vec{E} \cdot d\vec{D}_{el}$$

$$\delta W_{mag} = \vec{B} \cdot d\vec{D}_{mag}$$

Here the intensive field quantities are the electric and magnetic fields (\vec{E} and \vec{B}), while $d\vec{D}$ denotes the change of the total dipole moment, which is an extensive quantity.

We define

$$dW = \mu dN$$

as the work necessary to change the particle number by dN particles. The intensive field quantity is called the *chemical potential* and represents the resistance of the system against adding particles.

All different kinds of work have the generic property that they can be converted into each other without restrictions. For example, we can lift a weight with electrical energy or gain electrical energy from mechanical work with the help of a generator. There is no principle objection that these conversions do not proceed completely, i.e., with a rate of 100%, although real energy converters always have losses.

Sign convention

In physics (as opposed to engineering) we are generally interested in changes of the system and therefore consider work to be defined as the work done **ON** the system by its surroundings. Hence for a reversible change of volume of a system consisting of a fluid,

$$dW = -PdV$$

If dV is negative, the gas is compressed and the work done on it, $-PdV$, is positive.

Dissipative processes

Unlike for a reversible process where we can specify $dW = -PdV$, it is not possible to specify work done in terms of state variables of the system for dissipative processes, eg stirring. Although the work done may be quantified, this requires knowledge of external forces. Reversing the process, via controlling the surroundings, does not reverse the sign of the work done eg reversing the direction of stirring does not extract energy from the system. Therefore dissipative processes \Rightarrow **irreversible**. Irreversible processes where there is no direct dissipation (conversion of work into random motion) can also occur eg the irreversible flow of heat between bodies at different temperatures (we will see later that this represents a loss of potential to do work).

What is Heat

Newton: 1690

The rate of heat loss of a body is proportional to the temperature difference between the body and its surroundings.

Lavoisier: 1790

Heat consists of a self-repellent fluid, caloric, that flows from hotter bodies to colder bodies.

Joule and Thomson: 1851

Heat is not a substance, but a dynamical form of mechanical effect

If a THERMALLY ISOLATED system is brought from one equilibrium state to another, the work necessary is independent of the process used.

Heat is the exchange of energy between the system and the surroundings that cannot be identified as work (eg mechanical work).

LECTURE 5: THE FIRST LAW OF THERMODYNAMICS

Content of Lecture 5

5.1. Representations of the first law

5.1.1. Cycle

5.1.2. Process

5.2. Specific internal energy for general materials

5.3. Specific enthalpy for general materials

5.4. Specific heat capacity

5.5. Caloric equations of state

5.5.1. Ideal gases

5.5.2. Liquids and solids

5.5.3. General materials

5.6. Time-dependency

5.7. Final comments on conservation

5.1. Representations of the first law

There are a variety of ways to represent the first law of thermodynamics, also known as the principle of *conservation of energy*. Some of them are not obvious, but have withstood the scrutiny of detailed experiment. Perhaps the simplest, but also the most obtuse, is the following.

5.1.1 Cycle

- **FIRST LAW OF THERMODYNAMICS:** During any cycle, the cyclic integral of heat added to a system is proportional to the cyclic integral of work done by the system.

If we denote a cyclic integral by \oint , the mathematical representation of this law is

$$\mathcal{J} \oint \delta Q = \oint \delta W, \quad (Q \text{ in } \textit{cal}, W \text{ in } \textit{J}). \quad (5.1)$$

Here \mathcal{J} is a proportionality constant, sometimes known as the *mechanical equivalent of heat*. Now, during the development of thermodynamics, Q was measured in *cal*, where 1 *cal* represented the energy necessary to raise 1 *g* of water 1 °C, and W was measured in *J* which represented the work done in moving a 1 *kg* mass against a force of 1 *N*.

In the now-discredited caloric theory, heat was thought to be a fluid and not explicitly related to work. This theory began to lose credibility with the experiments conducted in Bavaria by the colorful American scientist Sir Benjamin Thompson¹ (Count Rumford). By doing work in boring a cannon immersed in water and boiling the water, Thompson was able to demonstrate that the work of boring was converted into heat. Thompson's image is shown in Fig. 5.1a. Thompson's etching of the cannon used in his experiment is reproduced in Fig. 5.1b.

In the 1840s there was considerable effort to relate mechanical and thermal energy and thus measure \mathcal{J} . There is some controversy over who first quantified this value. By many accounts Julius Robert von Mayer achieved the first success in 1842² though his exposition often lacked the mathematical and experimental support that many scientists demand. Mayer is pictured in Fig. 5.2. Contemporaneously, and with more publicity, Joule spent considerable effort in carefully measuring \mathcal{J} ^{3,4}. He estimated $\mathcal{J} = 4.41 \text{ J/cal}$, which has since been corrected to

$$\mathcal{J} = 4.1860 \frac{J}{cal}. \quad (5.2)$$

We give a portrait of Joule in Fig. 5.3a. A nineteenth century etching of Joule's device is given in Fig. 5.3b. A modern full-scale replica of Joule's apparatus designed and constructed by Mr. Leon Hluchota and Prof. Patrick F. Dunn, based upon Joule's original experimental display in the Science Museum, London, and in use in undergraduate laboratories at the University of Notre Dame, is shown in Fig. 5.3c.

Fig 5.1. A portrait of Sir Benjamin Thompson (Count Rumford)(1753-1814), American scientist whose cannon-boring experiments discredited the caloric theory and the image his cannon(1798)

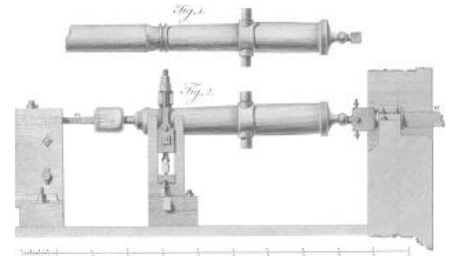
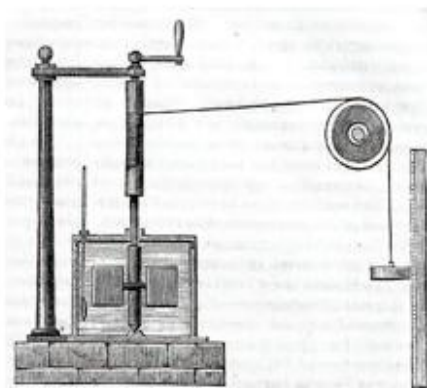


Fig 5.2. Julius Robert von Mayer (1814-1878), German physician and physicist who in 1842 said “Energy can be neither created nor destroyed.



a)



b)



c)

Fig 5.3. a) James Prescott Joule (1818-1889), English experimentalist who demonstrated the mechanical equivalent of heat; b) Sketch of Joule's original apparatus (1869); c) Operational full-scale replication of Joule's experiment to measure the mechanical equivalent of heat at the University of Notre Dame.

While Joule performed the key experiments, the critical acceptance of the first law is attributed by many to the work of Hermann von Helmholtz,⁵ pictured in Fig. 5.4. However, Truesdell notes that in this work Helmholtz restricts his conservation principle to kinetic and potential energies.⁶ The classical theoretical framework for the first law and more was firmly solidified by Rudolf Clausius.⁷ Clausius is depicted in Fig. 5.5.

Now, in this class, we will not bother much with the mechanical equivalent of heat, and simply insist that Q be measured in units of work. When Q has units of J , then $\mathcal{J} = 1$, and we recover our preferred form of the first law:

$$\oint \delta Q = \oint \delta W, \quad (Q \text{ in } J, W \text{ in } J). \quad (5.3)$$

Fig 5.4. Hermann Ludwig Ferdinand von Helmholtz (1821-1894), German physician and physicist who impacted nearly all of nineteenth century



Fig 5.5. Rudolf Julius Emmanuel Clausius (1822-1888), German theoretician who systematized classical thermodynamics into a science.



5.1.2 Process

We arrive at an alternate representation of the first law by the following analysis. Consider the sketch of Fig. 5.6. Now, consider two cycles, each passing through points 1 and 2, albeit

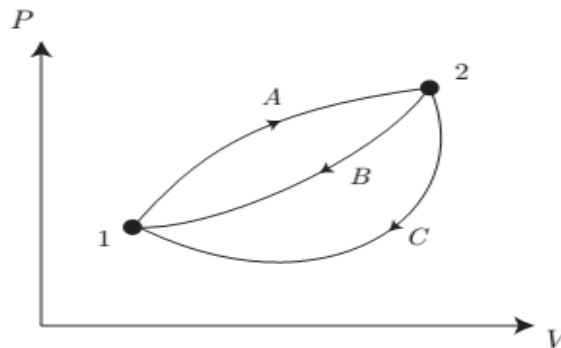


Figure 5.6: Sketch of $P - V$ diagram for various combinations of processes forming cyclic integrals.

via different paths:

- Cycle *I*: 1 to 2 on Path *A* followed by 2 to 1 on Path *B*,
- Cycle *II*: 1 to 2 on Path *A* followed by 2 to 1 on Path *C*.

The only difference between Cycles *I* and *II* is they take different return paths. Now, write the first law $\oint \delta Q = \oint \delta W$ for Cycle *I*:

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_B = \int_1^2 \delta W_A + \int_2^1 \delta W_B, \quad \text{Cycle } I. \quad (5.4)$$

For Cycle *II*, we have similarly

$$\int_1^2 \delta Q_A + \int_2^1 \delta Q_C = \int_1^2 \delta W_A + \int_2^1 \delta W_C, \quad \text{Cycle } II. \quad (5.5)$$

Now, subtract Eq. (5.5) from Eq. (5.4) to get

$$\int_2^1 \delta Q_B - \int_2^1 \delta Q_C = \int_2^1 \delta W_B - \int_2^1 \delta W_C. \quad (5.6)$$

Rearrange Eq. (5.6) to get

$$\int_2^1 (\delta Q - \delta W)_B = \int_2^1 (\delta Q - \delta W)_C. \quad (5.7)$$

Now, *B* and *C* are *arbitrary* paths; Eq. (5.7) asserts that the integral of $\delta Q - \delta W$ from 2 to 1 is *path-independent*. This is in spite of the fact that both *W* and, as we will see later, *Q* are path-dependent quantities. Therefore, we can deduce that this defines

- **ENERGY**: a thermodynamic property which is a theoretical construct suggested by the first law of thermodynamics as something to account for the difference between heat transfer and work in any process between the same start and end states.

Energy is a new extensive property of the system denoted by *E*. While we like to think we have intuition for what constitutes energy, it really is an elusive quantity. Viewed at another way, the Newtonian mechanical energy is easily visualized in terms of kinetic and potential energy, but it is not always conserved! Our new energy includes thermal energy, which we think we can easily feel, so we still have a good intuition for it. So we have generalized energy so that it is always conserved, at the expense of losing the ability to easily visualize it.

Recall that properties depend only on the state and not the path taken to arrive at the state. Let us then take the following definition for the differential of *E*:

$$\boxed{dE = \delta Q - \delta W}. \quad (5.8)$$

If we integrate from 1 to 2, we get

$$\int_1^2 dE = \int_1^2 \delta Q - \int_1^2 \delta W, \quad (5.9)$$

yielding

$$\boxed{E_2 - E_1 = {}_1Q_2 - {}_1W_2.} \quad (5.10)$$

Equation (5.10) is the alternate representation of the

- **FIRST LAW OF THERMODYNAMICS:** For a system undergoing a process, the change in energy is equal to the heat added to the system minus the work done by the system.

Now, we consider E to represent the *total energy* of the system. It has units of J . It includes energy which is

- potential,
- kinetic,
- thermal,
- chemical,
- electrical,
- magnetic,

- etc.

We will find it useful to lump all of the types of energy which are not potential or kinetic into a single term U , which we call

- **INTERNAL ENERGY:** that portion of total energy E which is not kinetic or potential energy. It includes thermal, chemical, electric, magnetic, and other forms of energy.

We take U to have units of J . We call the kinetic energy KE and the potential energy PE . So we take

$$\underbrace{E}_{\text{total energy}} = \underbrace{U}_{\text{internal energy}} + \underbrace{KE}_{\text{kinetic energy}} + \underbrace{PE}_{\text{potential energy}}. \quad (5.11)$$

In this course we shall mainly be concerned with changes of U which are associated with changes of the thermal energy of the system. A useful way to think of thermal energy is

- **THERMAL ENERGY:** kinetic energy associated with random motions of molecules at the *microscale*.

We can only observe this microscale kinetic energy with great difficulty. We usually have no hope of having any detailed knowledge of it, and so only consider it in the average. In fact, the temperature is a measure of the average microscale kinetic energy. We distinguish the thermal energy from KE , which we take to exist at the observable macroscale.

Each form of energy is an extensive property of the system. Taking differentials of Eq. (5.11), we get

$$dE = dU + d(KE) + d(PE). \quad (5.12)$$

So the first law, $dE = \delta Q - \delta W$, can be written as

$$dU + d(KE) + d(PE) = \delta Q - \delta W. \quad (5.13)$$

In the next two examples, let us consider two special cases of Eq. (5.13), which are familiar from Newtonian mechanics.

Now, since $dE = dU + d(KE) + d(PE)$ from Eq.(5.11), we get

$$dE = dU + mv \, dv + mg \, dz. \quad (5.34)$$

Integrate Eq. (5.34) from state 1 to state 2 to get

$$E_2 - E_1 = U_2 - U_1 + \frac{1}{2}m(v_2^2 - v_1^2) + mg(z_2 - z_1). \quad (5.35)$$

Now, substitute Eq. (5.35) into Eq. (5.10) to obtain

$$\underbrace{U_2 - U_1 + \frac{1}{2}m(v_2^2 - v_1^2) + mg(z_2 - z_1)}_{=E_2-E_1} = {}_1Q_2 - {}_1W_2. \quad (5.36)$$

Now, if m is a constant, as it will be for a system, we can divide both sides by m to get

$$u_2 - u_1 + \frac{1}{2}(v_2^2 - v_1^2) + g(z_2 - z_1) = {}_1q_2 - {}_1w_2. \quad (5.37)$$

Here, we have defined the new intensive variables

- $u \equiv U/m$, the internal energy per unit mass, also known as the *specific internal energy*. It has units kJ/kg . It is an intensive thermodynamic property.
- ${}_1q_2 \equiv {}_1Q_2/m$, the heat transfer per unit mass. It has units kJ/kg and is *not* a thermodynamic property.
- ${}_1w_2 \equiv {}_1W_2/m$, the work per unit mass. It has units kJ/kg and is *not* a thermodynamic property.

5.2. Specific internal energy for general materials

Just as P , v , and T are thermodynamic properties, so is u . In fact, it can be considered to be one of the necessary two properties necessary to define a third. So, for example, if we are given P and u , we could find $v = v(P, u)$ or $T = T(P, u)$.

More importantly, let us consider the most general form for u ; a form where u is a function of at most two independent thermodynamic variables, say T and v ,

$$u = u(T, v). \quad (5.38)$$

For materials such as water, $u(T, v)$ is tabulated. Note that the tables must presume a reference value for energy so as to give it an absolute nature. However, as long as we confine our thermodynamics to a single substance, *differences in energy will be the only quantities that have relevance in determining physical quantities of interest*. That is to say, the reference state will not be important for single material problems. This is not true for multiple material problems such as when chemical reactions are present.

Similar to v_f and v_g , the tables have

- u_f : the specific internal energy of a saturated liquid, and
- u_g : the specific internal energy of a saturated vapor.

Also similar to v , we have

$$u_{fg} = u_g - u_f. \quad (5.39)$$

We also get a similar analysis for quality x as for volume. For a two-phase mixture, the total energy of the mixture is the sum of the energies of the components:

$$U = U_{liq} + U_{vap}, \quad (5.40)$$

$$mu = m_{liq}u_f + m_{vap}u_g, \quad (5.41)$$

$$u = \frac{m_{liq}}{m}u_f + \frac{m_{vap}}{m}u_g, \quad (5.42)$$

$$u = \frac{m - m_{vap}}{m}u_f + \frac{m_{vap}}{m}u_g, \quad (5.43)$$

$$u = (1 - x)u_f + xu_g, \quad (5.44)$$

$$u = u_f + x(u_g - u_f), \quad (5.45)$$

$$u = u_f + xu_{fg}. \quad (5.46)$$

We can solve for x by inverting Eq. (5.46) to get

$$x = \frac{u - u_f}{u_{fg}}. \quad (5.47)$$

Let us consider the heat transfer for an isochoric process in which we also have $\Delta KE = \Delta PE = 0$. Because the process is isochoric ${}_1W_2 = \int_1^2 PdV = 0$. So the first law, Eq. (5.36), reduces to

$$U_2 - U_1 = {}_1Q_2, \quad (5.48)$$

$${}_1Q_2 = U_2 - U_1 = \Delta U. \quad (5.49)$$

The change in U gives the heat transfer for isochoric processes.

5.3. Specific enthalpy for general materials

Let us define a new thermodynamic property, *enthalpy*, in terms of known thermodynamic properties. The extensive total enthalpy H , and intensive specific enthalpy h are defined as

$$H \equiv U + PV, \quad (5.50)$$

$$h = \frac{H}{m} = \frac{U}{m} + P\frac{V}{m}. \quad (5.51)$$

Thus,

$$\boxed{h = u + Pv.} \quad (5.52)$$

Its most important feature is its utility in control volume analysis which will be fully discussed in Sec. 6.1.2.2.4; its underlying mathematical rationale will be given in Sec. 11.3.

The first written use of the word “enthalpy” is given by Porter^[8] who notes the term was introduced by the Dutch physicist and Nobel laureate Heike Kamerlingh Onnes (1853-1926). The word is from the Greek $\epsilon\nu\theta\acute{\alpha}\lambda\pi\epsilon\iota\nu$, meaning “to warm in.” We give an image of Porter’s citation of Onnes’ usage in Fig. 5.9.

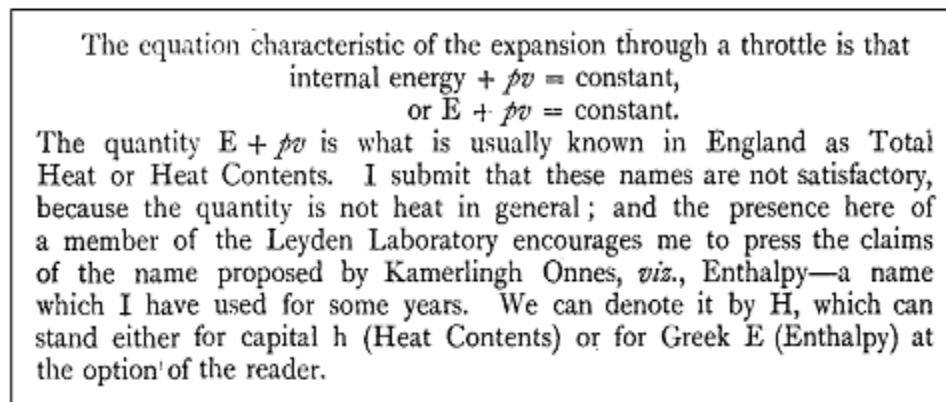


Figure 5.9: Image of first known printed use of the word “enthalpy” from Porter, 1922.

Eq. (5.52) is valid for general materials. It will be seen to be useful for many problems, though in principle, we could get by with u alone just as well. Now, since u , P , and v are thermodynamic properties, so then is h :

$$h = h(T, P). \quad (5.53)$$

Sometimes tables give h and we need to find u ; thus,

$$u = h - Pv. \quad (5.54)$$

Similar to u , we can easily show

$$h = h_f + xh_{fg}, \quad x = \frac{h - h_f}{h_{fg}}. \quad (5.55)$$

The enthalpy is especially valuable for analyzing isobaric processes. Consider a special isobaric process in which $P_1 = P_2 = P$, $\Delta KE = \Delta PE = 0$. Then the first law, Eq. (5.36), reduces to

$$U_2 - U_1 = {}_1Q_2 - {}_1W_2. \quad (5.56)$$

Since ${}_1W_2 = \int_1^2 PdV = P(V_2 - V_1)$ for the isobaric process, the first law reduces to

$$U_2 - U_1 = {}_1Q_2 - P(V_2 - V_1), \quad (5.57)$$

$$U_2 - U_1 = {}_1Q_2 - P_2V_2 + P_1V_1, \quad (5.58)$$

$${}_1Q_2 = \underbrace{(U_2 + P_2V_2)}_{=H_2} - \underbrace{(U_1 + P_1V_1)}_{=H_1}, \quad (5.59)$$

$${}_1Q_2 = H_2 - H_1 = \Delta H. \quad (5.60)$$

The change in H gives the heat transfer for isobaric processes.

5.4. Specific heat capacity

We loosely define the

- **SPECIFIC HEAT CAPACITY:** the amount of heat needed to raise the temperature of a unit mass of material by one degree.

The word is a relic of the discredited caloric theory of heat in which heat was thought to be a fluid which could somehow fill its container. We often simply call it the “specific heat.” We give the specific heat the symbol c . It has units $kJ/kg/K$. Its loose mathematical definition is

$$c \simeq \frac{1}{m} \frac{\delta Q}{\delta T}. \quad (5.61)$$

We also define the extensive heat capacity as $C = \delta Q/\delta T$, where C has units kJ/K . We will not use C explicitly from here on.

It turns out that since δQ is path-dependent, so is c . So let us specify two common paths:

- **SPECIFIC HEAT AT CONSTANT VOLUME:** c_v . We determine this on a path which is isochoric. On such a path, the first law holds that $\delta Q = dU$, since $\delta W = 0$. So we take

$$c_v = \frac{1}{m} \left. \frac{\partial U}{\partial T} \right|_v. \quad (5.62)$$

Since $u = U/m$, and we take m to be constant, we get

$$\boxed{c_v = \left. \frac{\partial u}{\partial T} \right|_v}. \quad (5.63)$$

Now, for general materials $u = u(T, v)$, so we see that

$$c_v = c_v(T, v), \quad (5.64)$$

that is to say, $c_v(T, v)$ is itself a thermodynamic property for general materials. It can vary with two independent variables. We shall see later for some materials it varies only with T , and for other materials, it is actually a constant.

- **SPECIFIC HEAT AT CONSTANT PRESSURE: c_P .** We determine this on a path which is isobaric. On such a path, the first law holds that $\delta Q = dH$. So we take

$$c_P = \left. \frac{1}{m} \frac{\partial H}{\partial T} \right|_P. \quad (5.65)$$

Since $h = H/m$, and we take m to be constant, we get

$$\boxed{c_P = \left. \frac{\partial h}{\partial T} \right|_P}. \quad (5.66)$$

Now, for general materials $h = h(T, P)$, so we see that

$$c_P = c_P(T, P), \quad (5.67)$$

that is to say, $c_P(T, P)$ is itself a thermodynamic property for general materials. It can vary with two independent variables. We shall see later for some materials it varies only with T , and for other materials, it is actually a constant.

- **SPECIFIC HEAT FOR INCOMPRESSIBLE MATERIALS: c .** Most liquids and solids under moderate to low pressure conditions ($P < 1 \text{ GPa}$) are well modeled as incompressible. Thus, in any heating process, there will be little if any associated work of compression. For such a material, there is no need to distinguish c_v and c_P , so we simply use c for the specific heat. We thus take

$$c(T) = \frac{du}{dT}. \quad (5.68)$$

Often, especially if the temperature changes are small, we can ignore the temperature variation of c for incompressible materials and simply take

$$c = \frac{du}{dT}. \quad (5.69)$$

More rigorous mathematical discussion of specific heat capacity will be given in Sec. [11.4](#)

5.5. Caloric equations of state

Recall that thermal equations of state are given by $P = P(T, v)$. We also have equations of state for the energy. We call such a relation a

- **CALORIC EQUATION OF STATE:** an equation which gives the energy as a function of two independent state variables. An example is the general form:

$$u = u(T, v). \quad (5.70)$$

In a later chapter we shall see there are a few restrictions on the form $u(T, v)$ can take. In a complicated fashion, it is not entirely independent of the thermal state equation $P = P(T, v)$.

One of the more confusing notions to beginning students of thermodynamics is which forms of energy and specific heat are appropriate for which materials. Here, we discuss them in more detail, moving from simple to complex.

5.5.1 Ideal Gases

For ideal gases, we have $Pv = RT$. Ideal gases can be either *calorically perfect* or *calorically imperfect*. For all ideal gases, be they calorically perfect or calorically imperfect, it will be proved in Sec. [11.4](#) that the caloric equation of state takes on a simpler form:

$$u = u(T). \quad (5.71)$$

Now, we can specify h for an ideal gas. From Eq. [\(5.52\)](#), $h = u + Pv$, and the ideal gas law, $Pv = RT$, we get

$$h = u(T) + RT. \quad (5.72)$$

Thus, the enthalpy of an ideal gas is a function of T only:

$$h = h(T). \quad (5.73)$$

Now, for the specific heats of an ideal gas, Eq. [\(5.63\)](#) gives

$$c_v(T, v) = \left. \frac{\partial u}{\partial T} \right|_v = \frac{d}{dT}(u(T)) = c_v(T). \quad (5.74)$$

Separating variables in Eq. [\(5.74\)](#), we can also say for an ideal gas

$$du = c_v(T)dT. \quad (5.75)$$

For c_P , Eq. [\(5.66\)](#) gives

$$c_P(T, P) = \left. \frac{\partial h}{\partial T} \right|_P = \frac{d}{dT}(h(T)) = c_P(T). \quad (5.76)$$

Separating variables in Eq. (5.76), we get then

$$dh = c_P(T)dT. \quad (5.77)$$

Now, we can differentiate Eq. (5.72) to get

$$dh = du + RdT. \quad (5.78)$$

Now, substitute Eqs. (5.75)(5.77) into Eq. (5.78) to get

$$c_P(T)dT = c_v(T)dT + RdT, \quad (5.79)$$

$$c_P(T) = c_v(T) + R. \quad (5.80)$$

$$\boxed{c_P(T) - c_v(T) = R.} \quad (5.81)$$

This is sometimes known as Mayer's relation. Last, let us define the *ratio of specific heats*, k , as

$$k = \frac{c_P}{c_v}. \quad (5.82)$$

For general materials $k = k(T, v)$. For an ideal gas, we have

$$k = \frac{c_v(T) + R}{c_v(T)} = 1 + \frac{R}{c_v(T)}. \quad (5.83)$$

So $k = k(T)$ for an ideal gas. We will see that $k(T)$ is often nearly constant. Since $R > 0$ and $c_v(T) > 0$, we must have $k > 1$ for an ideal gas. In a later chapter, it will later be seen this result extends to general gases.

5.5.1.1 Calorically perfect

A calorically perfect ideal gas (CPIG) has constant specific heat. Examples of CPIGs include noble and monatomic gases (e.g. He , Ne , Ar , O , H , N) over a wide range of temperatures and pressures, and more complex molecules (e.g. O_2 , N_2 , CO_2 , CH_4) over narrower bands of temperatures and pressures.

For the CPIG, c_v is a constant, so

$$\left. \frac{\partial u}{\partial T} \right|_v = c_v. \quad (5.84)$$

But for the ideal gas, $u = u(T)$, so the partial derivatives become total derivatives and

$$\frac{du}{dT} = c_v. \quad (5.85)$$

Integrating, we get the simple caloric equation of state:

$$\boxed{u(T) = u_o + c_v(T - T_o)}, \quad (5.86)$$

valid for CPIG.

Note that

$$u = u_o + c_v T - c_v T_o, \quad (5.87)$$

$$\underbrace{u + Pv}_{=h} = u_o + c_v T - c_v T_o + \underbrace{Pv}_{=RT}, \quad (5.88)$$

$$h = u_o + c_v T - c_v T_o + RT, \quad (5.89)$$

$$h = \underbrace{u_o + RT_o}_{=h_o} + \underbrace{(c_v + R)T}_{=c_P T} - \underbrace{(c_v T_o + RT_o)}_{=c_P T_o}, \quad (5.90)$$

$$h = h_o + c_P T - c_P T_o. \quad (5.91)$$

So

$$\boxed{h(T) = h_o + c_P(T - T_o)}, \quad (5.92)$$

valid for CPIG.

For a CPIG,

$$k = \frac{\bar{c}_P}{\bar{c}_v} = \frac{c_P}{c_v} = \text{constant}. \quad (5.93)$$

5.5.1.2 Calorically imperfect

For *calorically imperfect* ideal gases (CIIG), e.g. O_2 at moderate to high temperatures ($300 \text{ K} < T < 6000 \text{ K}$):

- $u = u(T)$,
- $c_v = c_v(T)$,
- $h = h(T)$,
- $c_P = c_P(T)$.

For such temperatures, our assumption of constant c_v is not as valid. But for ideal gases, we can still take $c_v = c_v(T)$, so

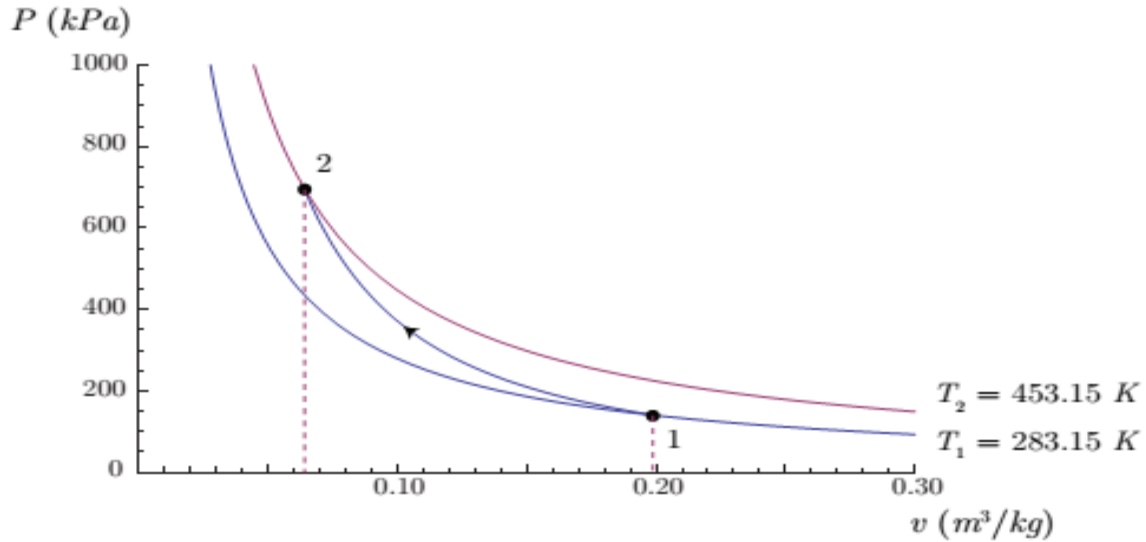


Figure 5.10: Plot of polytropic compression of Ar.

$$\frac{du}{dT} = c_v(T). \quad (5.115)$$

We can integrate via separation of variables to get

$$du = c_v(T)dT, \quad (5.116)$$

$$\int_1^2 du = \int_1^2 c_v(T)dT, \quad (5.117)$$

$$u_2 - u_1 = \int_1^2 c_v(T)dT. \quad (5.118)$$

We can interpret the difference in u as the area under the curve in a plot of $c_v(T)$ versus T as plotted in Fig. 5.11. More generally, we could say

$$\boxed{u(T) = u_o + \int_{T_o}^T c_v(\hat{T})d\hat{T}}, \quad (5.119)$$

valid for all ideal gases.

Here, \hat{T} is a dummy variable of integration. Similarly, we could show

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p(T)dT, \quad (5.120)$$

and more generally,

$$\boxed{h(T) = h_o + \int_{T_o}^T c_p(\hat{T})d\hat{T}}, \quad (5.121)$$

valid for all ideal gases.

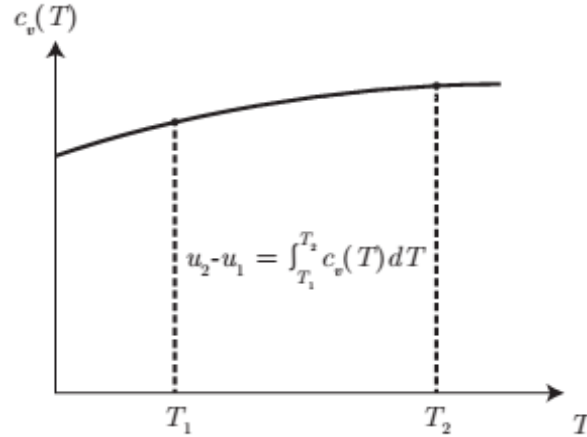


Figure 5.11: Relation between $u_2 - u_1$ and area under curve in a plot of $c_v(T)$ for calorically imperfect ideal gas.

Now, c_v , c_p and R all have units of $kJ/kg/K$. Let us consider the ratio

$$\frac{c_v}{R} = \frac{c_v M}{R M} = \frac{\frac{c_v}{M}}{\frac{R}{M}} = \frac{\bar{c}_v}{\bar{R}}. \quad (5.122)$$

The ratio is now in terms of molar specific properties with \bar{c}_v and \bar{R} having units of $kJ/kmole/K$. Note that \bar{R} is the universal gas constant. A plot of \bar{c}_v/\bar{R} versus T for a variety of simple molecules is given in Fig. 5.12. We note some remarkable facts:

- For monatomic gases, such as Ar , O , and H , $\bar{c}_v/\bar{R} = 3/2$ for a wide variety of temperatures.
- For diatomic gases, such as O_2 and H_2 for $T < 600 K$, $\bar{c}_v/\bar{R} \sim 5/2$, and for $T > 600 K$, $\bar{c}_v/\bar{R} \rightarrow 7/2$
- For larger molecules such as CO_2 or H_2O , \bar{c}_v/\bar{R} is larger still.

What we are seeing actually reflects some fundamental physics. We first note that statistical thermodynamics proves

- *Temperature is a measure of the average translational kinetic energy of a set of molecules.*

Now, we consider some features of Fig. 5.12

- Monatomic molecules, such as Ar , O or H have three fundamental modes of kinetic energy: translation in the x , y , and z directions. Each mode contributes $1/2$ to \bar{c}_v/\bar{R} , which sums to $3/2$.
- For diatomic molecules, we summarize the behavior in the sketch given in Fig. 5.13
 - At very low temperatures, diatomic molecules, such as H_2 or O_2 , act like monatomic molecules.

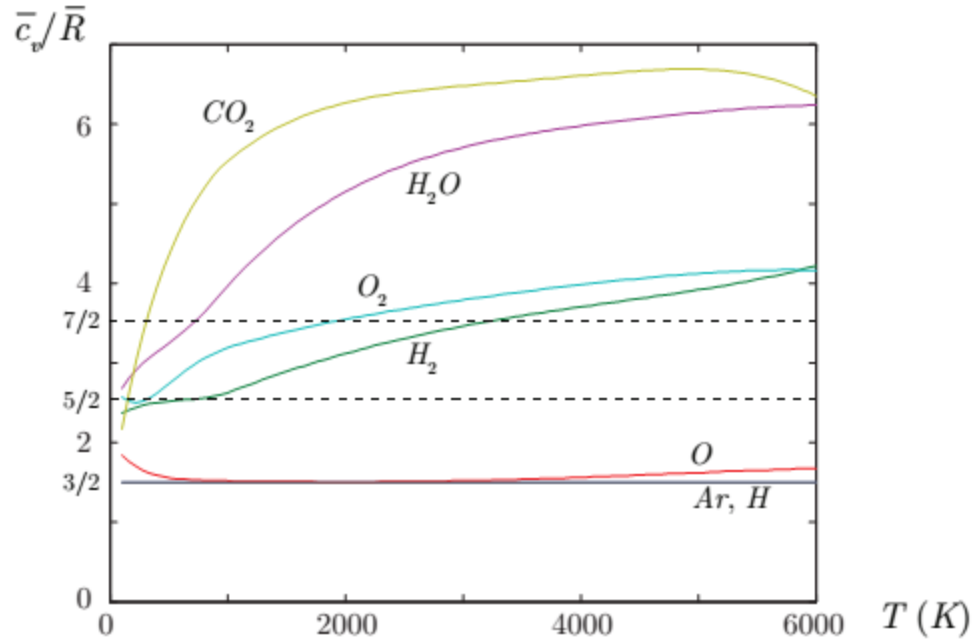


Figure 5.12: \bar{c}_v/\bar{R} as a function of T for several molecules.

- At low temperatures, diatomic molecules begin to rotate, and the rotational energy becomes an important component. In fact when energy is added to diatomic molecules, some is partitioned to translation and some is partitioned to rotation. There are two non-trivial axes of rotation, each adding $1/2$ to \bar{c}_v/\bar{R} , giving $\bar{c}_v/\bar{R} \sim 5/2$.
- At higher temperatures, diatomic molecules begin to vibrate as well, and this energy becomes an important component. There are two vibrational modes, one for kinetic energy and one for potential energy. Each adds another $1/2$ to \bar{c}_v/\bar{R} , giving $\bar{c}_v/\bar{R} \sim 7/2$ at high temperature.
- At higher temperatures still, the diatomic molecules begin to dissociate, e.g. $O_2 + O_2 \rightarrow 2O + O_2$.
- At even higher temperatures, its electrons are stripped, and it becomes an ionized plasma. This is important in engineering applications ranging from welding to atmospheric re-entry vehicles.
- For triatomic molecules such as H_2O or CO_2 , there are more modes of motion which can absorb energy, so the specific heat is higher still.

Feynman⁹ summarizes the argument that this preference for one type of energy over another (translation, rotational, vibrational) depending on temperature is surprising to those not

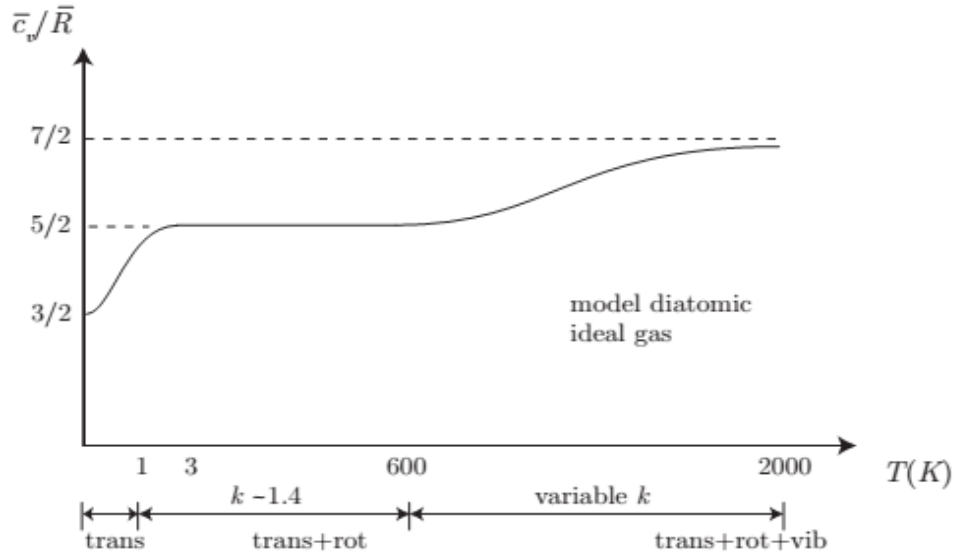


Figure 5.13: \bar{c}_v/\bar{R} as a function of T for a model diatomic gas. (Note a real gas would liquefy in the very low temperature region of the plot! So this model is really for a non-existent gas that has no liquid-inducing intermolecular forces.)

versed in quantum mechanics and violates standard assumptions of classical statistical mechanics. In fact, he notes that Maxwell had a hint of the problem as early as 1859, and stated this concern more directly in 1869. Maxwell summarized those concerns in an 1875 lecture, transcribed in *Nature*.¹⁰ Feynman argues that the reason for the energy partition observed in diatomic gases is a “failure of classical physics” and instead is a pure effect of quantum mechanics; that is to say $k = c_P(T)/c_v(T) = k(T)$ is a non-classical result! Employment of the theories of quantum and statistical mechanics allows an accounting for the observation that there is a preference of molecules to exist in lower energy states, and at those states, the discrete quantization is important. High energy vibrational states are less likely than translational states at low temperature. At higher temperature, there is a higher probability that all states are populated, and one recovers results consistent with classical physics.

Let us also recall that $c_P(T) - c_v(T) = R$; thus, $\bar{c}_P(T) - \bar{c}_v(T) = \bar{R}$. Let us summarize

- for monatomic gases,

$$c_v = \frac{3}{2}R, \quad (5.123)$$

$$c_P = c_v + R = \frac{5}{2}R, \quad (5.124)$$

$$\frac{c_P}{c_v} = k = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.6667. \quad (5.125)$$

- for diatomic gases at moderate temperature, $50 \text{ K} < T < 600 \text{ K}$,

$$c_v = \frac{5}{2}R, \quad (5.126)$$

$$c_P = c_v + R = \frac{7}{2}R, \quad (5.127)$$

$$\frac{c_P}{c_v} = k = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4. \quad (5.128)$$

To summarize, usually the most problematic case is whether or not specific heats vary with temperature in ideal gases. For low temperatures, the specific heat is well modeled as a constant; here the internal energy change is strictly proportional to the temperature change. For moderate to high temperatures, a temperature-variation of the specific heat is observed. Changes in internal energy are no longer strictly proportional to changes in temperature. The behavior is analogous to solid mechanics. At low strain ϵ , stress σ is proportional to strain, and the constant of proportionality is the modulus of elasticity E . For high strains, the linearity is lost; we could say the elastic modulus becomes a function of strain. We give a sketch in Fig. 5.14 of the comparison to solid mechanics

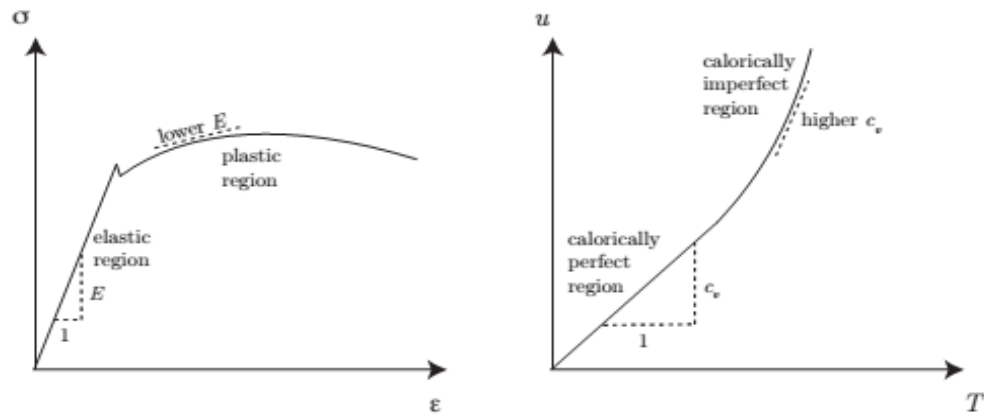


Figure 5.14: Sketch of comparison of stress-strain behavior in solids with ideal gas internal energy-temperature behavior.

There are four main ways to calculate changes in enthalpy for ideal gases:

- assumption of constant c_P evaluated at 298 K,
- assumption of constant c_P evaluated at an intermediate temperature,
- using a known analytic form of $c_P(T)$ in the direct integration of $\int_1^2 c_P(T)dT$, or
- estimation using the ideal gas tables.

5.5.2 Liquids and solids

Most liquids and solids for moderate pressures or below, $P < 1 \text{ GPa}$, are well modeled as incompressible. For such materials, we have caloric equations of state and specific heats of the form

- $u = u(T)$,
- $c = c(T)$.

For such a material

$$u(T) = u_o + \int_{T_o}^T c(\hat{T}) d\hat{T}, \quad (5.144)$$

and

$$\frac{du}{dT} = c(T). \quad (5.145)$$

Often, we can take a calorically perfect model in which c loses its temperature variation, and get the commonly used equations

$$\boxed{u(T) = u_o + c(T - T_o)}, \quad (5.146)$$

$$\boxed{\frac{du}{dT} = c}. \quad (5.147)$$

5.5.3 General materials

Examples of general materials include water and van der Waals gases. For such materials we have caloric equations of state and specific heats

- $u = u(T, v)$,
- $c_v = c_v(T, v)$,
- $h = h(T, P)$,

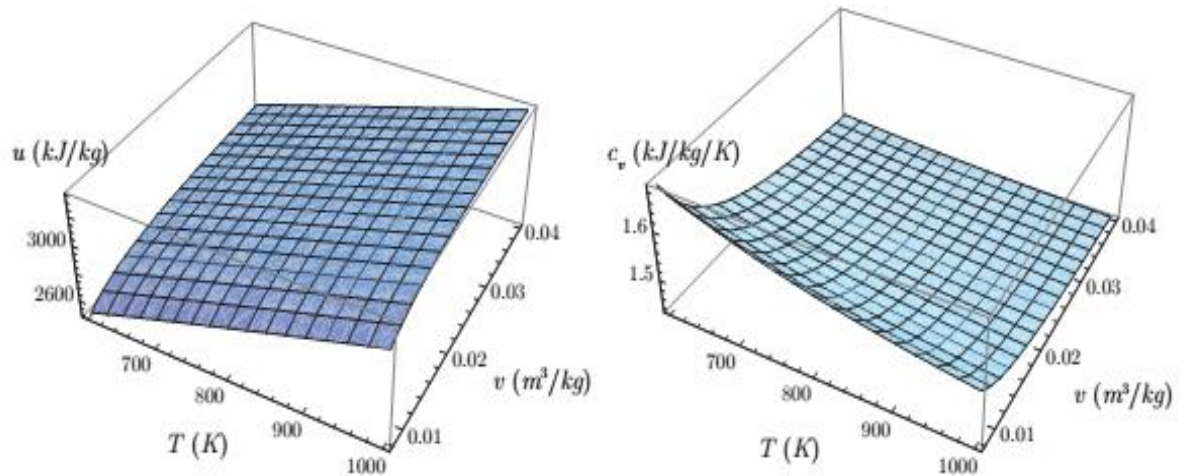


Figure 5.15: Sketch of $u = u(T, v)$, $c_v = c_v(T, v)$ using a Redlich-Kwong caloric state equation model for superheated water.

- $c_p = c_p(T, P)$.

A sketch of an estimate for $u(T, v)$ and $c_v(T, v)$ for superheated water is given in Fig. 5.15. Here, we selected a Redlich-Kwong model obeying

$$u(T, v) = \left(2863.75 \frac{\text{kJ}}{\text{kg}}\right) + \left(1.41 \frac{\text{kJ}}{\text{kg K}}\right) (T - (673.15 \text{ K})) - \left(65.743 \frac{\text{kJ K}^{1/2} \text{m}^3}{\text{kg kg}}\right) \left(\left(1.12304 \frac{\text{kg}}{\text{K}^{1/2} \text{m}^3}\right) - \frac{1}{\sqrt{Tv}}\right), \quad (5.161)$$

$$c_v(T, v) = \left(1.41 \frac{\text{kJ}}{\text{kg K}}\right) + \frac{\left(32.8715 \frac{\text{kJ K}^{1/2} \text{m}^3}{\text{kg kg}}\right)}{T^{3/2}v}. \quad (5.162)$$

This particular model ignores some of the potential temperature variation of c_v , but is useful for illustration purposes. It gives results not unlike those in portions of the steam tables. As an aside, the Redlich-Kwong thermal equation of state, see p. 63, for superheated water is

$$P = \frac{\left(0.461504 \frac{\text{kJ}}{\text{kg K}}\right) T}{v - \left(0.00117008 \frac{\text{m}^3}{\text{kg}}\right)} - \frac{43.8287 \frac{\text{kJ}}{\text{kg}} \frac{\text{K}^{1/2} \text{m}^3}{\text{kg}}}{v \left(v + \left(0.00117008 \frac{\text{m}^3}{\text{kg}}\right)\right) \sqrt{T}}. \quad (5.163)$$

Even more generally, u and h are tabulated for materials such as water.

5.6. Time-dependency

We venture gently away from classical thermodynamics into non-equilibrium thermodynamics. Let us admit time t into the differential form of the first law by scaling Eq. (5.13) by dt :

$$\frac{dU}{dt} + \frac{d}{dt}(KE) + \frac{d}{dt}(PE) = \frac{\delta Q}{dt} - \frac{\delta W}{dt}. \quad (5.178)$$

Since total energy $E = U + KE + PE$, we could also say

$$\frac{dE}{dt} = \frac{\delta Q}{dt} - \frac{\delta W}{dt}. \quad (5.179)$$

Often, we will use the Newtonian “dot” notation for time derivatives. A common form is

$$\boxed{\frac{dE}{dt} = \dot{Q} - \dot{W}}. \quad (5.180)$$

In this course, we will often neglect changes in KE and PE , in which case the time-dependent first law reduces to

$$\boxed{\frac{dU}{dt} = \dot{Q} - \dot{W}}. \quad (5.181)$$

Many times in this course, we will treat \dot{Q} and \dot{W} as constants. Problems become more interesting when they are variable. Such problems are also important. Now, Newton did consider some thermal problems. In fact Newton's law of cooling (see Eq. (4.115)) tells us that \dot{Q} is proportional to the surface area of a body and the temperature difference between the body and its environment:

$$\dot{Q} = -hA(T - T_\infty). \quad (5.182)$$

Note that heat flows into a body when it has a temperature less than its surroundings, $T < T_\infty$. Here, we have the

- HEAT TRANSFER COEFFICIENT, h , with units $W/m^2/K$.

Note $h \neq h$. Enthalpy is a different physical quantity with different units. While Eq. (5.182) is given the elevated name of "law," one must realize that it is by no means a law of the same status as the first law of thermodynamics. Rather, it is actually only a useful but fallible approximation; often h is not a constant but rather a complicated function of the local material's state and geometrical configuration. Its nuances are the subject of the discipline of convective heat transfer.

5.7. Final comments on conservation

We note the first law is often re-stated as energy is conserved. Let us reconcile this with our mathematical statement, $dE/dt = \dot{Q} - \dot{W}$. This equation tells us that the total energy E can change in response to heat and work crossing the system boundary. But conservation implies that a quantity does not change. We can recover the proper notion of conservation if we speak of an isolated system, which we recall is one that is not influenced by its surroundings. So for an isolated system there can, by definition be no work or heat transfer, so

$$\frac{dE}{dt} = 0, \quad \text{isolated system.} \quad (5.206)$$

Integrating, we find

$$E = \text{constant}, \quad \text{isolated system.} \quad (5.207)$$

Even more fundamentally, we can say, by its definition, that the mass m of a system is constant; thus, the mass of an isolated system must also be constant.

This theoretical formulation is often successful in describing nature for a wide variety of scenarios. However, it does not always succeed. It has been observed to fail for systems which move at a velocity close to the speed of light. For such systems, not only do energy and mass conservation principles fail, so do Newton's laws of mechanics. To realign theory with observation, it was necessary for Einstein, depicted in Fig. 5.22 to re-formulate a new, modified set of axioms. In a certain sense the new axioms are simple. For example one can replace Newton's second law with the seemingly simpler $d\mathbf{v}/dt = 0$, where \mathbf{v} is a new velocity vector; however, the coordinate axes associated with this vector are complicated.

Fig 5.22. Albert Einstein (1879-1955), German theoretical physicist who developed theories that explained data better than those of Newton



Another consequence of Einstein's reformulation was the remarkable results of mass-energy equivalence via the famous relation

$$E = mc^2, \quad (5.208)$$

where c is the speed of light in a vacuum. Another way of viewing Einstein's contributions is via a new conservation property: the mass-energy of an isolated system is constant. It is the conservation of mass-energy that is the key ingredient in both nuclear weapon systems as well as nuclear power generation.

NOTES

Experimentally it was found that

$$\oint (\delta w + \delta q) = 0$$

⇒ The sum ($w + q$) is independent of path

⇒ This implies that there is a state function whose differential is $\delta w + \delta q$

We define it as U , the "internal energy" or just "energy"

$$\therefore dU = \delta w + \delta q$$

For a cyclic process $\oint dU = 0$

For a change from state 1 to state 2,

$$\Delta U = \int_1^2 dU = U_2 - U_1 = q + w \quad \text{does not depend on path}$$



 each depends on path individually, but not the sum

For fixed n , we just need to know 2 properties, e.g. (T, V), to fully describe the system.

So $U = U(T, V)$

U is an extensive function (scales with system size).

$\bar{U} = \frac{U}{n}$ is molar energy (intensive function)



THE FIRST LAW

Mathematical statement:

$$dU = \delta q + \delta w$$

or

$$\Delta U = q + w$$

or

$$-\oint \delta q = \oint \delta w$$

Corollary: Conservation of energy

$$\Delta U_{system} = q + w$$

$$\Delta U_{surroundings} = -q - w$$

$$\Rightarrow \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

Clausius statement of 1st Law:

The energy of the universe is conserved.

The first law expresses the conservation of energy by including heat as a form of energy. It asserts that there exists a function of the state, *internal energy* U , whose change in any thermodynamic transformation is given by

$$\Delta U = \Delta Q - \Delta W$$

That is, ΔU is independent of the path of the transformation, although ΔQ and ΔW are path dependent. In a reversible infinitesimal transformation, the infinitesimal changes dQ and dW are not exact differentials, in the sense that they do not represent the changes of definite functions, but their difference

$$dU = dQ - dW$$

is an exact differential.

In other speaking

In an *arbitrary* thermodynamic transformation let ΔQ denote the net amount of heat absorbed by the system and ΔW the net amount of work done by the system. The first law of thermodynamics states that the quantity ΔU , defined by

$$\Delta U = \Delta Q - \Delta W \tag{1.1}$$

is the same for all transformations leading from a given initial state to a given final state.

This immediately defines a state function U , called the internal energy. Its value for any state may be found as follows. Choose an arbitrary fixed state as reference. Then the internal energy of any state is $\Delta Q - \Delta W$ in *any* transforma-

tion which leads from the reference state to the state in question. It is defined only up to an arbitrary additive constant. Empirically U is an extensive quantity. This follows from the saturation property of molecular forces, namely, that the energy of a substance is doubled if its mass is doubled.

The experimental foundation of the first law is Joule's demonstration of the equivalence between heat and mechanical energy—the feasibility of converting mechanical work completely into heat. The inclusion of heat as a form of energy leads naturally to the inclusion of heat in the statement of the conservation of energy. The first law is precisely such a statement.

In an infinitesimal transformation, the first law reduces to the statement that the differential

$$dU = dQ - dW \quad (1.2)$$

is exact. That is, there exists a function U whose differential is dU ; or, the integral $\int dU$ is independent of the path of the integration and depends only on the limits of integration. This property is obviously not shared by dQ or dW .

Given a differential of the form $df = g(A, B) dA + h(A, B) dB$, the condition that df be exact is $\partial g/\partial B = \partial h/\partial A$. Let us explore some of the consequences of the exactness of dU . Consider a system whose parameters are P, V, T . Any pair of these three parameters may be chosen to be the independent variables that completely specify the state of the system. The other parameter is then determined by the equation of state. We may, for example, consider $U = U(P, V)$. Then*

$$dU = \left(\frac{\partial U}{\partial P} \right)_V dP + \left(\frac{\partial U}{\partial V} \right)_P dV \quad (1.3)$$

The requirement that dU be exact immediately leads to the result

$$\frac{\partial}{\partial V} \left[\left(\frac{\partial U}{\partial P} \right)_V \right]_P = \frac{\partial}{\partial P} \left[\left(\frac{\partial U}{\partial V} \right)_P \right]_V \quad (1.4)$$

The following equations, expressing the heat absorbed by a system during an infinitesimal reversible transformation (in which $dW = P dV$), are easily obtained by successively choosing as independent variables the pairs (P, V) , (P, T) , and (V, T) :

$$dQ = \left(\frac{\partial U}{\partial P} \right)_V dP + \left[\left(\frac{\partial U}{\partial V} \right)_P + P \right] dV \quad (1.5)$$

$$dQ = \left[\left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \right] dT + \left[\left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \right] dP \quad (1.6)$$

$$dQ = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV \quad (1.7)$$

First Law of Thermodynamics

This leads to the general statement of the First Law of Thermodynamics, for infinitesimal changes:

$$dU = \delta W + \delta Q,$$

where both δW and δQ are path-dependent. For work done mechanically on a compressible fluid, First Law for infinitesimal reversible processes is:

$$dU = -PdV + \delta Q$$

Work: electrical, magnetic, gravitational etc.

Internal energy: kinetic and potential energy.

Potential energy includes chemical, nuclear, mass, gravitational.

The first law has time-reversal symmetry.

LECTURE 6: FIRST LAW ANALYSIS FOR A CONTROL VOLUME

Content of Lecture 6

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6.6.4. Compressible fluid mechanics equations

6.6.5. Heat transfer in incompressible static solids

Problems in previous chapters have focused on systems. These systems always were composed of the same matter. However, for a wide variety of engineering devices, for example

- flow in pipes,
- jet engines,
- heat exchangers,
- gas turbines,
- pumps,
- furnaces, or
- air conditioners,

a constant flow of new fluid continuously enters and exits the device. In fact, once the fluid has left the device, we often are not concerned with that fluid, as far as the performance of the device is concerned. Of course, we might care about the pollution emitted by the device and the long term fate of expelled particles. Pollution dispersion, in contrast to pollution-creation, is more a problem of fluid mechanics than thermodynamics.

Analysis of control volumes is slightly more complicated than for systems, and the equations we will ultimately use are slightly more complex. Unfortunately, the underlying mathematics and physics which lead to the development of our simplified control volume equations are highly challenging! Worse still, most beginning thermodynamics texts do not expose the student to all of the many nuances required for the simplification.

We will introduce no new axioms in this chapter. We shall simply formulate our mass and energy conservation axioms for a control volume configuration. A sketch of a generic apparatus for control volume analysis is given in Fig. 6.1

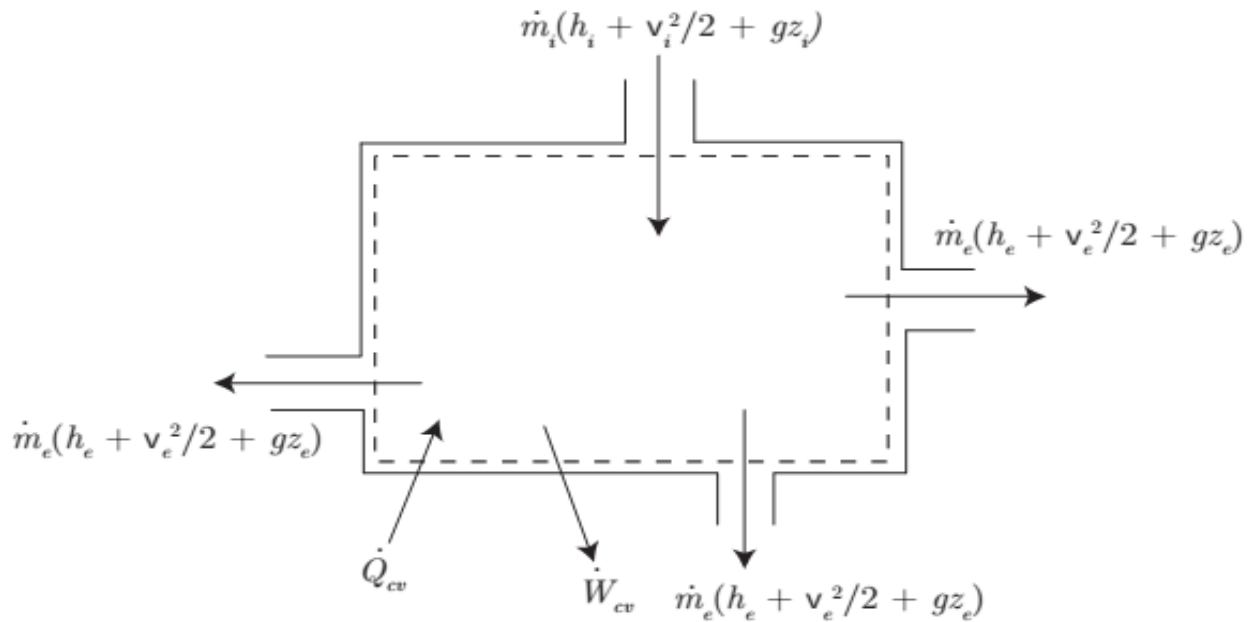


Figure 6.1: Sketch of generic configuration for control volume analysis.

6.1. Detailed derivations of control volume equations

This section will give a summary of the necessary mathematical operations necessary to cast the conservation of mass and energy principles in a traditional control volume formulation.

6.1.1 Relevant mathematics

We will use several theorems which are developed in vector calculus. Here, we give short motivations and presentations. The reader should consult a standard mathematics text for detailed derivations.

6.1.1.1 Fundamental theorem of calculus

The fundamental theorem of calculus is as follows

$$\int_{x=a}^{x=b} \phi(x) dx = \int_{x=a}^{x=b} \left(\frac{d\psi}{dx} \right) dx = \psi(b) - \psi(a). \quad (6.1)$$

It effectively says that to find the integral of a function $\phi(x)$, which is the area under the curve, it suffices to find a function ψ , whose derivative is ϕ , i.e. $d\psi/dx = \phi(x)$, evaluate ψ at each endpoint, and take the difference to find the area under the curve.

6.1.1.2 Divergence theorem

The divergence theorem, often known as Gauss's⁷ theorem, is the analog of the fundamental theorem of calculus extended to volume integrals. Gauss is depicted in Fig. 6.2. While it is



Fig 6.2. Johann Carl Friedrich Gauss (1777-1855), German mathematician

often attributed to Gauss who reported it in 1813, it is said that it was first discovered by Joseph Louis Lagrange in 1762⁸

Let us define the following quantities:

- $t \rightarrow$ time,
- $\mathbf{x} \rightarrow$ spatial coordinates,
- $V_a(t) \rightarrow$ arbitrary moving and deforming volume,
- $A_a(t) \rightarrow$ bounding surface of the arbitrary moving volume,
- $\mathbf{n} \rightarrow$ outer unit normal to moving surface, and
- $\phi(\mathbf{x}, t) \rightarrow$ arbitrary vector function of \mathbf{x} and t .

The divergence theorem is as follows:

$$\boxed{\int_{V_a(t)} \nabla \cdot \phi dV = \int_{A_a(t)} \phi \cdot \mathbf{n} dA.} \quad (6.2)$$

The surface integral is analogous to evaluating the function at the end points in the fundamental theorem of calculus.

If $\phi(\mathbf{x}, t)$ has the form $\phi(\mathbf{x}, t) = \mathbf{c}\phi(\mathbf{x}, t)$, where \mathbf{c} is a *constant* vector and ϕ is a scalar function, then the divergence theorem, Eq. (6.2), reduces to

$$\int_{V_a(t)} \nabla \cdot (\mathbf{c}\phi) dV = \int_{A_a(t)} (\mathbf{c}\phi) \cdot \mathbf{n} dA, \quad (6.3)$$

$$\int_{V_a(t)} \left(\underbrace{\phi \nabla \cdot \mathbf{c}}_{=0} + \mathbf{c} \cdot \nabla \phi \right) dV = \int_{A_a(t)} \phi (\mathbf{c} \cdot \mathbf{n}) dA, \quad (6.4)$$

$$\mathbf{c} \cdot \int_{V_a(t)} \nabla \phi \, dV = \mathbf{c} \cdot \int_{A_a(t)} \phi \mathbf{n} \, dA, \quad (6.5)$$

$$\mathbf{c} \cdot \underbrace{\left(\int_{V_a(t)} \nabla \phi \, dV - \int_{A_a(t)} \phi \mathbf{n} \, dA \right)}_{=0} = 0. \quad (6.6)$$

Now, since \mathbf{c} is arbitrary, the term in parentheses must be zero. Thus,

$$\boxed{\int_{V_a(t)} \nabla \phi \, dV = \int_{A_a(t)} \phi \mathbf{n} \, dA.} \quad (6.7)$$

Note if we take ϕ to be the scalar of unity (whose gradient must be zero), the divergence theorem reduces to

$$\int_{V_a(t)} \nabla(1) \, dV = \int_{A_a(t)} (1)\mathbf{n} \, dA, \quad (6.8)$$

$$0 = \int_{A_a(t)} (1)\mathbf{n} \, dA, \quad (6.9)$$

$$\int_{A_a(t)} \mathbf{n} \, dA = 0. \quad (6.10)$$

That is, the unit normal to the surface, integrated over the surface, cancels to zero when the entire surface is included.

We will use the divergence theorem (6.2) extensively. It allows us to convert sometimes difficult volume integrals into easier interpreted surface integrals. It is often useful to use this theorem as a means of toggling back and forth from one form to another.

6.1.1.3 Leibniz's rule

Leibniz's⁹ rule relates time derivatives of integral quantities to a form which distinguishes changes which are happening within the boundaries to changes due to fluxes through boundaries. Leibniz is depicted in Fig. 6.3.



Fig 6.3. Gottfried Wilhelm von Leibniz (1646-1716), German mathematician, philosopher and polymath who co-invented calculus

Let us consider the scenario sketched in Figure 6.4. Say we have some value of interest, Φ , which results from an integration of a kernel function ϕ over $V_a(t)$, for instance

$$\Phi = \int_{V_a(t)} \phi dV. \quad (6.11)$$

We are often interested in the time derivative of Φ , the calculation of which is complicated by the fact that the limits of integration are time-dependent. From the definition of the derivative, we find that

$$\frac{d\Phi}{dt} = \frac{d}{dt} \int_{V_a(t)} \phi dV = \lim_{\Delta t \rightarrow 0} \frac{\int_{V_a(t+\Delta t)} \phi(t+\Delta t) dV - \int_{V_a(t)} \phi(t) dV}{\Delta t}. \quad (6.12)$$

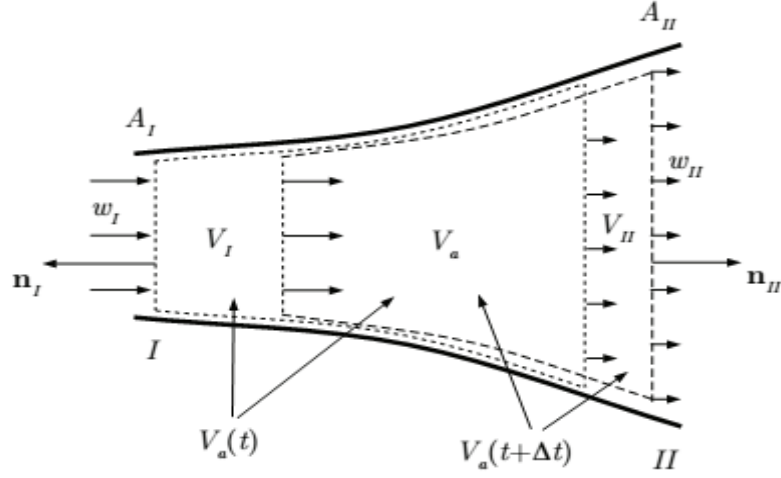


Figure 6.4: Sketch of the motion of an arbitrary volume $V_a(t)$. The boundaries of $V_a(t)$ move with velocity \mathbf{w} . The outer normal to $V_a(t)$ is $A_a(t)$. Here, we focus on just two regions: I , where the volume is leaving material behind, and II , where the volume is sweeping up new material.

Now, we have

$$V_a(t + \Delta t) = V_a(t) + V_{II}(\Delta t) - V_I(\Delta t). \quad (6.13)$$

Here, $V_{II}(\Delta t)$ is the amount of new volume swept up in time increment Δt , and $V_I(\Delta t)$ is the amount of volume abandoned in time increment Δt . So we can break up the first integral in the last term of Eq. (6.12) into

$$\int_{V_a(t+\Delta t)} \phi(t + \Delta t) dV = \int_{V_a(t)} \phi(t + \Delta t) dV + \int_{V_{II}(\Delta t)} \phi(t + \Delta t) dV - \int_{V_I(\Delta t)} \phi(t + \Delta t) dV, \quad (6.14)$$

which gives us then

$$\begin{aligned} \frac{d}{dt} \int_{V_a(t)} \phi dV = \\ \lim_{\Delta t \rightarrow 0} \frac{\int_{V_a(t)} \phi(t + \Delta t) dV + \int_{V_{II}(\Delta t)} \phi(t + \Delta t) dV - \int_{V_I(\Delta t)} \phi(t + \Delta t) dV - \int_{V_a(t)} \phi(t) dV}{\Delta t} \end{aligned} \quad (6.15)$$

Rearranging (6.15) by combining terms with common limits of integration, we get

$$\begin{aligned} \frac{d}{dt} \int_{V_a(t)} \phi dV &= \lim_{\Delta t \rightarrow 0} \frac{\int_{V_a(t)} (\phi(t + \Delta t) - \phi(t)) dV}{\Delta t} \\ &+ \lim_{\Delta t \rightarrow 0} \frac{\int_{V_{II}(\Delta t)} \phi(t + \Delta t) dV - \int_{V_I(\Delta t)} \phi(t + \Delta t) dV}{\Delta t}. \end{aligned} \quad (6.16)$$

Let us now further define

- $\mathbf{w} \rightarrow$ the velocity vector of points on the moving surface $V_a(t)$,

Now, the volume swept up by the moving volume in a given time increment Δt is

$$dV_{II} = \underbrace{\mathbf{w} \cdot \mathbf{n}}_{\text{positive}} \Delta t dA_{II} = \underbrace{w_{II} \Delta t}_{\text{distance}} dA_{II}, \quad (6.17)$$

and the volume abandoned is

$$dV_I = \underbrace{\mathbf{w} \cdot \mathbf{n}}_{\text{negative}} \Delta t dA_I = - \underbrace{w_I \Delta t}_{\text{distance}} dA_I. \quad (6.18)$$

Substituting into our definition of the derivative, Eq. (6.16), we get

$$\begin{aligned} \frac{d}{dt} \int_{V_a(t)} \phi dV &= \lim_{\Delta t \rightarrow 0} \int_{V_a(t)} \frac{(\phi(t + \Delta t) - \phi(t))}{\Delta t} dV \\ &+ \lim_{\Delta t \rightarrow 0} \frac{\int_{A_{II}(\Delta t)} \phi(t + \Delta t) w_{II} \Delta t dA_{II} + \int_{A_I(\Delta t)} \phi(t + \Delta t) w_I \Delta t dA_I}{\Delta t}. \end{aligned} \quad (6.19)$$

Now, we note that

- We can use the definition of the partial derivative to simplify the first term on the right side of (6.19),
- The time increment Δt cancels in the area integrals of (6.19), and
- $A_a(t) = A_I + A_{II}$,

so that

$$\underbrace{\frac{d}{dt} \int_{V_a(t)} \phi dV}_{\text{total time rate of change}} = \underbrace{\int_{V_a(t)} \frac{\partial \phi}{\partial t} dV}_{\text{intrinsic change within volume}} + \underbrace{\int_{A_a(t)} \phi \mathbf{w} \cdot \mathbf{n} dA}_{\text{net flux into volume}}. \quad (6.20)$$

This is the three-dimensional scalar version of *Leibniz's rule*. Say we have the special case in which $\phi = 1$; then Leibniz's rule (6.20) reduces to

$$\frac{d}{dt} \int_{V_a(t)} dV = \int_{V_a(t)} \underbrace{\frac{\partial}{\partial t}(1)}_{=0} dV + \int_{A_a(t)} (1) \mathbf{w} \cdot \mathbf{n} dA, \quad (6.21)$$

$$\frac{d}{dt} V_a(t) = \int_{A_a(t)} \mathbf{w} \cdot \mathbf{n} dA. \quad (6.22)$$

This simply says the total volume of the region, which we call $V_a(t)$, changes in response to net motion of the bounding surface.

Leibniz's rule (6.20) reduces to a more familiar result in the one-dimensional limit. We can then say

$$\frac{d}{dt} \int_{x=a(t)}^{x=b(t)} \phi(x, t) dx = \int_{x=a(t)}^{x=b(t)} \frac{\partial \phi}{\partial t} dx + \frac{db}{dt} \phi(b(t), t) - \frac{da}{dt} \phi(a(t), t). \quad (6.23)$$

As in the fundamental theorem of calculus (6.1), for the one-dimensional case, we do not have to evaluate a surface integral; instead, we simply must consider the function at its endpoints. Here, db/dt and da/dt are the velocities of the bounding surface and are equivalent to \mathbf{w} . The terms $\phi(b(t), t)$ and $\phi(a(t), t)$ are equivalent to evaluating ϕ on $A_a(t)$.

We can also apply the divergence theorem (6.2) to Leibniz's rule (6.20) to convert the area integral into a volume integral to get

$$\frac{d}{dt} \int_{V_a(t)} \phi dV = \int_{V_a(t)} \frac{\partial \phi}{\partial t} dV + \int_{V_a(t)} \nabla \cdot (\phi \mathbf{w}) dV. \quad (6.24)$$

Combining the two volume integrals, we get

$$\frac{d}{dt} \int_{V_a(t)} \phi dV = \int_{V_a(t)} \left(\frac{\partial \phi}{\partial t} + \nabla \cdot (\phi \mathbf{w}) \right) dV. \quad (6.25)$$

6.1.1.4 General transport theorem

Let B be an arbitrary extensive thermodynamic property, and β be the corresponding intensive thermodynamic property so that

$$dB = \beta dm. \quad (6.26)$$

The product of a differential amount of mass dm with the intensive property β give a differential amount of the extensive property. Since

$$dm = \rho dV, \quad (6.27)$$

where ρ is the mass density and dV is a differential amount of volume, we have

$$dB = \beta \rho dV. \quad (6.28)$$

If we take the arbitrary $\phi = \rho\beta$, Leibniz's rule, Eq. (6.20), becomes our general transport theorem:

$$\boxed{\frac{d}{dt} \int_{V_a(t)} \rho\beta dV = \int_{V_a(t)} \frac{\partial}{\partial t} (\rho\beta) dV + \int_{A_a(t)} \rho\beta (\mathbf{w} \cdot \mathbf{n}) dA.} \quad (6.29)$$

Applying the divergence theorem, Eq. (6.2), to the general transport theorem, Eq. (6.29), we find the alternate form

$$\boxed{\frac{d}{dt} \int_{V_a(t)} \rho\beta dV = \int_{V_a(t)} \left(\frac{\partial}{\partial t} (\rho\beta) + \nabla \cdot (\rho\beta \mathbf{w}) \right) dV.} \quad (6.30)$$

Fig 6.5. Osborne Reynolds (1842-1912), Anglo-Irish engineer



6.1.1.5 Reynolds transport theorem

Osborne Reynolds¹⁰ made many pioneering contributions to fluid mechanics. He is depicted in Fig. 6.5. Among other things, he wrote a treatise on the development of conservation principles in a general sense.¹¹ From this work, and after employing more modern notation, we arrive at what is now known as the Reynolds transport theorem if we force the arbitrary velocity of the moving volume to take on the velocity of a fluid particle, i.e. take

$$\mathbf{w} = \mathbf{v}. \quad (6.31)$$

In this case, our arbitrary volume is no longer arbitrary. Instead, it always contains the same fluid particles. We call this volume a

- MATERIAL VOLUME, $V_m(t)$: a volume which always contains the same fluid particles.

The proper way to generalize laws of nature which were developed for point masses is to consider collections of fixed point masses, which will always reside within a material volume. That said, it is simple to specialize the general transport theorem to obtain the Reynolds transport theorem. Here, we give two versions, the first using area integrals, and the second using volume integrals only. In this special case, Eqs. (6.29) and (6.30) become, respectively,

$$\frac{d}{dt} \int_{V_m(t)} \rho\beta \, dV = \int_{V_m(t)} \frac{\partial}{\partial t}(\rho\beta) \, dV + \int_{A_m(t)} \rho\beta (\mathbf{v} \cdot \mathbf{n}) \, dA, \quad (6.32)$$

$$\frac{d}{dt} \int_{V_m(t)} \rho\beta \, dV = \int_{V_m(t)} \left(\frac{\partial}{\partial t}(\rho\beta) + \nabla \cdot (\rho\beta\mathbf{v}) \right) \, dV. \quad (6.33)$$

The implications of these mathematical statements are summarized in the words of Reynolds: in Fig. 6.5

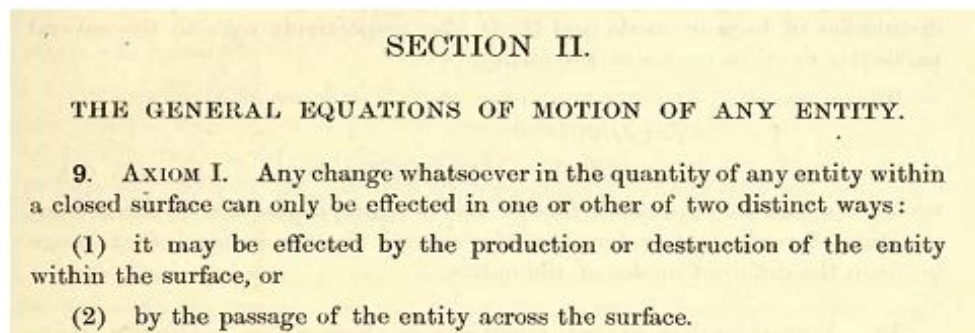


Figure 6.6: Image from Reynolds' 1903 study, p. 9, giving his key general axiom.

6.1.1.6 Fixed (control) volumes

If we take our arbitrary volume to be fixed in space, it is most often known as a

- **CONTROL VOLUME:** a fixed volume in space.

For control volumes

$$\mathbf{w} = \mathbf{0}. \quad (6.34)$$

Thus, the arbitrary volume loses its time dependency, so that

$$V_a(t) = V, \quad A_a(t) = A, \quad (6.35)$$

and the general transport theorem, Eq. (6.29), reduces to

$$\boxed{\frac{d}{dt} \int_V \rho\beta \, dV = \int_V \frac{\partial}{\partial t}(\rho\beta) \, dV.} \quad (6.36)$$

6.1.2 Conservation axioms

A fundamental goal of mechanics is to take the verbal notions which embody the basic axioms into usable mathematical expressions. First, we must list those axioms. The axioms themselves are simply principles which have been observed to have wide validity as long as length scales are sufficiently large to contain many molecules. Many of these axioms can be applied to molecules as well. The axioms cannot be proven. They are simply statements which have been useful in describing the universe.

A summary of the axioms in words is as follows

- *Mass conservation principle:* The time rate of change of mass of a material region is zero.
- *Linear momenta principle:* The time rate of change of the linear momenta of a material region is equal to the sum of forces acting on the region. This is Euler's generalization of Newton's second law of motion.
- *Angular momenta principle:* The time rate of change of the angular momenta of a material region is equal to the sum of the torques acting on the region. This was first formulated by Euler.
- *Energy conservation principle:* The time rate of change of energy within a material region is equal to the rate that energy is received by heat and work interactions. This is the first law of thermodynamics.
- *Entropy inequality:* The time rate of change of entropy within a material region is greater than or equal to the ratio of the rate of heat transferred to the region and the absolute temperature of the region. This is the second law of thermodynamics.

Here, we shall systematically convert two of these axioms, the mass conservation principle and the energy conservation principle, into mathematical form.

6.1.2.1 Mass

Mass is an extensive property for which we have

$$B = m, \quad \beta = 1. \quad (6.37)$$

The mass conservation axiom is simple to state mathematically. It is

$$\frac{d}{dt}m = 0. \quad (6.38)$$

A relevant material volume is sketched in Figure 6.7. We can define the mass enclosed within a material volume based upon the local value of density:

$$m = \int_{V_m(t)} \rho dV. \quad (6.39)$$

So the mass conservation axiom is

$$\frac{d}{dt} \int_{V_m(t)} \rho dV = 0. \quad (6.40)$$

Invoking the Reynolds transport theorem (6.32), $\frac{d}{dt} \int_{V_m(t)} [\] dV = \int_{V_m(t)} \frac{\partial}{\partial t} [\] dV + \int_{A_m(t)} \mathbf{v} \cdot \mathbf{n} [\] dA$, we get

$$\frac{d}{dt} \int_{V_m(t)} \rho dV = \int_{V_m(t)} \frac{\partial \rho}{\partial t} dV + \int_{A_m(t)} \rho \mathbf{v} \cdot \mathbf{n} dA = 0. \quad (6.41)$$

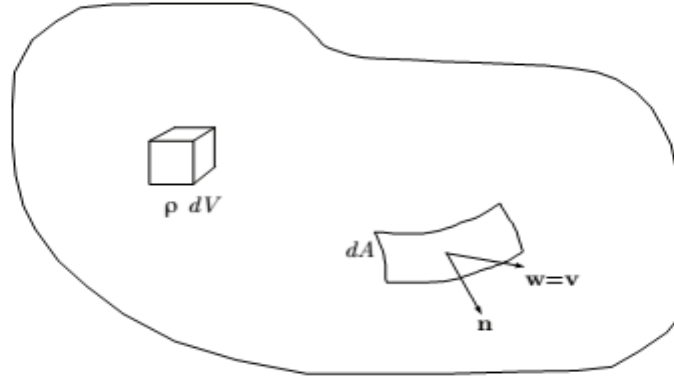


Figure 6.7: Sketch of finite material region $V_m(t)$, infinitesimal mass element ρdV , and infinitesimal surface element dA with unit normal \mathbf{n} , and general velocity \mathbf{w} equal to fluid velocity \mathbf{v} .

The first equality of Eq. (6.41) is simply a mathematical statement involving definitions; forcing either of the terms to equal zero is a statement of physics. Now, we invoke the divergence theorem, Eq. (6.2) $\int_{V(t)} \nabla \cdot [\] dV = \int_{A(t)} \mathbf{n} \cdot [\] dA$, to convert a surface integral to a volume integral to get the mass conservation axiom to read as

$$\int_{V_m(t)} \frac{\partial \rho}{\partial t} dV + \int_{V_m(t)} \nabla \cdot (\rho \mathbf{v}) dV = 0, \quad (6.42)$$

$$\int_{V_m(t)} \underbrace{\left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right)}_{=0} dV = 0. \quad (6.43)$$

Now, in an important step, we realize that the only way for this integral, which has absolutely arbitrary limits of integration, to always be zero, is for the integrand itself to always be zero. Hence, we have

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (6.44)$$

This is the important differential form of the mass conservation principle.

We can get a useful *control volume* formulation by integrating the mass conservation principle (6.44) over a *fixed* volume V :

$$\int_V \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) dV = \int_V 0 dV. \quad (6.45)$$

Now, the integral of 0 over a fixed domain must be zero. This is equivalent to saying $\int_a^b 0 dx = 0$, where the area under the curve of 0 has to be zero. So we have

$$\int_V \left(\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) \right) dV = 0. \quad (6.46)$$

Next apply the divergence theorem (6.2) to (6.46) to get

$$\int_V \frac{\partial \rho}{\partial t} dV + \int_A \rho \mathbf{v} \cdot \mathbf{n} dA = 0. \quad (6.47)$$

Applying now the result from (6.36) to (6.47), we see for the fixed volume that

$$\frac{d}{dt} \int_V \rho dV + \int_A \rho \mathbf{v} \cdot \mathbf{n} dA = 0. \quad (6.48)$$

We note now that at an inlet to a control volume that \mathbf{v} points in an opposite direction to \mathbf{n} , so we have

$$\mathbf{v} \cdot \mathbf{n} < 0, \quad \text{at inlets.} \quad (6.49)$$

At exits to a control volume \mathbf{v} and \mathbf{n} point in the same direction so that

$$\mathbf{v} \cdot \mathbf{n} > 0, \quad \text{at exits.} \quad (6.50)$$

If now, we take the simplifying assumption that ρ and \mathbf{v} have no spatial variation across inlets and exits, we get for a control volume with one inlet and one exit that

$$\frac{d}{dt} \int_V \rho dV + \rho_e |\mathbf{v}_e| A_e - \rho_i |\mathbf{v}_i| A_i = 0. \quad (6.51)$$

Here, the subscript i denotes inlet, and the subscript e denotes exit. Rearranging (6.51), we find

$$\frac{d}{dt} \int_V \rho dV = \rho_i |\mathbf{v}_i| A_i - \rho_e |\mathbf{v}_e| A_e. \quad (6.52)$$

We now define the mass in the control volume m_{cv} as

$$\boxed{m_{cv} = \int_V \rho dV.} \quad (6.53)$$

Here, (6.53) is equivalent to the equation on the top of p. 182 of BS. If we make the further simplifying assumption that ρ does not vary within V , we find that

$$\underbrace{\frac{dm_{cv}}{dt}}_{\text{rate of change of mass}} = \underbrace{\rho_i |\mathbf{v}_i| A_i}_{\text{mass rate in}} - \underbrace{\rho_e |\mathbf{v}_e| A_e}_{\text{mass rate out}}. \quad (6.54)$$

Here, m_{cv} is the mass enclosed in the control volume. If there is no net rate of change of mass the control volume is in *steady state*, and we can say that the mass flow in must equal the mass flow out:

$$\rho_i |\mathbf{v}_i| A_i = \rho_e |\mathbf{v}_e| A_e. \quad (6.55)$$

We define the *mass flow rate* \dot{m} as

$$\dot{m} = \rho |\mathbf{v}| A. \quad (6.56)$$

For steady flows with a single entrance and exit, we have

$$\dot{m} = \text{constant}. \quad (6.57)$$

For unsteady flows with a single entrance and exit, we can rewrite (6.54) as

$$\frac{dm_{cv}}{dt} = \dot{m}_i - \dot{m}_e. \quad (6.58)$$

For unsteady flow with many entrances and exits, we can generalize (6.54) as

$$\underbrace{\frac{dm_{cv}}{dt}}_{\text{rate of change of mass}} = \underbrace{\sum \rho_i |\mathbf{v}_i| A_i}_{\text{mass rate in}} - \underbrace{\sum \rho_e |\mathbf{v}_e| A_e}_{\text{mass rate out}}, \quad (6.59)$$

$$\boxed{\underbrace{\frac{dm_{cv}}{dt}}_{\text{rate of change of mass}} = \underbrace{\sum \dot{m}_i}_{\text{mass rate in}} - \underbrace{\sum \dot{m}_e}_{\text{mass rate out}}}. \quad (6.60)$$

Note that (6.60) is fully equivalent to BS's Eq. (6.1) (p. 181), but that it actually takes a good deal of effort to get to this point with rigor! For steady state conditions with many entrances and exits we can say

$$\sum \rho_i |\mathbf{v}_i| A_i = \sum \rho_e |\mathbf{v}_e| A_e. \quad (6.61)$$

Thus

$$\boxed{\sum \dot{m}_i = \sum \dot{m}_e}. \quad (6.62)$$

Here, (6.62) is the same as BS's (6.9), p. 186.

6.1.2.2 Energy

For energy, we must consider the *total energy* which includes internal, kinetic, and potential. Our extensive property B is thus

$$B = E = U + \frac{1}{2} m \mathbf{v} \cdot \mathbf{v} + mgz. \quad (6.63)$$

Here, we have assumed the fluid resides in a gravitational potential field in which the gravitational potential energy varies linearly with height z . The corresponding intensive property β is

$$\beta = e = u + \frac{1}{2}\mathbf{v} \cdot \mathbf{v} + gz. \quad (6.64)$$

We recall the first law of thermodynamics, which states the change of a material volume's total energy is equal to the heat transferred to the material volume less the work done by the material volume. Mathematically, this is stated as Eq. (5.8):

$$dE = \delta Q - \delta W. \quad (6.65)$$

We recall the total derivative is used for dE , since energy is a property and has an exact differential, while both heat transfer and work are not properties and do not have exact differentials. It is more convenient to express the first law as a rate equation, which we get by dividing (6.65) by dt to get

$$\frac{dE}{dt} = \frac{\delta Q}{dt} - \frac{\delta W}{dt}. \quad (6.66)$$

Recall that the upper case letters denote extensive thermodynamic properties. For example, E is total energy, inclusive of internal and kinetic and potential¹², with SI units of J . Let us consider each term in the first law of thermodynamics in detail and then write the equation in final form.

6.1.2.2.1 Total energy term For a fluid particle, the differential amount of total energy is

$$dE = \rho\beta dV = \rho \underbrace{\left(u + \frac{1}{2}\mathbf{v} \cdot \mathbf{v} + gz\right)}_{\beta} dV, \quad (6.67)$$

$$= \underbrace{\rho dV}_{\text{mass}} \underbrace{\left(u + \frac{1}{2}\mathbf{v} \cdot \mathbf{v} + gz\right)}_{\text{internal + kinetic + potential}}. \quad (6.68)$$

6.1.2.2.2 Work term Let us partition the work into work W_P done by a pressure force \mathbf{F}_P and work done by other sources, which we shall call W_{mv} , where the subscript “ mv ” indicates “material volume.”

$$W = W_P + W_{mv}. \quad (6.69)$$

Taking a time derivative, we get

$$\frac{\delta W}{dt} = \frac{\delta W_P}{dt} + \dot{W}_{mv}. \quad (6.70)$$

The work done by other sources is often called *shaft work* and represents inputs of such devices as compressors, pumps, and turbines. Its modeling is often not rigorous.

Recall that work is done when a force acts through a distance, and a work rate arises when a force acts through a distance at a particular rate in time (hence, a velocity is involved). Recall also that it is the dot product of the force vector with the position or velocity that gives the true work or work rate. In shorthand, we can say that the differential work done by the pressure force \mathbf{F}_P is

$$\delta W_P = \mathbf{F}_P \cdot d\mathbf{x}, \quad (6.71)$$

$$\frac{\delta W_P}{dt} = \mathbf{F}_P \cdot \frac{d\mathbf{x}}{dt} = \mathbf{F}_P \cdot \mathbf{v}. \quad (6.72)$$

$$\frac{\delta W_P}{dt} = \mathbf{F}_P \cdot \mathbf{v} > 0 \text{ for expansion}$$

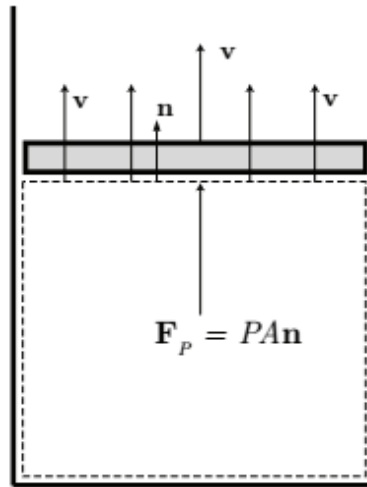


Figure 6.8: Sketch of fluid doing work.

Here, W has the SI units of J , and \mathbf{F}_P has the SI units of N . Now, let us consider the work done by the pressure force. In a piston-cylinder arrangement in which a fluid exists with pressure P within the cylinder and the piston is rising with velocity \mathbf{v} , the work rate done by the fluid is positive. We can think of the local stress vector in the fluid as pointing in the same direction as the fluid is moving at the piston surface, so that the dot product is positive. Now, we can express the pressure force in terms of the pressure by

$$\mathbf{F}_P = P\mathbf{A}\mathbf{n}. \quad (6.73)$$

Substituting (6.72) into (6.73), we get

$$\frac{\delta W_P}{dt} = P\mathbf{A}\mathbf{n} \cdot \mathbf{v}. \quad (6.74)$$

It is noted that we have been a little loose distinguishing local areas from global areas. Better stated, we should say for a material volume that

$$\frac{\delta W_P}{dt} = \int_{A_m(t)} P\mathbf{n} \cdot \mathbf{v} dA. \quad (6.75)$$

This form allows for P and \mathbf{v} to vary with location. This is summarized in the sketch of Figure 6.8.

6.1.2.2.3 Heat transfer term If we were considering temperature fields with spatial dependency, we would define a heat flux vector. This approach is absolutely necessary to describe many real-world devices, and is the focus of a standard undergraduate course in

heat transfer. Here, we will take a simplified assumption that the only heat fluxes are easily specified and are all absorbed into a lumped scalar term we will call \dot{Q}_{mv} . This term has units of $J/s = W$ in SI. So we have then

$$\frac{\delta Q}{dt} = \dot{Q}_{mv}. \quad (6.76)$$

6.1.2.2.4 The first law of thermodynamics Putting the words of the first law into equation form, we get

$$\frac{d}{dt} \underbrace{\int_{V_m(t)} \rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dV}_{E_{mv}} = \frac{\delta Q}{dt} - \frac{\delta W}{dt}. \quad (6.77)$$

We next introduce our simplification of heat transfer (6.76) and partition of work (6.70) along with (6.75) into (6.77) to get

$$\frac{d}{dt} \int_{V_m(t)} \rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dV = \dot{Q}_{mv} - \left(\dot{W}_{mv} + \int_{A_m(t)} P \mathbf{n} \cdot \mathbf{v} dA \right). \quad (6.78)$$

Now, we bring the pressure work integral to the right side of (6.78) to get

$$\frac{d}{dt} \int_{V_m(t)} \rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dV + \int_{A_m(t)} P \mathbf{n} \cdot \mathbf{v} dA = \dot{Q}_{mv} - \dot{W}_{mv}. \quad (6.79)$$

We next invoke the Reynolds transport theorem (6.32) into (6.79) to expand the derivative of the first integral so as to obtain

$$\underbrace{\int_{V_m(t)} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV + \int_{A_m(t)} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \mathbf{v} \cdot \mathbf{n} dA}_{dE_{mv}/dt} + \int_{A_m(t)} P \mathbf{n} \cdot \mathbf{v} dA = \dot{Q}_{mv} - \dot{W}_{mv}. \quad (6.80)$$

We next note that the two area integrals have the same limits and can be combined to form

$$\int_{V_m(t)} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV + \int_{A_m(t)} \left(\rho \left(\underbrace{u + \frac{P}{\rho}}_h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \mathbf{v} \cdot \mathbf{n} dA = \dot{Q}_{mv} - \dot{W}_{mv}. \quad (6.81)$$

We recall now the definition of enthalpy h , Eq. (5.52),

$$h = u + \frac{P}{\rho} = u + Pv. \quad (6.82)$$

Invoking (6.82) into (6.81), we get

$$\int_{V_m(t)} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV + \int_{A_m(t)} \left(\rho \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \mathbf{v} \cdot \mathbf{n} dA = \dot{Q}_{mv} - \dot{W}_{mv}. \quad (6.83)$$

Next use the divergence theorem (6.2) to rewrite (6.83) as

$$\int_{V_m(t)} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV + \int_{V_m(t)} \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV = \dot{Q}_{mv} - \dot{W}_{mv}. \quad (6.84)$$

Now, for convenience, let us define the specific control volume heat transfer and work q_{mv} and w_{mv} , each with SI units J/kg such that

$$\dot{Q}_{mv} = \int_{V_m(t)} \frac{\partial}{\partial t} (\rho q_{mv}) dV, \quad (6.85)$$

$$\dot{W}_{mv} = \int_{V_m(t)} \frac{\partial}{\partial t} (\rho w_{mv}) dV, \quad (6.86)$$

so that by substituting (6.85) and (6.86) into (6.84), we get

$$\begin{aligned} \int_{V_m(t)} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV + \int_{V_m(t)} \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) dV \\ = \int_{V_m(t)} \frac{\partial}{\partial t} (\rho q_{mv}) dV - \int_{V_m(t)} \frac{\partial}{\partial t} (\rho w_{mv}) dV. \end{aligned} \quad (6.87)$$

Now, all terms in (6.87) have the same limits of integration, so they can be grouped to form

$$\begin{aligned} \int_{V_m(t)} \left(\frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) + \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \right. \\ \left. - \frac{\partial}{\partial t} (\rho q_{mv}) + \frac{\partial}{\partial t} (\rho w_{mv}) \right) dV = 0. \end{aligned} \quad (6.88)$$

As with the mass equation, since the integral is zero, in general we must expect the integrand to be zero, giving us

$$\frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) + \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) - \frac{\partial}{\partial t} (\rho q_{mv}) + \frac{\partial}{\partial t} (\rho w_{mv}) = 0. \quad (6.89)$$

To get the standard control volume form of the equation, we then integrate (6.89) over a *fixed* control volume V to get

$$\begin{aligned} \int_V \left(\frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) + \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \right. \\ \left. - \frac{\partial}{\partial t} (\rho q_{mv}) + \frac{\partial}{\partial t} (\rho w_{mv}) \right) dV = 0. \end{aligned} \quad (6.90)$$

Now, defining the control volume heat transfer rate and work rate, \dot{Q}_{cv} and \dot{W}_{cv} ,

$$\dot{Q}_{cv} = \int_V \frac{\partial}{\partial t} (\rho q_{mv}) dV, \quad (6.91)$$

$$\dot{W}_{cv} = \int_V \frac{\partial}{\partial t} (\rho w_{mv}) dV, \quad (6.92)$$

we employ (6.91) and (6.92) in (6.90) to get

$$\int_V \left(\frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) + \nabla \cdot \left(\rho \mathbf{v} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) \right) \right) dV = \dot{Q}_{cv} - \dot{W}_{cv}. \quad (6.93)$$

Applying the divergence theorem (6.2) to (6.93) to convert a portion of the volume integral into an area integral, and (6.36) to bring the time derivative outside the integral for the fixed volume, we get

$$\underbrace{\frac{d}{dt} \int_V \rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dV}_{E_{cv}} + \int_A \rho \mathbf{v} \cdot \mathbf{n} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dA = \dot{Q}_{cv} - \dot{W}_{cv}. \quad (6.94)$$

We now define the total energy in the control volume as

$$E_{cv} = \int_V \rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dV. \quad (6.95)$$

Next assume that all properties across entrances and exits are uniform so that the area integral in (6.93) reduces to

$$\int_A \rho \mathbf{v} \cdot \mathbf{n} \left(h + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} + gz \right) dA = \sum \dot{m}_e \left(h_e + \frac{1}{2} \mathbf{v}_e \cdot \mathbf{v}_e + gz_e \right) - \sum \dot{m}_i \left(h_i + \frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i + gz_i \right). \quad (6.96)$$

Substituting (6.95) and (6.96) into (6.94), we get

$$\frac{dE_{cv}}{dt} + \sum \dot{m}_e \left(h_e + \frac{1}{2} \mathbf{v}_e \cdot \mathbf{v}_e + gz_e \right) - \sum \dot{m}_i \left(h_i + \frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i + gz_i \right) = \dot{Q}_{cv} - \dot{W}_{cv}. \quad (6.97)$$

Rearranging (6.97), we get

$$\underbrace{\frac{dE_{cv}}{dt}}_{\text{rate of CV energy change}} = \underbrace{\dot{Q}_{cv}}_{\text{CV heat transfer rate}} - \underbrace{\dot{W}_{cv}}_{\text{CV shaft work rate}} + \underbrace{\sum \dot{m}_i \left(h_i + \frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i + gz_i \right)}_{\text{total enthalpy rate in}} - \underbrace{\sum \dot{m}_e \left(h_e + \frac{1}{2} \mathbf{v}_e \cdot \mathbf{v}_e + gz_e \right)}_{\text{total enthalpy rate out}} \quad (6.98)$$

Here, (6.98) is equivalent to BS's Eq. (6.7), p. 185. Note that the so-called *total enthalpy* is often defined as

$$h_{tot} = h + \frac{1}{2}\mathbf{v} \cdot \mathbf{v} + gz. \quad (6.99)$$

Employing (6.99) in (6.98), we find

$$\boxed{\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum \dot{m}_i h_{tot,i} - \sum \dot{m}_e h_{tot,e}.} \quad (6.100)$$

Here, (6.100) is equivalent to BS's (6.8), p. 185.

If there is a single entrance and exit, we lose the summation, so that (6.98) becomes

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i \left(h_i + \frac{1}{2}\mathbf{v}_i \cdot \mathbf{v}_i + gz_i \right) - \dot{m}_e \left(h_e + \frac{1}{2}\mathbf{v}_e \cdot \mathbf{v}_e + gz_e \right). \quad (6.101)$$

If the flow is steady, we have $dE_{cv}/dt = 0$ and $\dot{m}_i = \dot{m}_e = \dot{m}$, so the first law with a single entrance and exit becomes

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m} \left(h_i - h_e + \frac{1}{2}(\mathbf{v}_i \cdot \mathbf{v}_i - \mathbf{v}_e \cdot \mathbf{v}_e) + g(z_i - z_e) \right). \quad (6.102)$$

Defining the specific control volume heat transfer and work as

$$q = \frac{\dot{Q}_{cv}}{\dot{m}}, \quad w = \frac{\dot{W}_{cv}}{\dot{m}}, \quad (6.103)$$

and substituting (6.103) into (6.102), we get

$$0 = q - w + h_i - h_e + \frac{1}{2}(\mathbf{v}_i \cdot \mathbf{v}_i - \mathbf{v}_e \cdot \mathbf{v}_e) + g(z_i - z_e). \quad (6.104)$$

Now, (6.104) can be rearranged to form BS's (6.13), p. 187:

$$\boxed{q + h_i + \frac{1}{2}\mathbf{v}_i \cdot \mathbf{v}_i + gz_i = w + h_e + \frac{1}{2}\mathbf{v}_e \cdot \mathbf{v}_e + gz_e.} \quad (6.105)$$

This looks more like the first law when we rearrange as

$$\left(h_e + \frac{1}{2}\mathbf{v}_e \cdot \mathbf{v}_e + gz_e \right) - \left(h_i + \frac{1}{2}\mathbf{v}_i \cdot \mathbf{v}_i + gz_i \right) = q - w. \quad (6.106)$$

If the flow is adiabatic, steady, has one entrance and one exit, and there is no shaft work, we find that the total enthalpy must remain constant:

$$h_i + \frac{1}{2}\mathbf{v}_i \cdot \mathbf{v}_i + gz_i = h_e + \frac{1}{2}\mathbf{v}_e \cdot \mathbf{v}_e + gz_e. \quad (6.107)$$

6.2. Mass conservation in brief

Here, we summarize the key equations for mass conservation derived in the previous section. We consider the mass enclosed in a fixed control volume V , Eq. (6.53):

$$m_{cv} = \int_V \rho dV. \quad (6.108)$$

The density ρ can vary throughout V . In this class, we will nearly always take it to be constant throughout the volume. If ρ is constant throughout V , then it can be brought outside the integral operator, yielding $m_{cv} = \rho \int_V dV = \rho V$. Our control volume will have a finite number of openings where fluid can enter and exit.

We state mass conservation for a control volume as

$$\underbrace{\frac{dm_{cv}}{dt}}_{\text{rate of change of mass}} = \underbrace{\sum \rho_i |\mathbf{v}_i| A_i}_{\text{mass rate in}} - \underbrace{\sum \rho_e |\mathbf{v}_e| A_e}_{\text{mass rate out}}, \quad (6.109)$$

$$\boxed{\underbrace{\frac{dm_{cv}}{dt}}_{\text{rate of change of mass}} = \underbrace{\sum \dot{m}_i}_{\text{mass rate in}} - \underbrace{\sum \dot{m}_e}_{\text{mass rate out}}.} \quad (6.110)$$

Equations (6.109, 6.110) were fully developed in the previous section where they appeared as Eqs. (6.59, 6.60). Here, the fluid at an inlet i has density ρ_i , velocity vector \mathbf{v}_i and flows through cross-sectional area A_i . An analogous set of variables exists at each exit e . Let us look at the units of the important quantity $\rho|\mathbf{v}|A$:

$$\rho|\mathbf{v}|A \rightarrow \frac{kg}{m^3} \frac{m}{s} \frac{m^2}{1} = \frac{kg}{s}. \quad (6.111)$$

Obviously, it is a rate of mass flow; consequently, we define the mass flow rate as

$$\dot{m} \equiv \rho|\mathbf{v}|A. \quad (6.112)$$

Often we will neglect the vector notation and take $|\mathbf{v}| = v$. Equation (6.110) expresses mathematically the notion of mass conservation for the control volume:

- *The time rate of accumulation of mass within the control volume is equal to the net rate of mass flow into the control volume.*

In short

$$\text{accumulation} = \text{in} - \text{out}.$$

In the important case in which there is no net accumulation rate, the so-called *steady state* limit, we get

$$\underbrace{\frac{dm_{cv}}{dt}}_{=0} = \sum \dot{m}_i - \sum \dot{m}_e. \quad (6.113)$$

$$\boxed{\sum \dot{m}_i = \sum \dot{m}_e.} \quad (6.114)$$

Eq. (6.114) is the same as Eq. (6.62). If there is a single entrance and exit, then we simply get

$$\dot{m}_i = \dot{m}_e = \dot{m} = \text{constant}. \quad (6.115)$$

6.3. Energy conservation in brief

We can state the first law of thermodynamics for a control volume as

$$\underbrace{\frac{dE_{cv}}{dt}}_{\text{rate of CV energy change}} = \underbrace{\dot{Q}_{cv}}_{\text{CV heat transfer rate}} - \underbrace{\dot{W}_{cv}}_{\text{CV shaft work rate}} + \underbrace{\sum \dot{m}_i \left(h_i + \frac{1}{2}v_i^2 + gz_i \right)}_{\text{total enthalpy rate in}} - \underbrace{\sum \dot{m}_e \left(h_e + \frac{1}{2}v_e^2 + gz_e \right)}_{\text{total enthalpy rate out}}. \quad (6.144)$$

Here, Eq. (6.144) is equivalent Eq. (6.98) and to BS's Eq. (6.7), p. 185. Note that the so-called *total enthalpy* is often defined as

$$h_{tot} = h + \frac{1}{2}v^2 + gz = u + \frac{1}{2}v^2 + gz + Pv. \quad (6.145)$$

Note that in this context, total enthalpy is on a per mass basis. The “total” comes from summing internal, kinetic, potential, and Pv terms. Employing (6.145) in (6.144), we find

$$\boxed{\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \sum \dot{m}_i h_{tot,i} - \sum \dot{m}_e h_{tot,e}.} \quad (6.146)$$

Here, Eq. (6.146) is equivalent to Eq. (6.100) and to BS's (6.8), p. 185. Eq. (6.146) expresses mathematically the notion of energy conservation for the control volume:

- *The time rate of accumulation of total energy within the control volume is equal the rate of heat transfer into the control volume minus the rate of work done leaving the control volume plus the net rate of total enthalpy entering the control volume.*

The new terms here are attributable to total enthalpy entering and exiting the control volume.

Again, the total enthalpy is the sum of the specific internal energy, the specific kinetic energy, the specific potential energy and the term Pv . It is easy to imagine that E_{cv} , which itself is composed of u , KE , and PE , is affected by the flow of u , KE , and PE into and out of the control volume. However the term Pv is unusual. It is multiplied by \dot{m} . Let us check the units:

$$\dot{m}Pv \rightarrow \left(\frac{kg}{s}\right) \left(\frac{kN}{m^2}\right) \left(\frac{m^3}{kg}\right) = \frac{kJ}{s} = kW. \quad (6.147)$$

It has the units of power. As shown in detail in the previous section,

- The term $\dot{m}Pv$ embedded within the control volume energy equation within h_{tot} accounts for the net work rate done by the fluid as it enters and exits the control surface bounding the control volume.
- The term \dot{W}_{cv} represents so-called shaft work and does not include work associated with the expansion of the working fluid.

If there is a single entrance and exit, we lose the summation, so that (6.144) becomes

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i \left(h_i + \frac{1}{2}v_i^2 + gz_i \right) - \dot{m}_e \left(h_e + \frac{1}{2}v_e^2 + gz_e \right). \quad (6.148)$$

If the flow is steady, we have $dE_{cv}/dt = 0$ and $\dot{m}_i = \dot{m}_e = \dot{m}$, so the first law with a single entrance and exit becomes

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m} \left(h_i - h_e + \frac{1}{2}(v_i^2 - v_e^2) + g(z_i - z_e) \right). \quad (6.149)$$

Defining the specific control volume heat transfer and work as

$$q = \frac{\dot{Q}_{cv}}{\dot{m}}, \quad w = \frac{\dot{W}_{cv}}{\dot{m}}, \quad (6.150)$$

and substituting (6.150) into (6.149), we get

$$0 = q - w + h_i - h_e + \frac{1}{2}(v_i^2 - v_e^2) + g(z_i - z_e). \quad (6.151)$$

Now, (6.151) can be rearranged to form BS's (6.13), p. 187:

$$q + h_i + \frac{1}{2}v_i^2 + gz_i = w + h_e + \frac{1}{2}v_e^2 + gz_e. \quad (6.152)$$

This looks more like the first law when we rearrange as

$$\underbrace{\left(h_e + \frac{1}{2}v_e^2 + gz_e \right)}_{\text{outlet}} = \underbrace{\left(h_i + \frac{1}{2}v_i^2 + gz_i \right)}_{\text{inlet}} + \underbrace{q - w}_{\text{CV heat and work}}. \quad (6.153)$$

If the flow is adiabatic, steady, has one entrance and one exit, and there is no shaft work, we find that the total enthalpy must remain constant:

$$h_i + \frac{1}{2}v_i^2 + gz_i = h_e + \frac{1}{2}v_e^2 + gz_e. \quad (6.154)$$

6.4. Some devices

Here, we will consider rudiments of control volume analysis for some common engineering devices.

6.4.1 Throttling device

A flow is throttled when, for example, it flows through a partially open valve. When it does so, we notice that there can be a significant pressure loss from one side of the partially open valve to the other. A sketch of a throttling device is given in Fig. 6.12

We model a throttling device as steady with one entrance and exit, with no control volume work or heat transfer. We neglect changes in area as well as potential energy. Mass conservation tells us

$$\underbrace{\frac{dm_{cv}}{dt}}_{=0} = \dot{m}_1 - \dot{m}_2, \quad (6.155)$$

$$0 = \dot{m}_1 - \dot{m}_2, \quad (6.156)$$

$$\dot{m}_1 = \dot{m}_2 = \dot{m}. \quad (6.157)$$

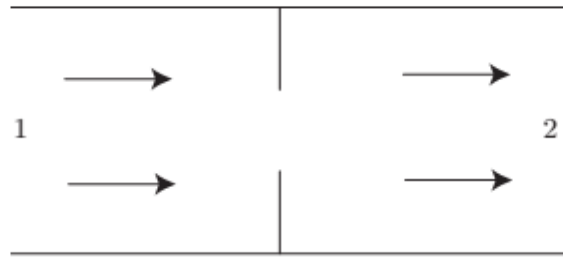


Figure 6.12: Sketch of throttling device.

Energy conservation tells us that

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_1 \left(h_1 + \frac{v_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{v_2^2}{2} + gz_2 \right), \quad (6.158)$$

$$0 = \dot{m} \left(h_1 - h_2 + \underbrace{\frac{v_1^2}{2} - \frac{v_2^2}{2}}_{\sim 0} + \underbrace{gz_1 - gz_2}_{=0} \right). \quad (6.159)$$

Now, in throttling devices there may be a change in velocity due to compressibility effects, but it is observed to be small when the flow velocity is much less than the speed of sound. We shall assume here the velocity is small relative to the speed of sound so as to recover $v_1 \sim v_2$ and thus

$$h_1 = h_2. \quad (6.160)$$

So, we can say that such a throttling device is one in which pressure drops and enthalpy remains constant.

6.4.2 Nozzles and diffusers

Similar to a throttling device, we model nozzles and diffusers as steady with one entrance and exit, with no control volume work. We may or may not neglect heat transfer. We neglect potential energy changes *but take kinetic energy changes into account*.

A nozzle is a device which induces a velocity increase; a diffuser is a device which induces a velocity decrease. For flows with subsonic velocities, nozzles have area decrease in the flow direction, while diffusers have area increases with the flow direction. We sketch these common configurations in Fig. 6.13. If one systematically applied the conservation of mass,

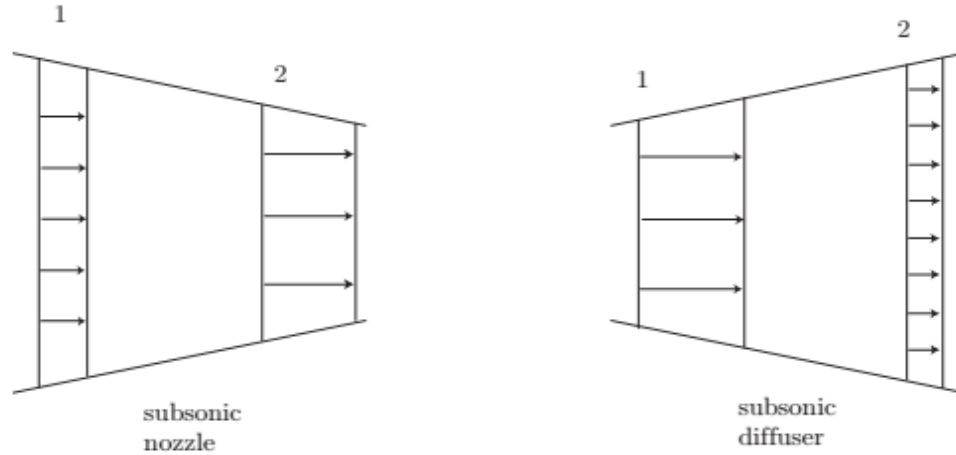


Figure 6.13: Sketch of subsonic nozzle and diffuser.

momentum, and energy principles, after detailed analysis, one finds the converse state of affairs for supersonic flow conditions. Supersonic nozzles have increasing area; supersonic diffusers have decreasing area. This is why in the design of rocket nozzles, the cross-sectional area broadens at the base. The broadening area induces a higher velocity, and induces a higher thrust for a supersonic rocket engine.

We analyze nozzles and diffusers as follows. Mass conservation tells us

$$\underbrace{\frac{dm_{cv}}{dt}}_{=0} = \dot{m}_1 - \dot{m}_2, \quad (6.163)$$

$$\dot{m}_1 = \dot{m}_2 = \dot{m}. \quad (6.164)$$

Energy conservation tells us

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \dot{Q}_{cv} - \underbrace{\dot{W}_{cv}}_{=0} + \dot{m}_1 \left(h_1 + \frac{v_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{v_2^2}{2} + gz_2 \right), \quad (6.165)$$

$$0 = \dot{Q}_{cv} + \dot{m} \left(h_1 - h_2 + \frac{v_1^2}{2} - \frac{v_2^2}{2} + \underbrace{gz_1 - gz_2}_{=0} \right), \quad (6.166)$$

$$0 = \frac{\dot{Q}_{cv}}{\dot{m}} + h_1 - h_2 + \frac{v_1^2}{2} - \frac{v_2^2}{2}. \quad (6.167)$$

If the nozzle or diffuser is also adiabatic, we get

$$h_1 + \frac{v_1^2}{2} = h_2 + \frac{v_2^2}{2}. \quad (6.168)$$

6.4.3 Turbine

A turbine is a device in which work is generated through expansion of a fluid as it passes through a fan-like device. The fluid interacts with the blades and turns the fan. Ultimately thermal and mechanical energy is transferred from the fluid into the rotational kinetic energy of the fan blades. A sketch of a turbine is given in Fig. 6.14. For a turbine, we typically

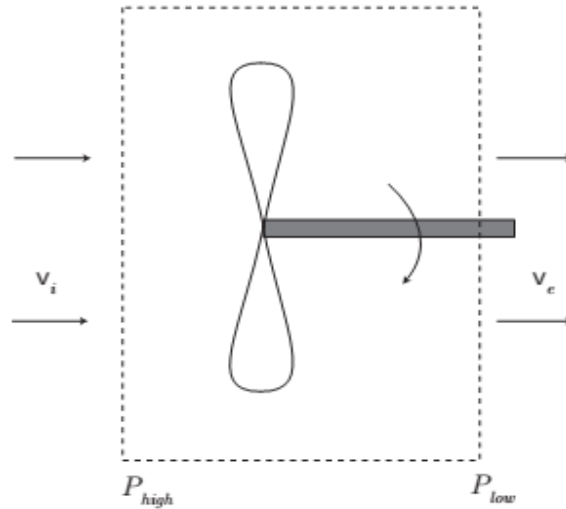


Figure 6.14: Highly simplified sketch of turbine.

neglect kinetic and potential energy changes of the fluid. We may or may not neglect heat transfer. We also neglect any unsteady effects. Mass conservation tells us

$$\underbrace{\frac{dm_{cv}}{dt}}_{=0} = \dot{m}_1 - \dot{m}_2, \quad (6.169)$$

$$\dot{m}_1 = \dot{m}_2 = \dot{m}. \quad (6.170)$$

Energy conservation tells us

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_1 \left(h_1 + \frac{v_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{v_2^2}{2} + gz_2 \right), \quad (6.171)$$

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m} \left(h_1 - h_2 + \underbrace{\frac{v_1^2}{2} - \frac{v_2^2}{2}}_{=0} + \underbrace{gz_1 - gz_2}_{=0} \right), \quad (6.172)$$

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}(h_1 - h_2), \quad (6.173)$$

$$\dot{W}_{cv} = \dot{Q}_{cv} + \dot{m}(h_1 - h_2). \quad (6.174)$$

We often neglect \dot{Q}_{cv} to get

$$\boxed{\dot{W}_{cv} = \dot{m}(h_1 - h_2)}. \quad (6.175)$$

On a per mass basis, we can scale by \dot{m} to get

$$w = h_1 - h_2. \quad (6.176)$$

For turbines, $h_1 > h_2$, so we get $w > 0$. The device is doing work.

6.4.4 Pumps and compressors

The analysis for a pump or compressor is effectively identical to that for a turbine. However the device operates in an opposite sense. Mechanical energy from either rotating (like a compressor in a jet engine) or reciprocating machinery (like a piston-cylinder arrangement) is transferred to the working fluid, raising its energetic state. We typically neglect changes in kinetic and potential energy of the fluid and consider the device to be in a steady state. We sometimes neglect heat transfer to the device.

The analysis is as follows. Mass conservation tells us

$$\underbrace{\frac{dm_{cv}}{dt}}_{=0} = \dot{m}_1 - \dot{m}_2, \quad (6.177)$$

$$\dot{m}_1 = \dot{m}_2 = \dot{m}. \quad (6.178)$$

Energy conservation tells us

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_1 \left(h_1 + \frac{v_1^2}{2} + gz_1 \right) - \dot{m}_2 \left(h_2 + \frac{v_2^2}{2} + gz_2 \right), \quad (6.179)$$

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m} \left(h_1 - h_2 + \underbrace{\frac{v_1^2}{2} - \frac{v_2^2}{2}}_{=0} + \underbrace{gz_1 - gz_2}_{=0} \right), \quad (6.180)$$

$$0 = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}(h_1 - h_2), \quad (6.181)$$

$$\dot{W}_{cv} = \dot{Q}_{cv} + \dot{m}(h_1 - h_2). \quad (6.182)$$

We often neglect \dot{Q}_{cv} to get

$$\boxed{\dot{W}_{cv} = \dot{m}(h_1 - h_2)}. \quad (6.183)$$

On a per mass basis, we can scale by \dot{m} to get

$$w = h_1 - h_2. \quad (6.184)$$

For pumps and compressors, $h_1 < h_2$, so we get $w < 0$. The device requires an input of work.

6.4.5 Heat exchanger

A heat exchanger is a device in which a working fluid trades its thermal energy with another working fluid. A sketch of a heat exchanger is given in Fig. 6.15. For heat exchangers, we

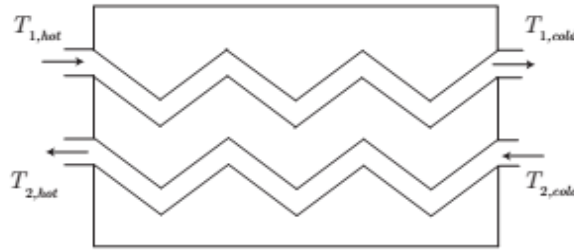


Figure 6.15: Sketch of counterflow heat exchanger.

typically neglect all work, as well as changes in kinetic and potential energy. Also

- there will be exchange of thermal energy between individual flow streams, but
- globally for the entire device, there will be no heat transfer with the environment.

Let us consider a counterflow heat exchanger. The mass balance for steady flow is trivial. The energy balance, neglecting changes in KE and PE states

$$\underbrace{\frac{dE_{cv}}{dt}}_{=0} = \underbrace{\dot{Q}_{cv}}_{=0} - \underbrace{\dot{W}_{cv}}_{=0} + \sum_i \dot{m}_i h_i - \sum_e \dot{m}_e h_e. \quad (6.185)$$

Applying this to the counterflow heat exchanger gives

$$\dot{m}_1 h_{1,hot} + \dot{m}_2 h_{2,cold} = \dot{m}_1 h_{1,cold} + \dot{m}_2 h_{2,hot}, \quad (6.186)$$

$$\dot{m}_1 (h_{1,hot} - h_{1,cold}) = \dot{m}_2 (h_{2,hot} - h_{2,cold}). \quad (6.187)$$

6.5. Introduction to the Rankine cycle

Consider the

- **RANKINE CYCLE:** a thermodynamic cycle which forms the foundation for most steam power plants.

The cycle was studied analytically by Rankine¹³ depicted in Fig. 6.17. We will consider



Fig 6.17. William John Macquorn Rankine (1820-1872), Scottish engineer who systematically studied and publish discussion of steam power cycles

additional nuances of the Rankine cycle in Sec. 10.1

The key features of the Rankine cycle are

- 1 \rightarrow 2: compression of a liquid by a pump,
- 2 \rightarrow 3: boiling of the liquid to form a vapor,
- 3 \rightarrow 4: expansion of the vapor through a turbine, and
- 4 \rightarrow 1: condensation of the vapor to liquid in a condenser.

A sketch of the Rankine cycle in the $P - v$ plane is given in Fig. 6.18. The Rankine

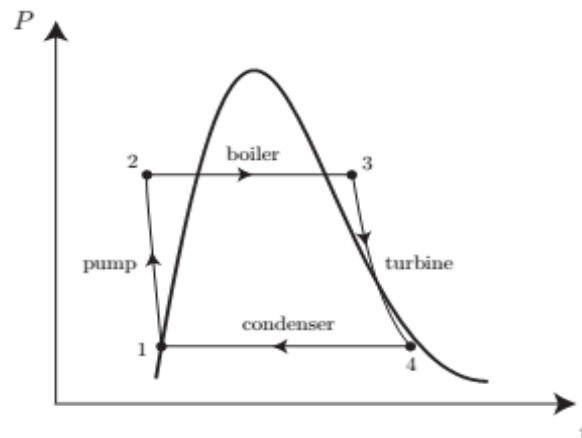


Figure 6.18: Sketch of Rankine cycle in the $P - v$ plane.

cycle forms the cornerstone of a wide variety of power generating devices in the world today. Whether the heat source comes from burning coal, natural gas, fuel oil, garbage, nuclear fission, solar energy, or some other source, it can always be used to boil water, which is

the key feature of the Rankine cycle. Most modern power plants are considerably more complicated than the simple outline given here. Some are equipped to use a variety of fuels. Often coal burning components are used continuously for so-called base loads and are supplemented during peak consumption hours by natural gas. Some modern plants use natural gas for base loads. Some cycles are equipped for district heating and cooling, some for electric power generation, some for nautical propulsion.

6.6. Preview: equation of continuum mechanics

This course focuses on mass and energy conservation coupled with equations of state for systems which are well modeled as equilibrium processes. We can do many important problems with these tools. However, there are many problems which we cannot do with these tools, e.g. problems with coupled time and space dependency, or problems with detailed material motion.

Let us, as a preview for future courses, write various related sets of partial differential equations which can couple equilibrium thermodynamics with mechanics.

6.6.1 Full set

We first give a summary of a reasonably complete and general set of equations for a continuum material. One way to write these equations is as follows:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad \text{mass,} \quad (6.265)$$

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \rho \mathbf{g} - \nabla P + \nabla \cdot \boldsymbol{\tau}, \quad \text{linear momenta,} \quad (6.266)$$

$$\boldsymbol{\tau}^T = \boldsymbol{\tau}, \quad \text{angular momenta,} \quad (6.267)$$

$$\begin{aligned} \frac{\partial}{\partial t} \left(\rho \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) \right) + \nabla \cdot \left(\rho \mathbf{v} \left(u + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) \right) &= -\nabla \cdot \mathbf{q} - \nabla \cdot (P \mathbf{v}) \\ &\quad + \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) + \rho \mathbf{v} \cdot \mathbf{g}, \\ &\quad \text{energy.} \end{aligned} \quad (6.268)$$

Equations (6.265-6.268) are the axioms of mass conservation, linear momentum conservation, angular momenta conservation, and energy conservation, respectively. They are valid for any pure material, be it solid, liquid, or gas, as long as we are at velocities small relative to the velocity of light. New variables here include the deviatoric stress tensor $\boldsymbol{\tau}$, and the heat flux

vector \mathbf{q} . The vector \mathbf{g} is the constant gravitational acceleration. It is easily modified for variable gravitational acceleration.

The conservation axioms are necessary but not sufficient to determine all flow variables. They must be supplemented by *constitutive relations*. Constitutive relations specify the actual material. A general set is given here.

$$P = P(\rho, T), \quad \text{thermal EOS}, \quad (6.269)$$

$$u = u(\rho, T), \quad \text{caloric EOS}, \quad (6.270)$$

$$\mathbf{q} = \mathbf{q}(T, \nabla T, \dots), \quad \text{heat flux}, \quad (6.271)$$

$$\boldsymbol{\tau} = \boldsymbol{\tau}(T, \nabla \mathbf{v}, \nabla \mathbf{x}, \dots), \quad \text{stress}. \quad (6.272)$$

Equation (6.269) is a thermal equation of state. An example is the ideal gas law $P = \rho RT$. Equation (6.270) is a caloric equation of state. An example is a calorically perfect ideal gas, $u = c_v(T - T_o) + u_o$. Equation (6.271) is a relation between the heat flux vector and other state variables. An example is Fourier's law, $\mathbf{q} = -\mathbf{k}\nabla T$. Equation (6.272) is a relation between the deviatoric stress and a variety of variables. For example, a Newtonian fluid obeying Stokes' assumption has $\boldsymbol{\tau} = \mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) - (1/3)(\nabla \cdot \mathbf{v})\mathbf{I}$. This relates stress to strain rate. On the other hand, the stress in a solid would be related to the strain, instead of the strain rate.

6.6.2 Static solids equations

For a static solid, we take $\mathbf{v} = \mathbf{0}$ and the density constant. The mass equation becomes irrelevant, as does the angular momenta equation. The linear momenta equation reduces to a force balance, since inertia is zero. We take the total stress tensor $\boldsymbol{\sigma} = \boldsymbol{\tau} - P\mathbf{I}$, where \mathbf{I} is the identity matrix.

$$\nabla \cdot \boldsymbol{\sigma} = -\rho \mathbf{g}, \quad \text{linear momenta.} \quad (6.273)$$

$$\boldsymbol{\sigma} = \frac{E}{1+\nu} \left(\mathbf{e} + \frac{\nu}{1-2\nu} \text{Tr}(\mathbf{e})\mathbf{I} \right), \quad \text{stress-strain relation.} \quad (6.274)$$

Here, E is the modulus of elasticity, ν is Poisson's ratio ($-1 \leq \nu \leq 1/2$), and \mathbf{e} is the strain.

6.6.3 Incompressible fluid mechanics equations

In the discipline of incompressible fluid mechanics, we typically take ρ to be a constant, we ignore the kinetic energy of the fluid, consider fluid properties such as viscosity and conductivity to be constant, and reduce our equations to the following set

$$\nabla \cdot \mathbf{v} = 0, \quad \text{mass}, \quad (6.275)$$

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = \rho \mathbf{g} - \nabla P + \mu \nabla^2 \mathbf{v}, \quad \text{linear momenta}, \quad (6.276)$$

$$\boldsymbol{\tau}^T = \boldsymbol{\tau}, \quad \text{angular momenta}, \quad (6.277)$$

$$\rho c_P \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \mathbf{k} \nabla^2 T, \quad \text{energy}, \quad (6.278)$$

$$\boldsymbol{\tau} = \mu(\nabla \mathbf{v} + (\nabla \mathbf{v})^T), \quad \text{stress-strain rate,} \quad (6.279)$$

$$\mathbf{q} = -\mathbf{k}\nabla T, \quad \text{Fourier's law} \quad (6.280)$$

The thermodynamic state equations are not particularly important here. Moreover, the mass and linear momenta equations form an independent set. The energy equation is coupled to mass and momenta equations because of the velocity vector.

6.6.4 Compressible fluid mechanics equations

In compressible aerodynamics, we account for density changes and thermodynamics, but usually neglect gravity, viscosity and heat conduction. Our equations reduce to, for a CPIG,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad \text{mass,} \quad (6.281)$$

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla P, \quad \text{linear momenta,} \quad (6.282)$$

$$\left(\frac{\partial u}{\partial t} + \mathbf{v} \cdot \nabla u \right) = -P \left(\frac{\partial v}{\partial t} + \mathbf{v} \cdot \nabla v \right), \quad \text{energy,} \quad (6.283)$$

$$P = \rho RT, \quad \text{thermal state,} \quad (6.284)$$

$$u = c_v T + u_o, \quad \text{caloric state.} \quad (6.285)$$

Notice the energy equation is simply the familiar $du/dt = -Pdv/dt$, when d/dt is interpreted as $\partial/\partial t + \mathbf{v} \cdot \nabla$.

6.6.5 Heat transfer in incompressible static solids

For heat transfer in static solids, we require $\mathbf{v} = \mathbf{0}$. Moreover, there is no work. We take a calorically perfect solid with constant thermal conductivity \mathbf{k} which obeys Fourier's law $\mathbf{q} = -\mathbf{k}\nabla T$ and get the first law of thermodynamics to reduce to the simple scalar equation known to Fourier in the early nineteenth century:

$$\rho c \frac{\partial T}{\partial t} = \mathbf{k} \nabla^2 T, \quad \text{energy.} \quad (6.286)$$

LECTURE 7: THE SECOND LAW OF THERMODYNAMICS

Content of Lecture 7

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Conservation of mass and energy are fine concepts that allow us to quantify and predict well many phenomena which are observed in nature. And if a phenomenon can be repeated, it becomes subject to prediction, and can be thought of as a science.

However, *conservation of mass and energy, by themselves, admit as possibilities phenomena which are not observed in nature!* For instance consider an isolated system composed of two equal masses of liquid water. See Fig. 7.1. The first is at $T_A = 310\text{ K}$, the second is at

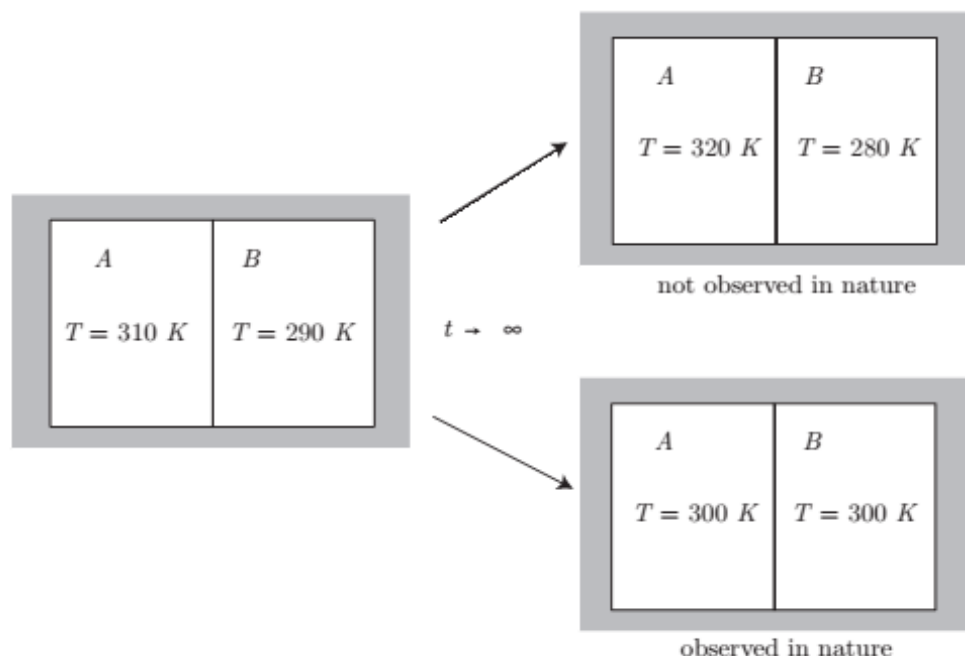


Figure 7.1: Sketch of two scenarios, both of which satisfy mass and energy conservation.

$T_B = 290\text{ K}$. A long time elapses. Because the combined system is isolated, there are no external heat or work exchanges with the environment. But we will allow heat exchanges between mass A and mass B. Consider two possibilities, both admitted by mass and energy conservation, as $t \rightarrow \infty$:

- $T_A \rightarrow 320\text{ K}$, $T_B \rightarrow 280\text{ K}$. The thermal energy that is gained by A is lost by B, such that the net energy is conserved and the first law is satisfied. *This is never observed in nature.*
- $T_A \rightarrow 300\text{ K}$, $T_B \rightarrow 300\text{ K}$. The thermal energy that is lost by A is gained by B, so once again the first law is satisfied. *This is always observed in nature.*

So mass conservation and the first law of thermodynamics, both of which speak to this *gedankenexperiment*, are insufficient to guarantee that we will predict what is observed in nature. We need another axiom!

In a similar way, there are a variety of phenomena which may satisfy mass and energy conservation, but are not observed in nature. Some include

- water running uphill without an external assist,
- CO_2 and H_2O reacting spontaneously to form CH_4 and O_2 , and
- air separating into its constituents spontaneously.

7.1. Statements of the second law

The *second law of thermodynamics* is an attempt to provide a single all-encompassing statement which expands our thermodynamic theory so as to predict the just-described behavior. Though our statement of the second law will be simple enough, it will be obtuse and sometimes difficult to reconcile with nature. It is also a profound concept which has wide ranging ramifications. Its origins are firmly rooted in the engineering sciences, as it was motivated by optimization of steam engines. However, it has found applications in many realms of physics, chemistry, ecology, economics, computer science, and other fields.

In his influential essay contrasting scientific and humanistic cultures, C. P. Snow¹ sees understanding of the second law as an indicator of scientific literacy and goes on to chide his humanist colleagues:

A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics, the law of entropy. The response was cold: it was also negative. Yet I was asking something which is about the scientific equivalent of: ‘Have you read a work of Shakespeare’s?’ I now believe that if I had asked an even simpler question —such as, What do you mean by mass, or acceleration, which is the scientific equivalent of saying, ‘Can you read?’ —not more than one in ten of the highly educated would have felt that I was speaking the same language. So the great edifice of modern physics goes up, and the majority of the cleverest people in the western world have about as much insight into it as their Neolithic ancestors would have had.

Let us summarize some more reasons for studying the second law:

- It predicts the direction in time of processes.
- It aids in determining equilibrium conditions.
- It allows one to determine peak performance of practical devices.
- It enables one to frame analysis of the factors which inhibit the realization of peak performance.
- It allows a rational definition of the absolute temperature scale.
- It has implications beyond engineering in physics, philosophy, economics, computer science, etc.

7.1.1 Entropy-based statement

There are many ways to state the second law of thermodynamics. One statement is as follows:

- **SECOND LAW OF THERMODYNAMICS:** The entropy of an isolated system can never decrease with time.

This definition begs the question, what is entropy? A formal definition will be deferred to the next chapter. Let us loosely define it here as a measure of the so-called randomness (or disorder) of a system, with high randomness corresponding to high entropy. Low randomness or low disorder often corresponds to low entropy.

Interpreted in another way, structure or order requires energy input to be realized, while over time, without continued maintenance, structure and order decay. The formulation of the second law we adopt will be robust enough to prevent us from predicting water to run uphill, methane to spontaneously form from carbon dioxide and water, or air to separate into its constituents. It will also be seen to be an important principle for predicting the optimal behavior of a wide variety of engineering devices.

All that said, it should be noted that the equivalence of entropy with disorder, while useful and common, is likely not universal. Certainly Wright² characterizes it as “a highly

²P. G. Wright, 1970, “Entropy and disorder,” *Contemporary Physics*, 11(6): 581-588.

contentious opinion” and discusses counter-examples, especially as related to molecular level phenomena. Wright’s arguments are reinforced by Styer³ who concludes that the notion of “entropy as disorder” be used only in conjunction with the notion of “entropy as freedom.” Freedom here is to be interpreted as the ability to acquire a variety of states: if only one state is available, freedom is severely restricted, and entropy is low; if many states are available, freedom is widespread, and entropy is high. Both terms, “disorder” and “freedom” are shown by Styer to have alternate interpretations which render both imperfect metaphors for entropy.

³D. F. Styer, 2000, “Insight into entropy,” *American Journal of Physics*, 68(12): 1090-1096.

7.1.2 Clausius statement

Clausius, the German mathematical physicist who probably did the most to cast thermodynamics on a scientific basis, gives a more precise statement of the second law:

- **SECOND LAW OF THERMODYNAMICS:** “Heat cannot, of itself, pass from a colder to a hotter body.”⁴

⁴R. Clausius, 1879, *The Mechanical Theory of Heat*, Macmillan, London, p. 78.

The original German version appeared earlier⁵ and is reproduced in Fig. 7.2.

⁵R. Clausius, 1854, “Ueber eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie,” *Annalen der Physik und Chemie*, 169(12): 481-506.

Dieser Grundsatz, auf welchem die ganze folgende Entwicklung beruht, lautet: *es kann nie Wärme aus einem kälteren in einen wärmeren Körper übergehen, wenn nicht gleichzeitig eine andere damit zusammenhängende Änderung eintritt.* Er wird durch Alles, was wir über den Wärme-

Figure 7.2: Image of the [original 1854 appearance](#) of the Clausius form of the second law.

The Clausius formulation of the second law is easy to understand in engineering terms and is illustrated schematically in Fig. [7.3](#). Note that air conditioners move heat from cold regions to hot regions, but that work input is required.

7.1.3 Kelvin-Planck statement

Another statement of the second law is inspired by statements of the nineteenth century scientists, Kelvin and Planck, depicted in Fig. [7.4](#). The so-called Kelvin-Planck statement, a modern rendition of earlier statements, is often given as

- **SECOND LAW OF THERMODYNAMICS:** It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of work to its surroundings while receiving an energy transfer by heat from a single thermal reservoir.

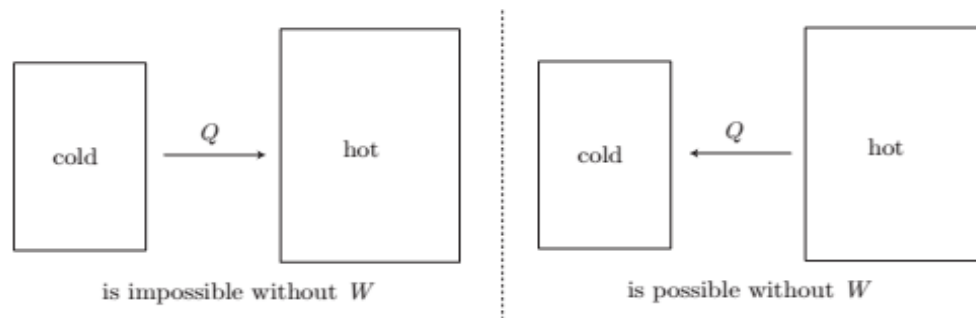
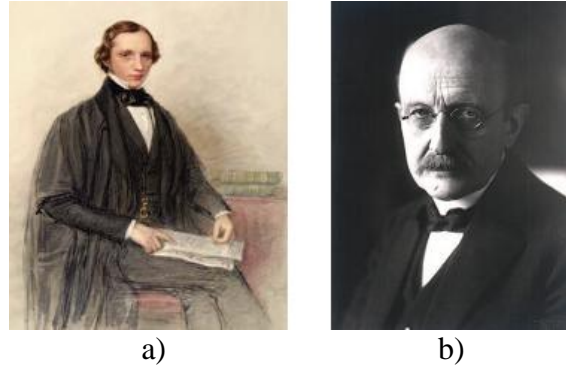


Figure 7.3: Schematic of the Clausius statement of the second law of thermodynamics. Thomson’s original 1851 statement^{[6](#)} is somewhat different. Planck’s 1897 statement^{[7](#)} is closer. Both are reproduced in Fig. [7.5](#).

⁶[W. Thomson \(later Lord Kelvin\), 1851](#), “On the dynamical theory of heat, with numerical results deduced from Mr. Joule’s equivalent of a thermal unit, and M. Regnault’s observations on steam,” *Transactions of the Royal Society of Edinburgh*, 20: 261-268; 289-298.

⁷[M. Planck, 1897](#), *Vorlesungen über Thermodynamik*, Walter de Gruyter, Berlin; reprinted in [English translation](#) as *Treatise on Thermodynamics*, Dover, New York, p. 89.

Fig 7.4. a) William Thomson (Lord Kelvin)(1824-1907), Ulster-born Scottish scientist who had profound on nineteenth century science including thermodynamics; b) Max Carl Ernst Ludwig Planck (1858-1947), German physicist



<p><i>It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects*.</i></p>	<p><i>It is impossible to construct an engine which will work in a complete cycle, and produce no effect except the raising of a weight and the cooling of a heat-reservoir.*</i></p>
a) Kelvin	b) Planck

Fig 7.5. Images of a) Thomson’s 1851 and b) Planck’s 1897 statements of the second law of thermodynamics

The Kelvin-Planck formulation of the second law is easy to understand in engineering terms and is illustrated schematically in Fig. 7.6. For the schematic of Fig. 7.6, the first law, neglecting changes in kinetic and potential energy, states that

$$U_2 - U_1 = Q - W. \tag{7.1}$$

But we have specified that the process is a cycle, so $U_1 = U_2$, and thus the first law holds

$$Q = W. \tag{7.2}$$

Now, the second law, for this scenario, holds that positive Q cannot be delivered, which gives, for an engine in contact with a *single* thermal reservoir,

$$Q \leq 0, \quad W \leq 0. \tag{7.3}$$

In informal language, the Kelvin-Planck statement says

- you can turn all the work into heat, but
- you cannot turn all the heat into work.

7.1.4 Carathéodory statement

Another form of the second law was given by the mathematician and advocate for the axiomatic approach to thermodynamics, Carathéodory, depicted in Fig. 7.7. The Carathéodory statement⁸ is

⁸C. Carathéodory, 1909, “Untersuchungen über die Grundlagen der Thermodynamik,” *Mathematische Annalen*, 67: 355-386.

- **SECOND LAW OF THERMODYNAMICS:** In the neighborhood of any equilibrium state of a thermodynamic system, there are equilibrium states that are adiabatically inaccessible.

Demonstration of its equivalence to other statements is not straightforward, and we shall not consider it in any further detail in these notes; nevertheless, the notions embodied in this statement as well as the school of thought in thermodynamics which has grown around the work of its author has benefits associated with casting thermodynamics in the context of more general mathematical ideas, thus making results from modern mathematics more easily applicable to thermodynamics. The work of Carathéodory is often dismissed as somehow too mathematical. Indeed, his approach to thermodynamics in general requires a mathematical sophistication beyond that needed to understand the more common Clausius or Kelvin-Planck formulations. The interested reader can consult a relevant discussion⁹

⁹M. W. Zemansky, 1966, "Kelvin and Caratheodory—a reconciliation," *American Journal of Physics*, 34(10): 914-920.

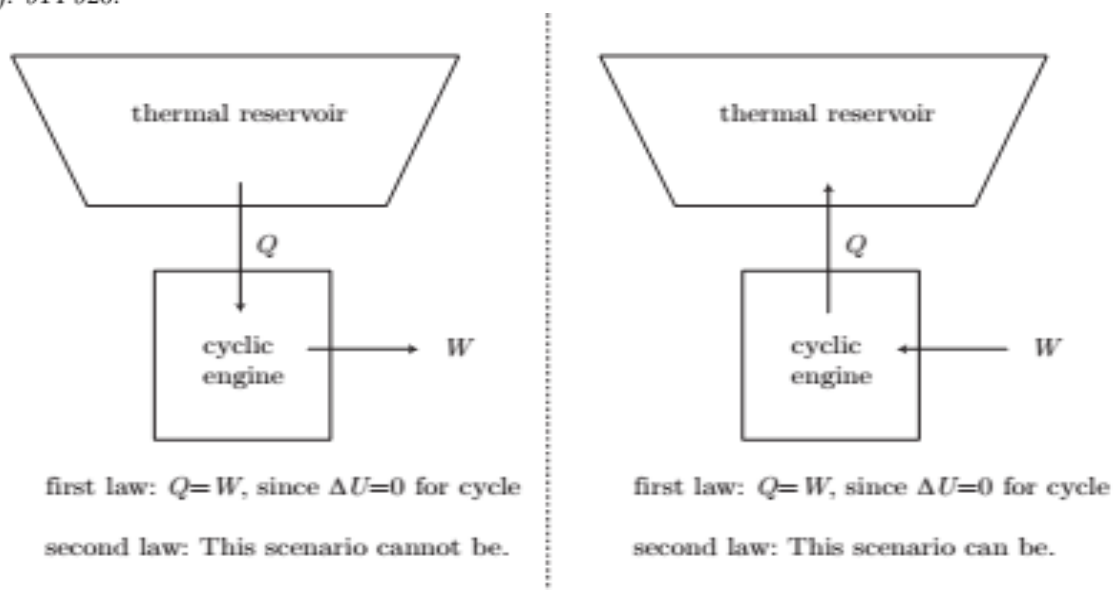


Fig 7.6. Schematic of the Kelvin-Planck statement of the second law of thermodynamics

7.1.5 Judeo-Christian statement

One finds in Genesis 3:19 the admonition given by the Catholic church in its Ash Wednesday services,

- MODULATED SECOND LAW OF THERMODYNAMICS: Remember man that thou art dust, and unto dust thou shalt return.

7.1.6 Historian-inspired statement

The great American historian and generalist, Henry Brooks Adams (1838-1918) grandson and great-grandson of American presidents, wrote a detailed and entertaining essay on the second law. Among his many comments is included¹⁰

- ADAMS' SECOND LAW OF THERMODYNAMICS: "...but to the vulgar and ignorant historian it meant only that the ash-heap was constantly increasing in size."

¹⁰H. B. Adams, 1910, *A Letter to American Teachers of History*, J. H. Furst, Washington.

7.1.7 Literature-inspired statement

Though he probably did not intend it for engineering, the Nobel literature laureate Chinua Achebe's most famous novel has a title which also serves as a rough-and-ready statement of the second law:

- INFORMAL SECOND LAW OF THERMODYNAMICS: Things fall apart.

The title of the novel is drawn from a line in Nobel literature laureate William Butler Yeats' apocalyptic 1921 poem, *The Second Coming*.



Fig 7.7. Constantin Carathéodory (1873-1950), Greek mathematician

7.1.8 Food service-inspired statement

- SECOND LAW OF THERMODYNAMICS, SPECIAL CASE: Untended food rots.

7.2. Reversible and irreversible processes

We shall find it useful to have in hand definitions for so-called reversible and irreversible processes. Let us take

- REVERSIBLE PROCESS: A process in which it is possible to return both the system and surroundings to their original states.
- IRREVERSIBLE PROCESS: A process in which it is impossible to return both the system and surroundings to their original states.

Now, it may be possible to restore the system to its original state but not the surroundings (or the surroundings to its original state but not the system). Such a process is irreversible.

We shall often study reversible processes as they represent an ideal of the most we can ever hope to achieve. Some common engineering idealizations of reversible processes include

- frictionless motion,
- ideal inviscid flow of a fluid over an airfoil.

Now, everything in the real world deviates from the ideal. In flow over a wing, friction in the form of viscosity causes local irreversible heating of the air near the wing and the wing itself. Often in the real world these irreversibilities are confined to small regions and often do not largely affect the motion of the body.

If the world in which we live were reversible, we would realize some benefits, but ultimately life would be impossible. In a reversible world

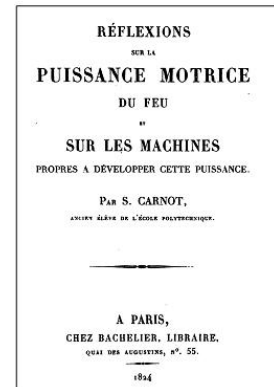
- Pendulum clocks would never need to be rewound.
- Electricity would flow without generating heat; thus, computer fans would be unnecessary, among other things, but
- We would not be able to walk!

7.3. Analysis of Carnot heat engines

Here, we will present what amounts to a version of the discussion of the 1850s inspired by the original work of Carnot¹¹ depicted along with his writings in Fig. 7.8 for heat engines.

¹¹S. Carnot, 1824, *Réflexions sur la Puissance Motrice du Feu et sur les Machines propres à Développer cette Puissance*, Bachelier, Paris. (English translation, 2005, *Reflections on the Motive Power of Fire*, Dover, Mineola, New York). 1897 English translation.

Fig 7.8. Sadi Nicolas Léonard Carnot (1796-1832), French engineer whose analysis formed the basis for modern thermodynamics and the title page from his *magnum opus*

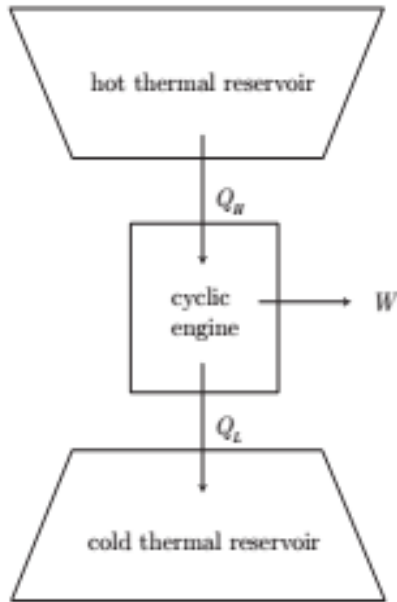


Carnot's 1824 work was done before any formal notions of the first and second laws had been systematized.

The informal statement of the Kelvin-Planck version of the second law is that you cannot turn all the heat into work. Now, an engineer often wants to harvest as much as possible of the thermal energy of combustion and convert it into mechanical energy. Kelvin-Planck simply says we cannot have it all. But it lets us have some! In fact if we only harvest a portion of the thermal energy for work and reject the rest in the form of thermal energy, we can satisfy the second law. We show this schematically in Fig. 7.9. The first law for this system is

$$U_2 - U_1 = Q_H - Q_L - W. \quad (7.4)$$

Note that here, we are thinking of W , Q_H , and Q_L as all positive. If we were rigorous with our sign convention, we would have reversed the arrow on Q_L since our sign convention always has positive work entering the system. However,



first law: $W = Q_H - Q_L$, since $\Delta U = 0$ for cycle

second law: This scenario can be.

Fig 7.9. Schematic of a realizable heat engine

- following a common practice, the rigorous sign convention is traditionally abandoned for analysis of heat engines!

Now, we are requiring a cyclic process, so $U_1 = U_2$; thus, Eq. (7.4) reduces to

$$W = Q_H - Q_L. \quad (7.5)$$

Now, recall we previewed the idea of thermal efficiency, η , in Eq. (6.229):

$$\eta = \frac{\text{what you want}}{\text{what you pay for}}. \quad (7.6)$$

We recast it for the scenario of Fig. 7.9 where we want W and we pay for Q_H :

$$\eta = \frac{W}{Q_H}. \quad (7.7)$$

Now, we use Eq. (7.5) to eliminate W in Eq. (7.7) and get

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}. \quad (7.8)$$

Equation (7.8) is analogous to the earlier Eq. (6.235). Now, if $Q_L = 0$, we get $\eta = 1$, and our engine does a perfect job in converting all the heat into work. But if $Q_L = 0$, we violate the Kelvin-Planck version of the second law! So we must reject *some* heat. Another version of the Kelvin-Planck statement then is

$$\eta = 1 - \frac{Q_L}{Q_H} < 1. \quad (7.9)$$

It is possible to prove the following corollary to the Kelvin-Planck statement:

$$\eta_{\text{irreversible}} \leq \eta_{\text{reversible}}, \quad (7.10)$$

for cycles operating between the same thermal reservoirs.

And there is a second corollary, applicable for two different cycles, both reversible, and both operating between the same thermal reservoirs:

$$\eta_{\text{reversible},1} = \eta_{\text{reversible},2}. \quad (7.11)$$

7.4. The absolute temperature scale

The second corollary to the Kelvin-Planck statement holds that all reversible engines operating between the same thermal reservoirs have the same η . *This is independent of any details of the cycle or the materials involved.* This implies that

- *The thermal efficiency, η , should depend only on the character of the reservoirs involved.*

Specifically, we will define η in terms of what we will call the TEMPERATURE of the reservoir. This is the classical macroscopic interpretation of temperature. Later statistical theories give it the additional interpretation as a measure of the average translational kinetic energy of molecules of the system. But that is not our approach here! Now, we might suppose that this new thermodynamic property, temperature, should somehow be a measure of how much heat is transferred from one reservoir to another. Moreover, each reservoir will have its own temperature. The hot reservoir will have temperature T_H ; the cold reservoir will have temperature T_L . So we are then saying that

$$\eta = \eta(T_H, T_L). \quad (7.19)$$

As of yet, this functional form is unspecified. Substituting this form into our earlier Eq. (7.8), we get

$$\eta(T_H, T_L) = 1 - \frac{Q_L}{Q_H}. \quad (7.20)$$

This can only be true if Q_L and Q_H have some relation to T_L and T_H . So let us propose a useful definition. We insist that our temperatures take the form of that for a Carnot cycle

$$\boxed{\frac{T_L}{T_H} = \frac{Q_L}{Q_H}}. \quad (7.21)$$

This is just a definition that cannot be argued. Its utility will be seen as its justification, but nothing more. Eq. (7.21) is valid only in the context of a Carnot cycle, and not for other cycles.

Our logic train is that we observe heat engines, such as steam engines seen by Carnot in the early 1800s, doing work as a result of heat transfers. That effect, work, must have a cause. And we are going to assert that the cause is affiliated with a temperature difference.

So far our temperature has been defined only in terms of a ratio. Let us make an arbitrary choice to avoid ratios. We take, for convenience, the temperature of the triple point of water to be 273.15 K. Thus for any system, the local T is

$$T = (273.15 \text{ K}) \left(\frac{Q}{Q_{\text{triple point}}}_{\text{reversible cycle}} \right). \quad (7.22)$$

This implies we can connect our heat engine to a reservoir maintained at the triple point temperature of water, and measure the associated Q s for the heat engine. With our definition, Eq. (7.21), our thermal efficiency, Eq. (7.8), becomes

$$\boxed{\eta = 1 - \frac{T_L}{T_H}}. \quad (7.23)$$

This famous formula is the thermal efficiency for an idealized heat engine; it is not valid for other heat engines. This formula is not found in Carnot's original work; nor is it straightforwardly presented in the later works of the 1850s. Clausius puts most of the pieces in place¹² so much so that Müller and Müller¹³ attribute the formula to him; but it is not directly seen in his 1854 study; see Truesdell¹⁴

Note

$$\lim_{T_L \rightarrow 0} \eta = 1, \quad (7.24)$$

$$\lim_{T_H \rightarrow \infty} \eta = 1. \quad (7.25)$$

These two statements have practical importance. While we would like to drive our efficiency to be as close to unity as possible, nature limits us. Generally, we have little to no control over the environmental temperature T_L , so it is a lower bound, usually around $T_L \sim 300 \text{ K}$. And material properties for engines limit T_H . For many metals, $T_H \sim 1500 \text{ K}$ is approaching values where material strength is lost. So a practical upper bound based on these numbers tells us $\eta \sim 1 - (300 \text{ K})/(1500 \text{ K}) = 0.8$ is maybe the most we can expect. We plot η as a function of T_H for fixed $T_L = 300 \text{ K}$ in Fig. 7.12. For real systems, with irreversible features, the values are much worse.

¹²R. Clausius, 1854, "Ueber eine veränderte Form des aweiten Hauptsatzes der mechanischen Wärmetheorie," *Annalen der Physik und Chemie*, 169(12): 481-506.

¹³I. Müller and W. H. Müller, 2009, *Fundamentals of Thermodynamics and Applications with Historical Annotations and many Citations from Avogadro to Zernelo*, Springer, Berlin, p. 131.

¹⁴C. Truesdell, 1980, *The Tragicomical History of Thermodynamics, 1822-1854*, Springer, New York, p. 330.

7.5. Analysis of Carnot refrigerators and heat pumps

A refrigerator or heat pump is a device which, with work input, moves thermal energy from cold regions to hot regions. Without the work input, this could not be achieved, as it would violate the Clausius statement of the second law of thermodynamics. We show this schematically in Fig. 7.13. For a refrigerator, we define a coefficient of performance β , sometimes called *COP*, as

$$\beta = \frac{\text{what you want}}{\text{what you pay for}} = \frac{Q_L}{W}, \quad \text{Carnot refrigerator.} \quad (7.26)$$

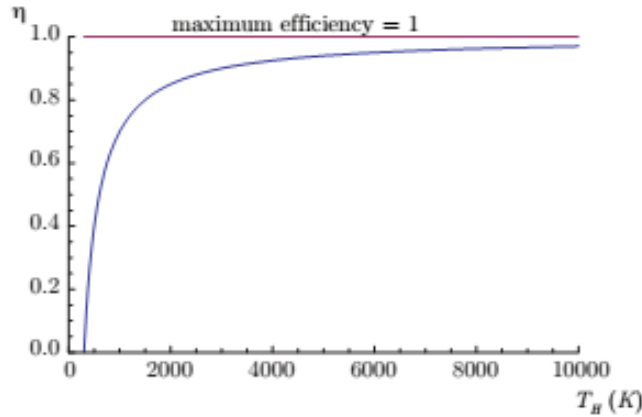


Fig 7.12. Plot of idealized thermal efficiency as a function of thermal reservoir temperature with $T_L = 300\text{K}$

Now, the first law for this cycle gives $W = Q_H - Q_L$, so

$$\beta = \frac{Q_L}{Q_H - Q_L} = \frac{1}{\frac{Q_H}{Q_L} - 1} = \frac{1}{\frac{T_H}{T_L} - 1}, \quad \text{Carnot refrigerator.} \quad (7.27)$$

Note that

$$\beta \geq 0, \quad (7.28)$$

for $T_H/T_L \geq 1$. In addition, it is possible to have $\beta > 1$ if $T_H/T_L < 2$. Since we reserve efficiencies to have $0 \leq \eta \leq 1$, the *COP* is not really an efficiency. But it is a useful measure that is used as an industry standard for refrigerators.

For heat pumps, we want to bring Q_H into a warm room from a cold outdoors to make the warm room warmer. So it has a related *COP*, which we define as β' :

$$\beta' = \frac{Q_H}{W}, \quad \text{Carnot heat pump.} \quad (7.29)$$

Again the first law gives $W = Q_H - Q_L$, so

$$\beta' = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}} = \frac{1}{1 - \frac{T_L}{T_H}}, \quad \text{Carnot heat pump.} \quad (7.30)$$

For $T_L/T_H \leq 1$, we have $\beta' \geq 1$.

Note for both refrigerators and heat pumps, as $W \rightarrow 0$, both $\beta \rightarrow \infty$ and $\beta' \rightarrow \infty$, and we transfer thermal energy from a cold reservoir to a hot one, in violation of the Clausius statement of the second law.

7.6. Rejected thermal energy on a national scale

We see that the second law characterizes the necessary rejection of heat in processes involving heat and work. Let us briefly examine this on a national scale. Figure 7.15 reports US energy usage in 2011 from a wide variety of sources directed to a wide variety of applications. The basic unit of energy here is the *quad* where $1 \text{ quad} = 10^{15} \text{ Btu} = 1.055 \times 10^{18} \text{ J} = 1.055 \text{ EJ}$, where *EJ* is an “exajoule.” Much can be gleaned from this chart. Overall US energy use is estimated at 97.3 *quad* for the year indicated. As far as the second law is concerned, electricity generation rejects 26.6 *quad* waste heat per annum and transportation rejects 20.3 *quad* waste heat per annum. In total, 55.6 *quad* is rejected, and 41.7 *quad* is directed towards a useful intended purpose. Thus, the thermal efficiency of the US in 2011 was

$$\eta_{US} = \frac{41.7 \text{ quad}}{(41.7 \text{ quad}) + (55.6 \text{ quad})} = 0.429. \quad (7.34)$$

Example

If all the waste heat in the US in 2011 were directed into Lake Michigan, find its temperature rise.

In more convenient units the waste heat for a given year is

$$Q = (55.6 \text{ quad}) \left(\frac{1.055 \times 10^{18} \text{ J}}{\text{quad}} \right) = 5.87 \times 10^{19} \text{ J}. \quad (7.35)$$

Now, Lake Michigan has a volume of 4900 km^3 . Therefore the mass of water in Lake Michigan is roughly

$$m = \rho V = \left(997 \frac{\text{kg}}{\text{m}^3} \right) (4900 \text{ km}^3) \left(\frac{10^3 \text{ m}}{\text{km}} \right)^3 = 4.88 \times 10^{15} \text{ kg}. \quad (7.36)$$

If all the waste energy were dumped into Lake Michigan, we could expect from a first law analysis to find a temperature rise of

$$\Delta T = \frac{Q}{mc_P} = \frac{5.87 \times 10^{19} \text{ J}}{(4.88 \times 10^{15} \text{ kg}) \left(4180 \frac{\text{J}}{\text{kg K}} \right)} = 2.88 \text{ K}. \quad (7.37)$$

For comparison, Lake Ontario would have received roughly an 8 K temperature rise. Locally on the University of Notre Dame campus, both St. Mary’s and St. Joseph’s Lakes would be vaporized many times over.

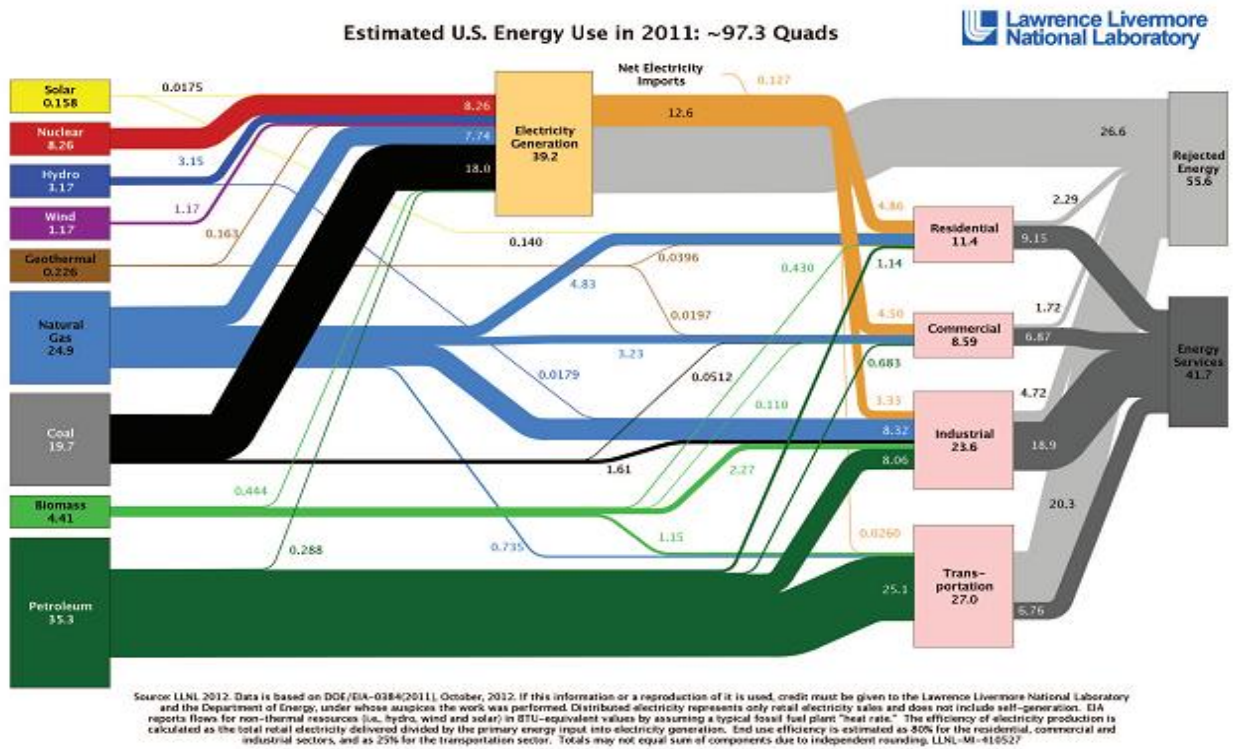


Fig 7.15. Chart of distribution of energy sources and usage in the US in 2011. Data from Lawrence Livermore National Laboratory

NOTES

The Second Law

- ▲ First Law showed the equivalence of work and heat

$$\Delta U = q + w, \oint dU = 0 \text{ for cyclic process} \Rightarrow q = -w$$

Suggests engine can run in a cycle and convert heat into useful work.

- ▲ Second Law
 - Puts restrictions on useful conversion of q to w
 - Follows from observation of a directionality to natural or spontaneous processes
 - Provides a set of principles for
 - determining the direction of spontaneous change
 - determining equilibrium state of system

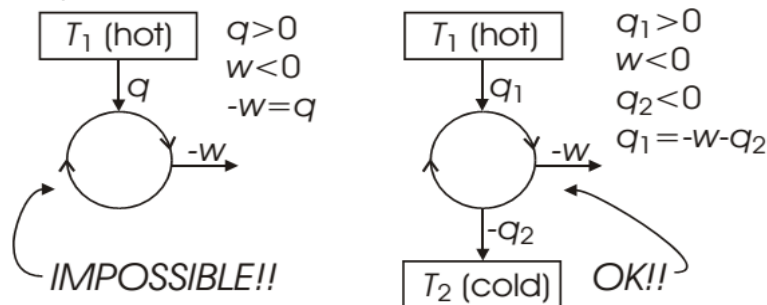
Heat reservoir

Definition: A very large system of uniform T , which does not change regardless of the amount of heat added or withdrawn.

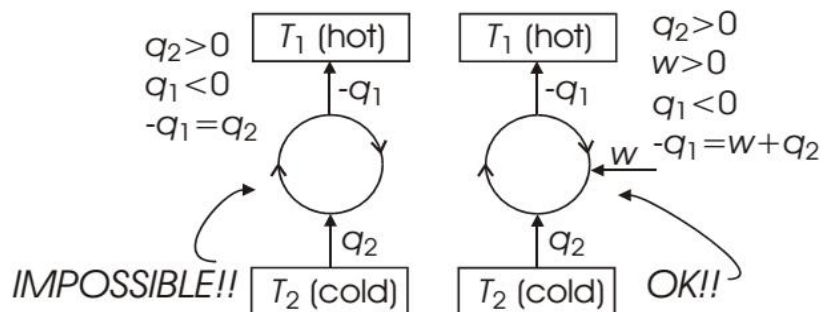
Also called heat bath. Real systems can come close to this idealization.

Different statements of the Second Law

Kelvin: It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without at the same time transferring some heat to a colder reservoir.



Clausius: It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir without at the same time converting some work into heat.



Alternative Clausius statement:

All spontaneous processes are irreversible.

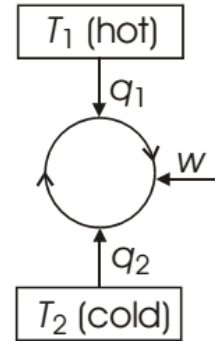
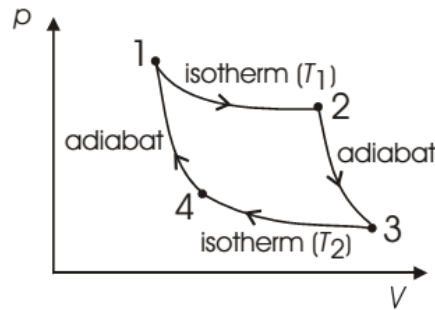
(e.g. heat flows from hot to cold spontaneously and irreversibly)

Kelvin and Clausius statements are specialized to heat engines.
 Mathematical statement is very abstract.

Link them through analytical treatment of a heat engine.

The Carnot Cycle - a typical heat engine

All paths are reversible



- 1 → 2 isothermal expansion at T_1 (hot) $\Delta U = q_1 + w_1$
- 2 → 3 adiabatic expansion ($q = 0$) $\Delta U = w'_1$
- 3 → 4 isothermal compression at T_2 (cold) $\Delta U = q_2 + w_2$
- 4 → 1 adiabatic compression ($q = 0$) $\Delta U = w'_2$

$$\text{Efficiency} = \frac{\text{work output to surroundings}}{\text{heat in at } T_1 \text{ (hot)}} = \frac{-(w_1 + w'_1 + w_2 + w'_2)}{q_1}$$

$$1^{\text{st}} \text{ Law} \Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -(w_1 + w'_1 + w_2 + w'_2)$$

$$\therefore \text{Efficiency} \equiv \varepsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

Kelvin: $q_2 < 0 \rightarrow \text{Efficiency} \equiv \varepsilon < 1$ (< 100%)

$$-w = q_1 \varepsilon = \text{work output}$$

Note: if cycle were run in reverse, then $q_1 < 0$, $q_2 > 0$, $w > 0$.
It's a refrigerator!

Carnot cycle for an ideal gas

$$1 \rightarrow 2 \quad \Delta U = 0; \quad q_1 = -w_1 = \int_1^2 p dV = RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

$$2 \rightarrow 3 \quad q = 0; \quad w'_1 = C_V (T_2 - T_1)$$

$$\text{Rev. adiabat} \quad \Rightarrow \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$3 \rightarrow 4 \quad \Delta U = 0; \quad q_2 = -w_2 = \int_3^4 p dV = RT_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$4 \rightarrow 1 \quad q = 0; \quad w'_2 = C_V (T_1 - T_2)$$

$$\text{Rev. adiabat} \quad \Rightarrow \quad \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)}$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \Rightarrow \frac{q_2}{q_1} = -\frac{T_2}{T_1}$$

$$\text{or} \quad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq_{\text{rev}}}{T} = 0$$

links heat engines to mathematical statement

Efficiency

$$\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

→ 100% as $T_2 \rightarrow 0$ K

For a heat engine (Kelvin): $q_1 > 0, w < 0, T_2 < T_1$

$$\text{Total work out} = -w = \varepsilon q_1 = \left(\frac{T_1 - T_2}{T_1} \right) q_1 \Rightarrow (-w) < q_1$$

Note: In the limit $T_2 \rightarrow 0 \text{ K}$, $(-w) \rightarrow q_1$, and $\varepsilon \rightarrow 100\%$ conversion of heat into work. 3rd law will state that we can't reach this limit!

For a refrigerator (Clausius): $q_2 > 0, w > 0, T_2 < T_1$

$$\text{Total work in} = w = \left(\frac{T_2 - T_1}{T_1} \right) q_1$$

$$\text{But } \frac{q_1}{T_1} = -\frac{q_2}{T_2} \Rightarrow w = \left(\frac{T_1 - T_2}{T_2} \right) q_2$$

Note: In the limit $T_2 \rightarrow 0 \text{ K}$, $w \rightarrow \infty$. This means it takes an infinite amount of work to extract heat from a reservoir at $0 \text{ K} \Rightarrow 0 \text{ K}$ cannot be reached (3rd law).

Kelvin Statement. There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a given heat reservoir and to convert it entirely into work.

Clausius Statement. There exists no thermodynamic transformation whose *sole* effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir.

In both statements the key word is "sole." An example suffices to illustrate the point. If an ideal gas is expanded reversibly and isothermally, work is done by the gas. Since $\Delta U = 0$ in this process, the work done is equal to the heat absorbed by the gas during the expansion. Hence a certain quantity of heat is converted entirely into work. This is not the sole effect of the transformation, however, because the gas occupies a larger volume in the final state. This process is allowed by the second law.

The Kelvin statement *K* and the Clausius statement *C* are equivalent. To prove this we prove that if the Kelvin statement is false, the Clausius statement is false, and vice versa.

Proof that K False \Rightarrow C False Suppose K is false. Then we can extract heat from a reservoir at temperature T_1 and convert it entirely into work, with no other effect. Now we can convert this work into heat and deliver it to a reservoir at temperature $T_2 > T_1$ with no other effect. (A practical way of carrying out this particular step is illustrated by Joule's experiment on the equivalence of heat and energy.) The net result of this two-step process is the transfer of an amount of heat from a colder reservoir to a hotter one with no other effect. Hence C is false. ■

Proof that C False \Rightarrow K False First define an *engine* to be a thermodynamic system that can undergo a cyclic transformation (i.e., a transformation whose final state is identical with the initial state), in which system does the following things, and only the following things:

- (a) absorbs an amount of heat $Q_2 > 0$ from reservoir T_2 ;
- (b) rejects an amount of heat $Q_1 > 0$ to reservoir T_1 , with $T_1 < T_2$;
- (c) performs an amount of work $W > 0$.

Suppose C is false. Extract Q_2 from reservoir T_1 and deliver it to reservoir T_2 , with $T_2 > T_1$. Operate an engine between T_2 and T_1 for one cycle, and arrange the engine so that the amount of heat extracted by the engine from T_2 is exactly Q_2 . The net result is that an amount of heat is extracted from T_1 and entirely converted into work, with no other effect. Hence K is false. ■

Carnot's theorem

The second law immediately implies that a Carnot engine cannot be 100% efficient, for otherwise all the heat absorbed from the upper reservoir would be converted into work in one cycle of operation. There is no other effect, since the system returns to its original state.

According to the Carnot's theorem

No engine operating between two given temperatures is more efficient than a Carnot engine.

Proof Since only two reservoirs are present, a Carnot engine simply means a reversible engine. What we assert then, is that an irreversible engine cannot be more efficient than a reversible one.

Consider a Carnot engine C and an engine X (not necessary reversible) working between the reservoirs T_2 and T_1 , with $T_2 > T_1$, as shown in Figure 2.5. We shall run C in reverse, as a refrigerator \bar{C} , and feed the work output of X to \bar{C} . Table 2.1 shows a balance sheet of heat transfer in one cycle of joint operation.

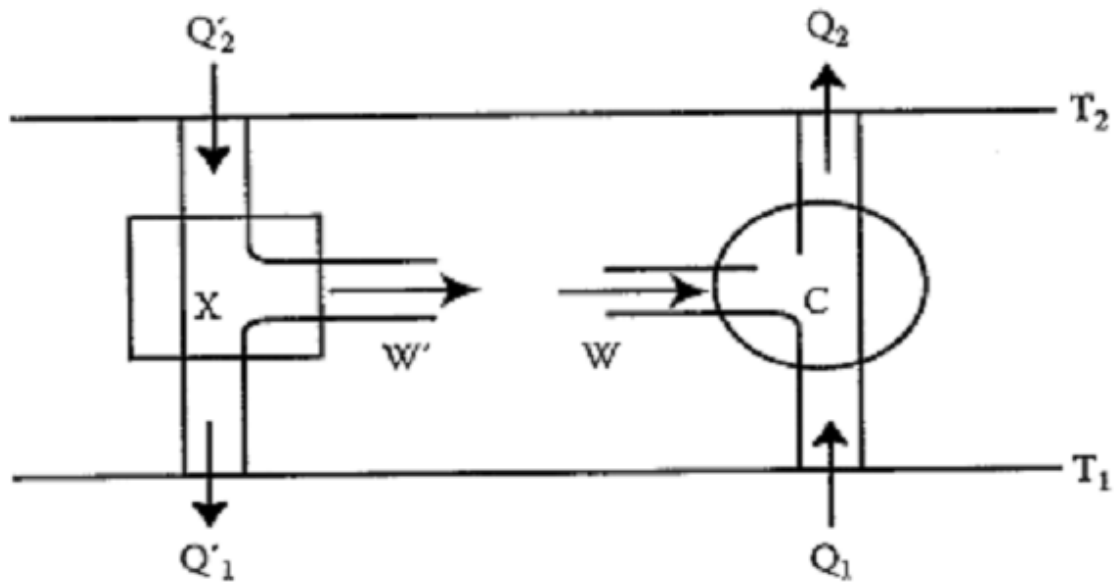
The total work output is

$$W_{\text{tot}} = (Q'_2 - Q'_1) - (Q_2 - Q_1)$$

Now arrange to have $Q'_2 = Q_2$. Then, no net heat was extracted from the reservoir T_2 , which can be ignored. An amount of heat $Q_1 - Q'_1$ was extracted from the reservoir T_1 and converted entirely into work with no other effect. This would violate the second

Balance Sheet of Heat Transfer

Engine	From T_2	To T_1
X	Q'_2	Q'_1
\bar{C}	$-Q_2$	$-Q_1$



Driving a Carnot refrigerator \bar{C} with an arbitrary engine X .

law, unless $Q_1 \leq Q'_1$. Dividing both sides of this inequality by Q_2 , and using the fact $Q'_2 = Q_2$, we have

$$\frac{Q_1}{Q_2} \leq \frac{Q'_1}{Q'_2}$$

Therefore $1 - (Q_1/Q_2) \geq 1 - (Q'_1/Q'_2)$, or

$$\eta_C \geq \eta_X$$

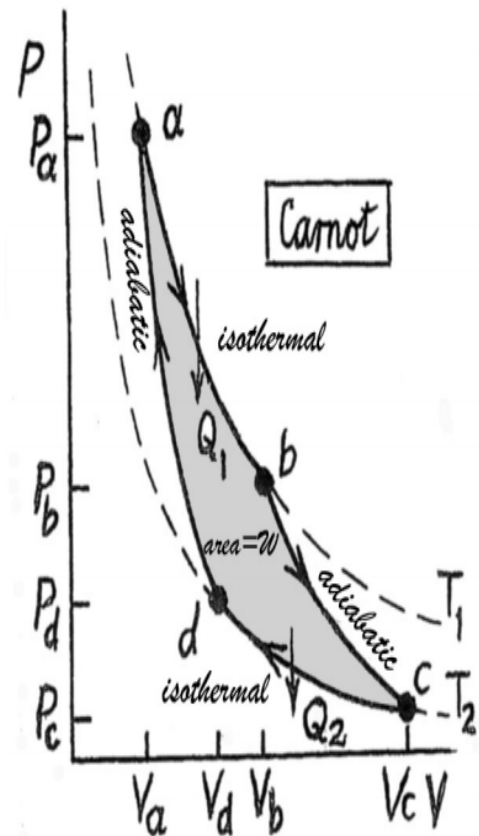
As a corollary, all Carnot engines have the same efficiency, since X may be a Carnot engine. This shows that the Carnot engine is universal, in that it depends only on the temperatures involved, and not on the working substance.

Absolute scale of temperature

- (a) The definition of the absolute scale of temperature is independent of the specific properties of any substance. It depends only on a property that is common to all substances, the second law of thermodynamics.
- (b) The limit $\theta = 0$ is the greatest lower bound of the temperature scale and is called the absolute zero. Actually no Carnot engine exists with absolute zero as the temperature of the lower reservoir, for that would violate the second law. The absolute zero exists only in a limiting sense.
- (c) The absolute Kelvin scale θ is identical with the ideal-gas temperature scale T , if $T > 0$. This is easily proved by using an ideal gas to form a Carnot engine. From now on we do not distinguish between the two and denote the absolute temperature by T .

The Carnot cycle and engine

The four-stage Carnot cycle is shown. Any fluid known as the **working substance** may be taken around the cycle. The surroundings consist of two constant temperature heat reservoirs, one at T_1 and the other at $T_2 < T_1$, and some means (such as pistons) to allow the exchange of mechanical energy with other devices. The system and surroundings comprise the hypothetical *Carnot engine*. It operates reversibly between the two heat reservoirs, with, in each cycle, heat Q_1 entering at T_1 , Q_2 leaving at T_2 and work W being delivered. If the working substance is not an ideal gas, the shapes of the isotherms and adiabatics will be (slightly) different from those shown.



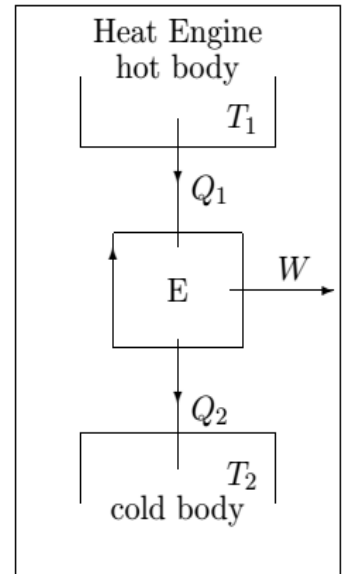
The efficiency of a heat engine

A generalised engine is illustrated schematically opposite. *This engine still operates in cycles, with its working substance always returning to the same thermodynamic state at the end of each cycle.* Thermodynamic efficiency analysis is done in work/heat *per cycle*: in reality the *power* produced is often more important:

$$\text{Power} = \text{Work per cycle} \times \text{cycles per second}$$

Q_1 , Q_2 and W are heat supplied to, heat rejected by and work done **by** the working substance. The work done **on** the working substance is $-W$, and the First Law takes the form $\Delta U = Q_1 - Q_2 + (-W) = 0$ for each complete cycle. From this, $W = Q_1 - Q_2$, and the efficiency η of the engine is defined by

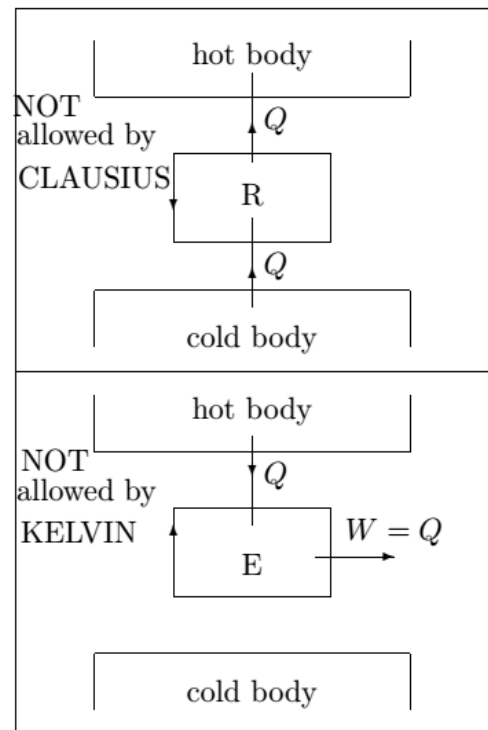
$$\eta = W/Q_1 = 1 - Q_2/Q_1$$



The Clausius statement:

It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body

The “R” on the diagram, of the forbidden device, denotes “refrigerator”.



The Kelvin-Planck statement

It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.

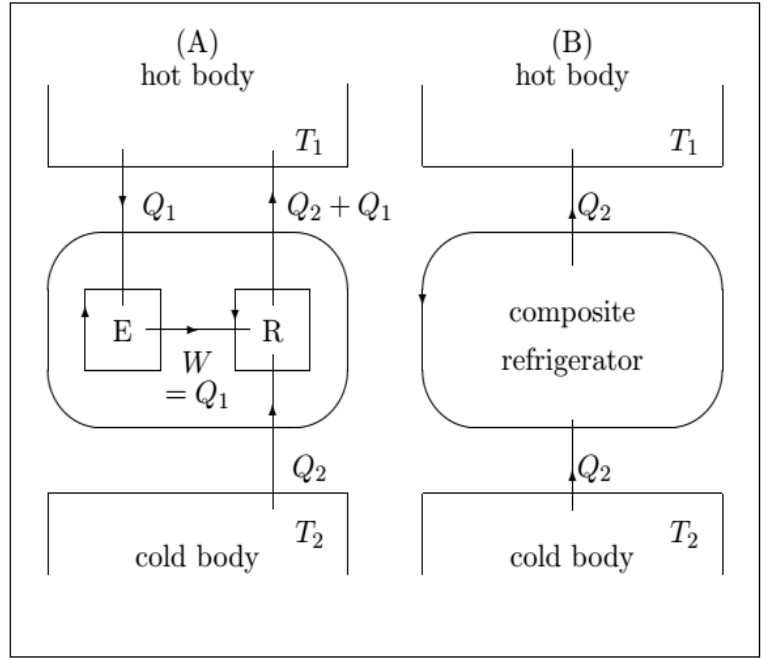
The “E” on the diagram, of the forbidden device, denotes “engine”.

Note the use of *body* rather than *heat reservoir*, meaning that engines can be considered to operate between two bodies (one a source and the other a sink of heat) of which the hotter one cools and the colder one heats up whilst the engine is running.

The equivalence of the Clausius and the Kelvin-Planck statements

This is traditionally proved by showing that if either statement is false, so is the other.

Suppose Kelvin-Planck's statement is false. Then an engine (E) can drive a refrigerator (R), as sketched opposite, where W (equal to Q_1 from the 1st law applied to E) is just sufficient to operate one cycle of R. If R extracts Q_2 from the cold body, it will deliver heat $Q_1 + Q_2$ (1st law applied to R) to the hot body, each cycle. E+R can be treated as a composite refrigerator, whose only effect is to transfer heat Q_2 from a colder to a hotter body, requiring Clausius's statement to also be false. (The similar proof that if Clausius's statement is false so too is Kelvin's is left as an exercise).

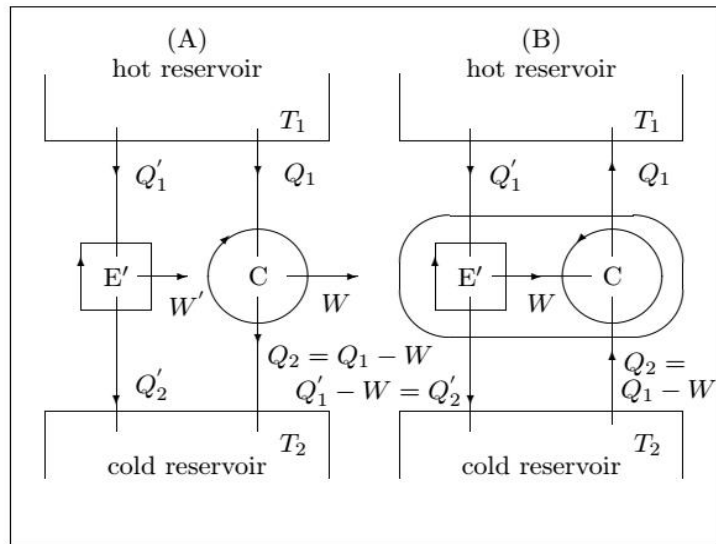


Carnot's theorem and a corollary

Carnot's Theorem is

No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

To prove this we will examine how the efficiency of a hypothetical engine E' is restricted by Clausius's statement of the 2nd law.



Let the hypothetical engine E' (efficiency η') and a Carnot engine C (efficiency η_C) operate between the same heat reservoirs at temperatures T_1 and $T_2 < T_1$; sketch (A) above. All stages of the Carnot engine are reversible, so it can be driven backwards. If the engines are adjusted so that $W' = |W|$, then, **assuming** $\eta' > \eta$, $W'/Q'_1 = W/Q'_1 > W/Q_1$ leads to $Q_1 > Q'_1$. That means (see diagrams) that the composite device (sketch (B)) would act as a refrigerator which each cycle extracts heat $Q_1 - Q'_1$ from the lower temperature reservoir and delivers exactly the same heat to the higher temperature reservoir *without exchanging mechanical work with any other device*. This contradicts Clausius's statement of the 2nd law, so the assumption $\eta' > \eta_C$ cannot be valid. It is necessary to consider also the possibility $\eta' = \eta_C$, for which, from the diagram, $Q'_1 = Q_1$. The composite device achieves nothing: heat flows are zero and there is no work exchanged. The conclusion is that the efficiency η for any real engine must therefore satisfy

$$\eta \leq \eta_C$$

The corollary follows: make the composite device from two Carnot engines, C_a and C_b , with the first one, efficiency η_{c_a} driving the second one, efficiency η_{c_b} , backwards. Carnot's Theorem leads to $\eta_{c_a} \leq \eta_{c_b}$. However, for C_b driving C_a backwards, $\eta_{c_b} \leq \eta_{c_a}$. The only option is $\eta_{c_a} = \eta_{c_b}$, hence the corollary:

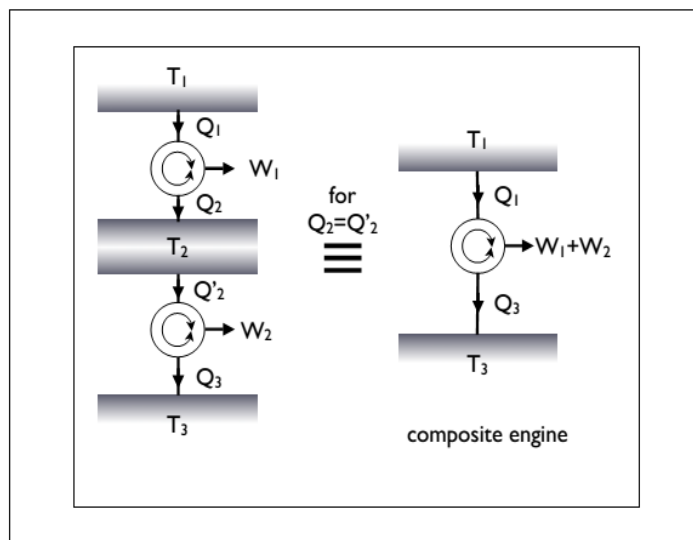
All Carnot engines operating between the same two reservoirs have the same efficiency (INDEPENDENT of the working substance).

Another Corollary: Existence of a thermodynamic temperature

We have shown that the thermodynamic efficiency of all *reversible* heat engines operating between the same two temperature reservoirs is equal (independent of the choice of working substance or process). This efficiency, $\eta = 1 - \frac{Q_2}{Q_1}$, can therefore only depend on the temperature of the reservoirs. The ratio Q_1/Q_2 is therefore some universal function f of T_1 and T_2 : $Q_1/Q_2 = f(T_1, T_2)$. We can say more about the functional form of f by considering the following:

Consider two reversible engines as shown (any working substance). Per cycle, the first removes heat from reservoir at T_1 and rejects heat at T_2 doing work W_1 . The size and rate of the processes of the second engine are scaled so that it is synchronised with the first engine removing heat $Q'_2 = Q_2$ per cycle from the reservoir at T_2 doing some work W_2 and rejecting heat Q_3 to a reservoir at T_3 with $T_1 > T_2 > T_3$.

For this arrangement the heat entering and leaving the reservoir at T_2 balance and so no reservoir is in fact required. The overall process is thus equivalent to the composite engine shown on the right of the figure. For the two individual engines:



$$\frac{Q_1}{Q_2} = f(T_1, T_2) \tag{1}$$

$$\frac{Q_2}{Q_3} = f(T_2, T_3) \tag{2}$$

While for the composite

$$\frac{Q_1}{Q_3} = f(T_1, T_3) \quad (3)$$

with f the same universal function in all 3 expressions. Multiplying EQN 1 by EQN 2, Q_2 cancels giving an expression for Q_1/Q_3 that can be compared with EQN 3:

$$\frac{Q_1}{Q_3} = \boxed{f(T_1, T_2) \cdot f(T_2, T_3) = f(T_1, T_3)}$$

The only way the boxed expression can be satisfied is if the function f factorises,

$$f(T_1, T_2) = \frac{\theta(T_1)}{\theta(T_2)}$$

with $\theta(T)$ a universal function of temperature for a given choice of temperature scale. We have thus found a ‘natural’ temperature scale, θ , called thermodynamic temperature, that can be expressed as a function of our arbitrary practical temperature scale. It is shown in the next topic that $\theta \equiv T_{IG}$ ie $\theta(T_{IG}) = T_{IG}$.

LECTURE 8: ENTROPY

Content of Lecture 8

- 8.1. Theoretical development
- 8.2. Second law in terms of entropy
 - 8.3. The Gibbs equation
 - 8.4. Entropy for ideal gases
 - 8.4.1. Calorically perfect
 - 8.4.2. Calorically imperfect
- 8.5. Entropy for an incompressible solid or liquid
 - 8.6. Iso-curves
 - 8.6.1. Isochores
 - 8.6.2. Isobars
 - 8.6.3. Isentropes
- 8.7. Isentropic relations for an ideal gas
 - 8.7.1. Calorically perfect
 - 8.7.2. Calorically imperfect
- 8.8. Two cycles
 - 8.8.1. Carnot
 - 8.8.2. Otto
- 8.9. Entropy of thermo-mechanical mixing
- 8.10. Probabilistic approach to entropy
- 8.11. Summary statement of thermodynamics

Much as the new property energy arose via consideration of the first law of thermodynamics, we will find it useful to introduce

- **ENTROPY:** a thermodynamic property which provides a quantitative measure of the disorder of a given thermodynamic state,

from consideration of the second law of thermodynamics. The word itself was coined by Clausius^[1] who based it on the combination of $\epsilon\nu$ - (en-) “to put into,” and $\tau\rho\sigma\pi\eta$ (tropē), “turn” or “conversion.” The Greek here is a modification of the original Greek of Clausius, who employed η $\tau\rho\sigma\pi\eta$. An image of the first use of the word is given in Fig. 8.1.

In some ways entropy is simply a mathematical convenience and a theoretical construct. However, its resilience is due to the fact that it is useful for engineers to summarize important design concepts for thermal systems such as steam power plants, automobile engines, jet engines, refrigerators, heat pumps, and furnaces.

^[1]R. Clausius, 1865, “Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie,” *Annalen der Physik und Chemie*, 125(7): 353-390.

8.1. Theoretical development

Let us motivate the property of entropy by considering Fig. 8.2 Here, we perform our analysis on a differential basis. We have a thermal reservoir at T_{res} which delivers a small amount of heat $\delta Q'$ to a reversible cyclic engine, labeled "1." This engine delivers a small amount of work $\delta W'$ and rejects a small amount of heat δQ to another reservoir at variable T , labeled "2." This reservoir itself delivers a different small amount of work δW to the surroundings. Let us examine the implications of our temperature definition and the second law of thermodynamics on this scenario.

Fig 8.1. Image capturing the first use of the word entropy, from R. Clausius, 1865

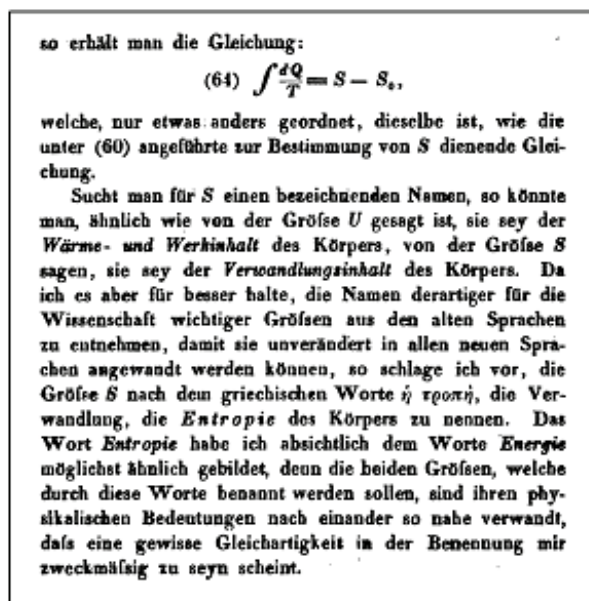
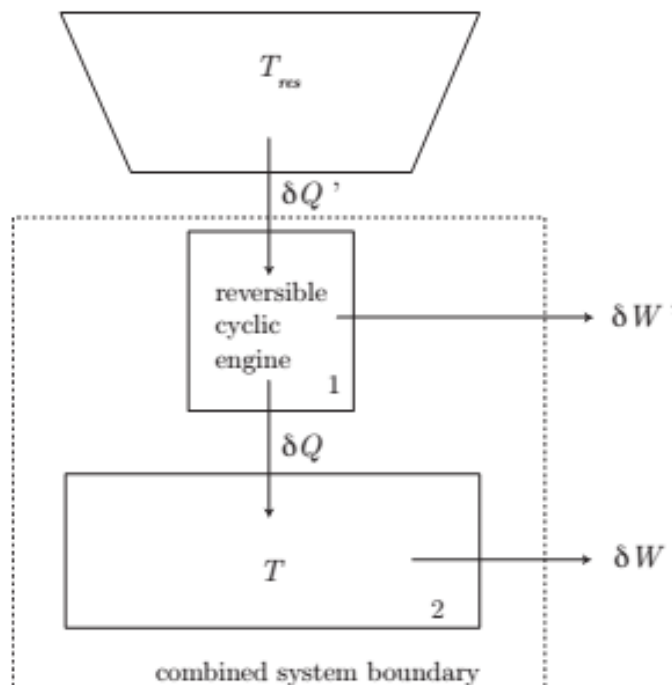


Fig 8.2. Sketch of heat engine configuration to motivate the development of entropy



We first apply Eq. (7.21) to the configuration of Fig. 8.2:

$$\frac{\delta Q'}{\delta Q} = \frac{T_{res}}{T}. \quad (8.1)$$

Thus

$$\frac{\delta Q'}{T_{res}} = \frac{\delta Q}{T}. \quad (8.2)$$

Now, let us take the combined system, enclosed within the dotted box, to be composed of 1 and 2. The first law in differential form for the combined system is

$$dE = (\delta Q') - (\delta W + \delta W'). \quad (8.3)$$

Note that we have not yet required the process be cyclic. Also note that δQ is *internal* and so does not cross the boundary of the combined system and is not present in our first law formulation. Rearrange Eq. (8.3) to get

$$\delta W + \delta W' = \delta Q' - dE. \quad (8.4)$$

Now, use Eq. (8.2) to eliminate $\delta Q'$ in Eq. (8.4):

$$\delta W + \delta W' = T_{res} \frac{\delta Q}{T} - dE. \quad (8.5)$$

Now, let us let this configuration undergo a thermodynamic cycle, indicated by the operation \oint applied to Eq. (8.5):

$$\oint \delta W + \oint \delta W' = \oint T_{res} \frac{\delta Q}{T} - \underbrace{\oint dE}_{=0}. \quad (8.6)$$

Because E is a thermodynamic property, its cyclic integral is zero. But Q and W are not properties, so they have non-zero values when integrated through a cycle. Performing the integration of Eq. (8.6) and realizing that, by definition, T_{res} is a constant, we get

$$W + W' = T_{res} \oint \frac{\delta Q}{T}. \quad (8.7)$$

Now, we can apply the Kelvin-Planck form of the second law of thermodynamics to the configuration of Fig. 8.2; thus, we require simply that

$$W + W' \leq 0. \quad (8.8)$$

That is, we cannot convert all the heat to work, but we can convert all the work to heat. Since Kelvin-Planck tells us $W + W' \leq 0$, Eq. (8.7) tells us

$$T_{res} \oint \frac{\delta Q}{T} \leq 0. \quad (8.9)$$

And since $T_{res} > 0$, we can divide Eq. (8.9) by it without changing the sense of the inequality to get a mathematical representation of the second law of thermodynamics:

$$\oint \frac{\delta Q}{T} \leq 0, \quad (8.10)$$

second law of thermodynamics.

If all processes are reversible, we lose the inequality, and get simply

$$\oint \frac{\delta Q}{T} = 0, \quad (8.11)$$

all processes reversible.

Now, let us reconsider Fig. 5.6 recast here as Fig. 8.3, which was used for development of the path-independent thermodynamic property E . Here, we will use similar concepts to develop the thermodynamic property of entropy. Let us restrict our discussion to reversible

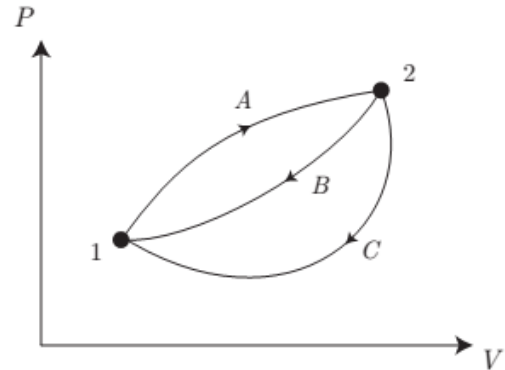


Fig 8.3. Sketch of P-V diagram for various combinations of processes forming cyclic integrals

processes, which are the best we could hope for in an ideal world. So we demand that Eq. (8.11) holds.

Now, from Fig. 8.3, consider starting from 1, proceeding on path A to 2, and returning to 1 via path B . The cyclic integral $\oint \delta Q/T = 0$ decomposes to

$$\left(\int_1^2 \frac{\delta Q}{T} \right)_A + \left(\int_2^1 \frac{\delta Q}{T} \right)_B = 0. \quad (8.12)$$

Now, perform the same exercise going from 1 to 2 on path A and returning on path C , yielding

$$\left(\int_1^2 \frac{\delta Q}{T} \right)_A + \left(\int_2^1 \frac{\delta Q}{T} \right)_C = 0. \quad (8.13)$$

Now, subtract Eq. (8.13) from Eq. (8.12) to get

$$\left(\int_2^1 \frac{\delta Q}{T}\right)_B - \left(\int_2^1 \frac{\delta Q}{T}\right)_C = 0. \quad (8.14)$$

Thus

$$\left(\int_2^1 \frac{\delta Q}{T}\right)_B = \left(\int_2^1 \frac{\delta Q}{T}\right)_C. \quad (8.15)$$

We can reverse direction and recover the same result, since $\int_2^1 = -\int_1^2$:

$$\left(\int_1^2 \frac{\delta Q}{T}\right)_B = \left(\int_1^2 \frac{\delta Q}{T}\right)_C. \quad (8.16)$$

Since paths B and C are different and arbitrary, but $\int_1^2 \delta Q/T$ is the same on either path, the integral must be *path-independent*. It therefore defines a thermodynamic property of the system. We define that property as entropy, S , an extensive thermodynamic property:

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}.} \quad (8.17)$$

Note the units of S must be kJ/K in the SI system. We also can scale by the constant mass m to get the corresponding intensive variable $s = S/m$:

$$\boxed{s_2 - s_1 = \int_1^2 \frac{\delta q}{T}.} \quad (8.18)$$

The units for s are $kJ/kg/K$; note they are the same as c_p , c_v , and R . In differential form, we can say

$$\boxed{ds = \frac{\delta q}{T}.} \quad (8.19)$$

This leads us to

$$\boxed{\delta q = T ds.} \quad (8.20)$$

Integrating Eq. (8.20), we get

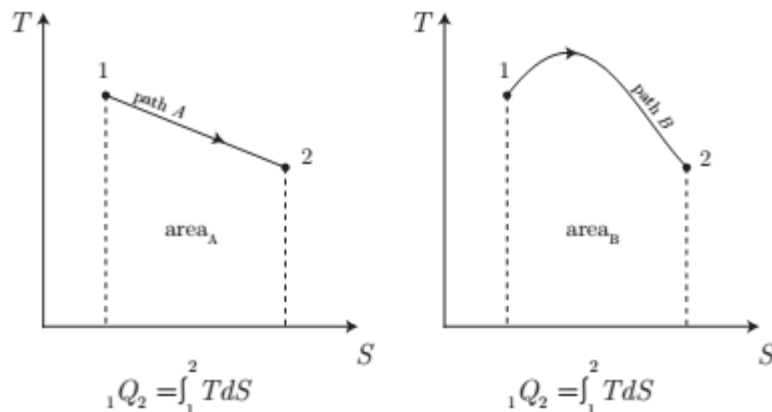
$$\int_1^2 \delta q = \int_1^2 T ds. \quad (8.21)$$

Thus, we get

$$\boxed{{}_1q_2 = \int_1^2 T ds.} \quad (8.22)$$

This is the heat transfer equivalent to ${}_1w_2 = \int_1^2 P dv$. So we see the heat transfer for a process from 1 to 2 is given by the area under the curve in the $T - s$ plane; see Fig. 8.4. Note if our

Fig 8.4. Sketch of process in the $T - S$ plane, with the associated heat transfer



process lies on a so-called

- **ISENTROPE:** a line on which entropy s is constant,

then by Eq. (8.22), ${}_1q_2 = 0$; thus, the process is adiabatic. Now, Eq. (8.22) only applies for a reversible process. Combining these notions, we summarize with the important equivalence:

$$\boxed{\text{isentropic} = \text{adiabatic} + \text{reversible.}}$$

For problems in which no chemical reactions are present, we will find ourselves interested only in entropy differences. For problems with chemical reactions, the absolute values of entropy will be important. Such values can be obtained by consideration of the

- **THIRD LAW OF THERMODYNAMICS:** “every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances,”

quoted here from Lewis and Randall² The law, another axiom of thermodynamics, was developed over several years by Nernst³ depicted in Fig. 8.5. It will not be considered

²G. N. Lewis and M. Randall, 1923, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, p. 448.

³e.g. W. H. Nernst, 1906, Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen, *Nachrichten von der Königlich-Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-physikalische Klasse*, Weidmannsche Buchhandlung, Berlin.

Fig 8.5. Walther Hermann Nernst (1864-1941), German physical chemist who developed the third law of thermodynamics



further here.

Because entropy is a thermodynamic property, it can be used to help determine the state. That is we can say any of the following:

$$s = s(T, v), \quad s = s(T, P), \quad s = s(v, x), \quad P = P(T, s), \quad v = v(P, s), \quad \dots \quad (8.23)$$

For two-phase mixtures, we have, as expected,

$$s = s_f + x s_{fg}, \quad s = s_f + x(s_g - s_f), \quad s = (1 - x)s_f + x s_g, \quad x = \frac{s - s_f}{s_{fg}}. \quad (8.24)$$

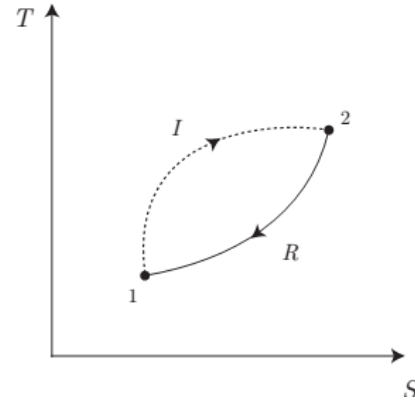
8.2. Second law in terms of entropy

We now have a statement of the second law, $\oint \delta Q/T \leq 0$, valid for reversible or irreversible heat transfer, and a definition of entropy $S_2 - S_1 = \int_1^2 \delta Q/T$, provided the heat transfer is reversible. The two seem similar. Let us combine them to cast the second law in terms of entropy. Consider the cycle in the $T - S$ diagram of Fig. 8.6. We start at 1, and proceed to 2 along path I , which represents an irreversible process. We return from 2 to 1 along path R , which represents a reversible process. The second law, Eq. (8.10), holds

$$\oint \frac{\delta Q}{T} \leq 0, \quad (8.25)$$

$$0 \geq \oint \frac{\delta Q}{T}. \quad (8.26)$$

Fig 8.6. Sketch of cycle in the $T - S$ plane composed of irreversible process I from 1 to 2, followed by reversible process R from 2 back to 1



The equality implies all processes are reversible; the inequality implies some portion of the process is irreversible. Now, for a reversible process we also have

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}. \quad (8.27)$$

Since the process is reversible, we reverse to get

$$S_1 - S_2 = \int_2^1 \frac{\delta Q}{T}. \quad (8.28)$$

Now, apply the second law, Eq. (8.10), to the scenario of Fig. 8.6

$$0 \geq \left(\int_1^2 \frac{\delta Q}{T} \right)_I + \left(\int_2^1 \frac{\delta Q}{T} \right)_R. \quad (8.29)$$

Now, substitute Eq. (8.28) into Eq. (8.29) to eliminate the integral along R to get

$$0 \geq \left(\int_1^2 \frac{\delta Q}{T} \right)_I + S_1 - S_2, \quad (8.30)$$

$$S_2 - S_1 \geq \left(\int_1^2 \frac{\delta Q}{T} \right)_I. \quad (8.31)$$

More generally, we can write the second law of thermodynamics as

$$\boxed{S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}.} \quad (8.32)$$

If $1 \rightarrow 2$ is reversible, the equality holds; if $1 \rightarrow 2$ is irreversible, the inequality holds.

Now, *if the system is isolated*, there can be no heat transfer interactions and $\delta Q = 0$. So

$$\boxed{S_2 - S_1 \geq 0,} \quad (8.33)$$

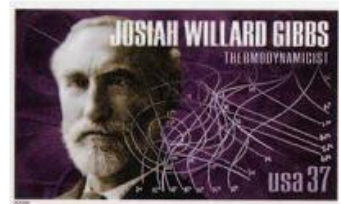
isolated system.

This implies 2 occurs later in time than 1. Thus, for isolated systems, the entropy increases as time moves forward.

8.3. The Gibbs equation

We are now in a position to obtain one of the most important relations in thermodynamics, the Gibbs equation, named for the great nineteenth century American engineer, physicist, chemist, and mathematician, depicted in Fig. 8.11

Fig 8.11. Josiah Willard Gibbs (1839-1903), American mechanical engineer who revolutionized the science of classical and statistical thermodynamics



The Gibbs equation is a re-capitulation of the first law of thermodynamics. It is taken in the limit that

- all processes are assumed to be reversible.

And we shall only consider the Gibbs equation for simple compressible substances, neglecting changes in kinetic and potential energy, though other forms are possible.

We first recall the differential form of the first law, Eq. (5.8), $dE = \delta Q - \delta W$, neglect⁴ changes in KE and PE , so that $dE = dU$, and then consider this on a per mass basis, obtaining

$$du = \delta q - \delta w. \quad (8.58)$$

Now, for a simple compressible substance undergoing pressure-volume work, we have Eq. (4.34) cast on a per mass basis, $\delta w = Pdv$. For the same substance undergoing simultaneous reversible heat transfer, we have from Eq. (8.20), $\delta q = Tds$. So we can recast Eq. (8.58) as the

⁴The justification of neglecting changes in KE and PE is rarely stated. If we retained the total energy, we would be led ultimately to $ds = de/T + (P/T)dv$. Moreover, we would conclude that changes in KE or PE could lead to a change in entropy. However, we choose to specifically retain an accounting for mechanical energy via Newton's second law. Detailed analysis of Newton's second law would show that work done by certain classes of forces, *e.g.* gravity forces and forces due to pressure differences, was reversible, and does not dissipate mechanical energy. That class of change of KE and PE should not be thought of as entropy-generating, because of its reversibility. However, work done by other types of forces, *e.g.* viscous shear forces, does dissipate mechanical energy into thermal energy. Such a conversion is irreversible, and should contribute to an entropy change. These notions are best understood in the context of the full mass, momenta, and energy equations for a continuum. Details may be found in <http://www.nd.edu/~powers/ame.60635/notes.pdf>.

Gibbs equation⁵:

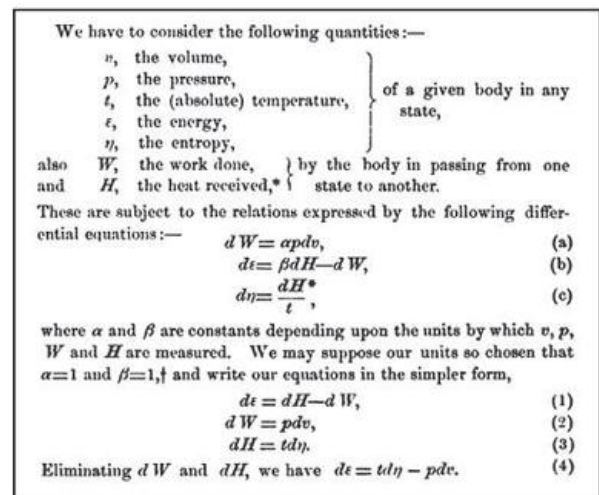
$$\boxed{du = Tds - Pdv.} \quad (8.59)$$

Gibbs presented this now famous equation in an obscure journal, which was the only journal in which he ever published. A reproduction from that journal of the page where his equation first appeared⁶ is given in Fig. 8.12

⁵In this usage, similar to that given by BS, we are not alone, but may be in the minority. Some texts call Eq. (8.59) the "first Gibbs equation." Perhaps a more common name for a variant of Eq. (8.59) is the "Fundamental Thermodynamic Relation," which is commonly described for the extensive analog, $dU = TdS - PdV$.

⁶J. W. Gibbs, 1873, "Graphical methods in the thermodynamics of fluids," *Transactions of the Connecticut Academy of Arts and Sciences*, 2: 309-342.

Fig 8.12. An image of the 1873 first appearance of the Gibbs equation in print



Note that the Gibbs equation is generally valid for all materials. We have said nothing about either a thermal or caloric equation of state. It is thus valid for ideal gases, non-ideal gases, liquids, solids, or two-phase mixtures. And though we considered reversible processes in its derivation, once we have it, we note that only properties are defined, and so we do not have to restrict ourselves to reversible processes. It is commonly rearranged in a way which allows the entropy to be determined:

$$\boxed{Tds = du + Pdv.} \quad (8.60)$$

The Gibbs equation can also be written in terms of enthalpy. Recall Eq. (5.52), $h = u + Pv$, also valid for general materials. Elementary calculus then tells us

$$h = u + Pv, \quad (8.61)$$

$$dh = du + Pdv + vdP, \quad (8.62)$$

$$du = dh - Pdv - vdP. \quad (8.63)$$

Substitute Eq. (8.63) into the Gibbs relation Eq. (8.60) to yield

$$Tds = dh - Pdv - vdP + Pdv, \quad (8.64)$$

$$Tds = dh - vdP. \quad (8.65)$$

So we can say⁷

$$\boxed{dh = Tds + vdP.} \quad (8.66)$$

8.4. Entropy for ideal gases

Let us find how to write the entropy for an ideal gas. We first use the Gibbs equation, Eq. (8.60), to solve for ds to get

$$ds = \frac{du}{T} + \underbrace{\frac{P}{T}}_{=R/v} dv. \quad (8.74)$$

Now, ideal gases have $Pv = RT$, so $P/T = R/v$, so we have

$$ds = \frac{du}{T} + \frac{R}{v} dv. \quad (8.75)$$

Now, ideal gases also have from Eq. (5.75), $du = c_v(T)dT$, so

$$ds = \frac{c_v(T)dT}{T} + R\frac{dv}{v}. \quad (8.76)$$

We will first consider a CPIG, and then a CIIG.

8.4.1 Calorically perfect

For a CPIG, c_v is a constant, and Eq. (8.76) reduces to

$$ds = \frac{c_v dT}{T} + R\frac{dv}{v}. \quad (8.77)$$

This is easily integrated as follows

$$\int_1^2 ds = \int_1^2 \frac{c_v dT}{T} + \int_1^2 R \frac{dv}{v}, \quad (8.78)$$

$$\int_1^2 ds = c_v \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v}. \quad (8.79)$$

So we get

$$\boxed{s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}.} \quad (8.80)$$

In general for a CPIG we can say

$$\boxed{s(T, v) = s_o + c_v \ln \frac{T}{T_o} + R \ln \frac{v}{v_o},} \quad (8.81)$$

where o denotes a reference state. We can invert to solve for T/T_o as follows

$$\frac{T(s, v)}{T_o} = \left(\frac{v_o}{v}\right)^{R/c_v} \exp\left(\frac{s - s_o}{c_v}\right). \quad (8.82)$$

Since $R/c_v = (c_P - c_v)/c_v = k - 1$, we also write

$$\boxed{\frac{T(s, v)}{T_o} = \left(\frac{v_o}{v}\right)^{k-1} \exp\left(\frac{s - s_o}{c_v}\right).} \quad (8.83)$$

Now, we can also rearrange Eq. (8.66) to get

$$ds = \frac{dh}{T} - \frac{v}{T} dP. \quad (8.84)$$

Now, the ideal gas gives us $v/T = R/P$, and the calorically perfect assumption gives us $dh = c_P dT$, with c_P a constant. Thus, Eq. (8.84) reduces to

$$ds = c_P \frac{dT}{T} - R \frac{dP}{P}. \quad (8.85)$$

We integrate Eq. (8.85) to get

$$\int_1^2 ds = c_P \int_1^2 \frac{dT}{T} - R \int_1^2 \frac{dP}{P}. \quad (8.86)$$

Thus,

$$\boxed{s_2 - s_1 = c_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}.} \quad (8.87)$$

In general, for a CPIG we can say

$$\boxed{s(T, P) = s_o + c_P \ln \frac{T}{T_o} - R \ln \frac{P}{P_o},} \quad (8.88)$$

where o denotes a reference state. We can invert Eq. (8.88) to form

$$\frac{T(s, P)}{T_o} = \left(\frac{P}{P_o}\right)^{R/c_P} \exp\left(\frac{s - s_o}{c_P}\right). \quad (8.89)$$

Since $R/c_P = (c_P - c_v)/c_P = 1 - 1/k = (k - 1)/k$, we have

$$\boxed{\frac{T(s, P)}{T_o} = \left(\frac{P}{P_o}\right)^{(k-1)/k} \exp\left(\frac{s - s_o}{c_P}\right)}. \quad (8.90)$$

8.4.2 Calorically imperfect

For the CIIG, we integrate Eq. (8.76) to get

$$\int_1^2 ds = \int_1^2 \frac{c_v(T)dT}{T} + R \int_1^2 \frac{dv}{v}. \quad (8.91)$$

This gives

$$\boxed{s_2 - s_1 = \int_1^2 \frac{c_v(T)dT}{T} + R \ln \frac{v_2}{v_1}}. \quad (8.92)$$

For the CIIG, we have Eq. (5.77), $dh = c_P(T)dT$, along with the ideal gas result $v/T = R/P$; thus, Eq. (8.84) reduces to

$$ds = \frac{c_P(T)dT}{T} - R \frac{dP}{P}. \quad (8.93)$$

Integrating, we get

$$\boxed{s_2 - s_1 = \int_1^2 \frac{c_P(T)dT}{T} - R \ln \frac{P_2}{P_1}}. \quad (8.94)$$

In general we can say

$$s = s_o + \underbrace{\int_{T_o}^T \frac{c_P(\hat{T})d\hat{T}}{\hat{T}}}_{=s_T^o} - R \ln \frac{P}{P_o}. \quad (8.95)$$

Here, the “hat” notation indicates a dummy variable of integration. Here, s_T^o is a function of temperature and represents the entropy when the pressure is evaluated at its reference value of $P = P_o$. In BS, Table A.8 gives tabular values of s_T^o . Note that

- in this course a superscript o denotes evaluation at a reference pressure. Typically $P_o = 100 \text{ kPa}$.

So for the CIIG, we have

$$\boxed{s(T, P) = s_o + \underbrace{\int_{T_o}^T \frac{c_P(\hat{T})d\hat{T}}{\hat{T}}}_{=s_T^o} - R \ln \frac{P}{P_o} = s_T^o - R \ln \frac{P}{P_o}}. \quad (8.96)$$

We could also say

$$\boxed{s_2 - s_1 = s_{T_2}^o - s_{T_1}^o - R \ln \frac{P_2}{P_1}}. \quad (8.97)$$

8.5. Entropy for an incompressible solid or liquid

For an incompressible solid or liquid we have $dv = 0$, so the Gibbs equation, Eq. (8.59), reduces to

$$Tds = du. \quad (8.129)$$

If we take $du = cdT$, we get

$$Tds = cdT, \quad (8.130)$$

$$ds = \frac{cdT}{T}, \quad (8.131)$$

$$s - s_o = \int_{T_o}^T \frac{c(\hat{T})d\hat{T}}{\hat{T}}. \quad (8.132)$$

And if the solid or liquid is calorically perfect with c a true constant, we get

$$s - s_o = c \ln \frac{T}{T_o}. \quad (8.133)$$

8.6. Iso-curves

8.6.1 Isochores

To identify isochores, let us consider Eq. (8.60),

$$Tds = du + P \underbrace{dv}_{=0}, \quad (8.134)$$

$$Tds = du, \quad (8.135)$$

$$T = \left. \frac{\partial u}{\partial s} \right|_v. \quad (8.136)$$

This is valid for a general material. If we have an ideal gas, then $du = c_v(T)dT$, and on an isochore, Eq. (8.60) becomes

$$Tds = \underbrace{du}_{=c_v(T)dT} + P \underbrace{dv}_{=0}, \quad (8.137)$$

$$Tds = c_v(T)dT, \quad (8.138)$$

$$\frac{T}{c_v(T)} = \left. \frac{\partial T}{\partial s} \right|_v. \quad (8.139)$$

Thus, the slope of an isochore in the $T - s$ plane for an ideal gas is T/c_v .

8.6.2 Isobars

To identify isobars, let us consider Eq. (8.65),

$$Tds = dh - \underbrace{v}_{=0} dP, \quad (8.140)$$

$$Tds = dh, \quad (8.141)$$

$$T = \left. \frac{\partial h}{\partial s} \right|_P. \quad (8.142)$$

This is valid for a general material. Iff we have an ideal gas, then $dh = c_p(T)dT$, and on an isobar, Eq. (8.65) becomes

$$Tds = \underbrace{dh}_{=c_p(T)dT} - \underbrace{v}_{=0} dP, \quad (8.143)$$

$$Tds = c_p(T)dT, \quad (8.144)$$

$$\frac{T}{c_p(T)} = \left. \frac{\partial T}{\partial s} \right|_P. \quad (8.145)$$

Thus, the slope of an isobar in the $T - s$ plane for an ideal gas is T/c_p . Since $c_p(T) > c_v(T)$, *the slope of the isochore is greater than the slope of an isobar at a given point.*

For air as a CPIG with $k = 7/5$, $R = 0.287 \text{ kJ/kg/K}$, the scenario is sketched in Fig. 8.14. For materials such as water, the behavior is similar. The slope of the isochore is greater at a given point than that of an isobar.

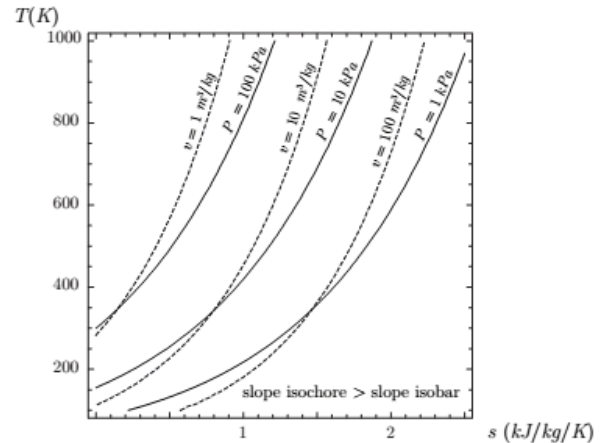


Fig 8.14. Sketch of isochores and isobars in the $T - s$ plane for CPIG air, $k = 7/5$, $R = 0.287 \text{ kJ/kg/K}$, $s_0 = 0 \text{ kJ/kg/K}$

8.6.3 Isentropes

We introduce an

- **ISENTROPE:** a curve on which entropy is constant.

For general materials, we identify isentropes by considering Eq. (8.60) with $ds = 0$:

$$T \underbrace{ds}_{=0} = du + Pdv, \quad (8.146)$$

$$0 = du + Pdv, \quad (8.147)$$

$$du = -Pdv. \quad (8.148)$$

Because there is no heat transfer on an isentrope, for such a process, all of the Pdv work goes into changing the internal energy of the system. We could also say

$$\left. \frac{\partial u}{\partial v} \right|_s = -P. \quad (8.149)$$

Similarly,

$$T \underbrace{ds}_{=0} = dh - vdP, \quad (8.150)$$

$$0 = dh - vdP, \quad (8.151)$$

$$dh = vdP. \quad (8.152)$$

We could also say

$$\left. \frac{\partial h}{\partial P} \right|_s = v. \quad (8.153)$$

8.7. Isentropic relations for an ideal gas

Here, we will consider algebraic relations for ideal gases undergoing isentropic processes. The results are simple for CPIGs and a little more complicated for CIIGs.

8.7.1 Calorically perfect

Let us consider the important case of a CPIG undergoing an isentropic process. Start with the Gibbs equation, Eq. (8.60), $Tds = du + Pdv$. Now, for an isentropic CPIG, we have $ds = 0$, $P = RT/v$, and $du = c_v dT$, so we get

$$0 = c_v dT + \frac{RT}{v} dv, \quad (8.154)$$

$$0 = c_v \frac{dT}{T} + R \frac{dv}{v}, \quad (8.155)$$

$$-c_v \frac{dT}{T} = R \frac{dv}{v}, \quad (8.156)$$

$$-c_v \int_1^2 \frac{dT}{T} = R \int_1^2 \frac{dv}{v}, \quad (8.157)$$

$$-c_v \ln \frac{T_2}{T_1} = R \ln \frac{v_2}{v_1}, \quad (8.158)$$

$$\ln \frac{T_2}{T_1} = \frac{R}{c_v} \ln \frac{v_1}{v_2}, \quad (8.159)$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{v_1}{v_2} \right)^{R/c_v}, \quad (8.160)$$

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{v_1}{v_2} \right)^{k-1}, \quad (8.161)$$

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1}. \quad (8.162)$$

Now, since $T = Pv/R$, we can also say

$$\frac{\frac{P_2 v_2}{R}}{\frac{P_1 v_1}{R}} = \left(\frac{v_1}{v_2} \right)^{k-1}, \quad (8.163)$$

$$\frac{P_2 v_2}{P_1 v_1} = \left(\frac{v_1}{v_2} \right)^{k-1}, \quad (8.164)$$

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^k, \quad (8.165)$$

$$\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = \left(\frac{v_1}{v_2} \right)^{k-1}. \quad (8.166)$$

We can summarize by combining Eqs. (8.162)–(8.166) to get an important result, which we emphasize *is valid for isentropic calorically perfect ideal gases only*:

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = \left(\frac{v_1}{v_2} \right)^{k-1}}. \quad (8.167)$$

Another useful form is given by rearranging Eq. (8.166) to get the result, again *valid for isentropic calorically perfect ideal gases only*:

$$\boxed{P_1 v_1^k = P_2 v_2^k}. \quad (8.168)$$

We see that the isentropic relation between P and v is that for a polytropic process, see p. 87, with the polytropic exponent $n = k$. Recall for an ideal gas undergoing an isothermal process, we have $P_1 v_1 = P_2 v_2$, which is polytropic with $n = 1$.

8.7.2 Calorically imperfect

Consider now an isentropic relation for a CIIG. Recall from Eq. (8.96) that there is no simple way to write the algebraic form of the entropy, which relies on an integral, available in tabular form. Consideration of CIIGs usually relies on an unusual combination of table look-up and equations.

We can use Eq. (8.96) to write the entropy at states 1 and 2 as

$$s_1 = s_{T_1}^o - R \ln \frac{P_1}{P_o}, \quad (8.275)$$

$$s_2 = s_{T_2}^o - R \ln \frac{P_2}{P_o}. \quad (8.276)$$

Recall o denotes the reference pressure, and s_T^o is a temperature-dependent function, which is available in tabular form. So the entropy difference, $s_2 - s_1$, is

$$s_2 - s_1 = s_{T_2}^o - s_{T_1}^o - R \left(\ln \frac{P_2}{P_o} - \ln \frac{P_1}{P_o} \right), \quad (8.277)$$

$$= s_{T_2}^o - s_{T_1}^o - R \ln \left(\frac{P_2 P_o}{P_o P_1} \right), \quad (8.278)$$

$$= s_{T_2}^o - s_{T_1}^o - R \ln \left(\frac{P_2}{P_1} \right). \quad (8.279)$$

If the process is isentropic, we have $s_2 = s_1$, and so

$$0 = s_{T_2}^o - s_{T_1}^o - R \ln \frac{P_2}{P_1}, \quad (8.280)$$

$$s_{T_2}^o - s_{T_1}^o = R \ln \frac{P_2}{P_1}. \quad (8.281)$$

8.8. Two cycles

In this section, we describe two important thermodynamic cycles. The most scientifically important is the *Carnot cycle*, and we spend some effort in its exposition. We contrast this with the *Otto cycle*, which is used to model the operation of gasoline engines.

8.8.1 Carnot

Motivated by a practical desire to improve French industry in the aftermath of military defeats of earlier decades, Nicolas L eonard Sadi Carnot (1796-1832), (son of the mathematician and architect of the military success of the early French revolution, Lazare Carnot) developed an *impractical* engine with great theoretical importance. Though the so-called Carnot engine has never been built, it represents the best heat engine which could be built, and imposes useful restrictions for practical engineers with visions of unrealizable efficiencies. Most importantly, the analysis of Carnot demonstrates how perpetual motion machines of the first and second kind cannot exist. Those of the first kind violate the first law of thermodynamics; those of the second kind violate the second law of thermodynamics.

Let us use a piston-cylinder arrangement to illustrate a Carnot cycle. See the sketch of Fig. 8.24. A sketch of the process in both the $P - v$ and $T - s$ planes for a CPIG is given in Fig. 8.25.

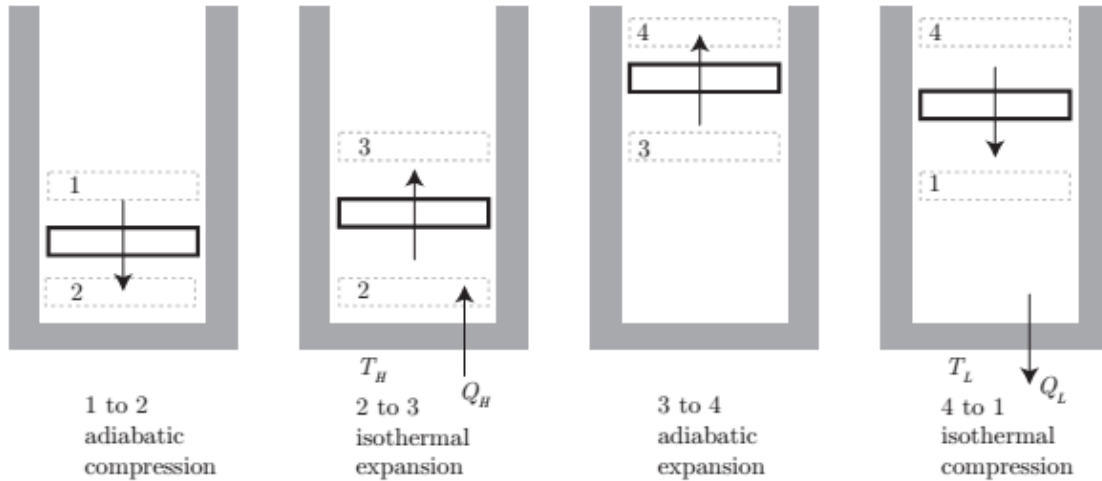


Fig 8.24. Sketch of Carnot cycle piston-cylinder device

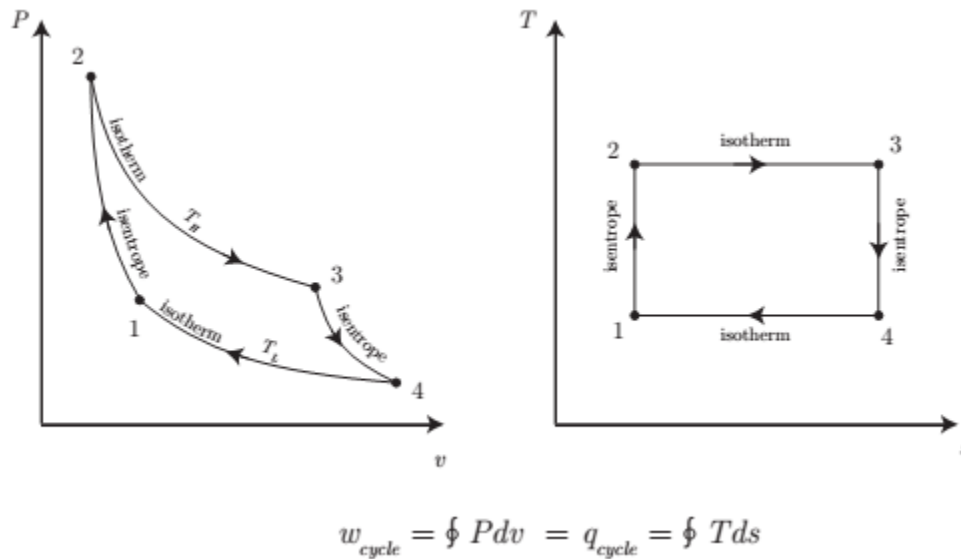


Fig 8.25. Sketch of a Carnot cycle for a CPIG represented in the $P - v$ and $T - s$ planes

The Carnot cycle is defined in four stages. Here, we use a different identification of the states 1, 2, 3, and 4 than do BS to be consistent with more common notation that will be used later for other engines by BS and most other texts. The four stages are

- 1 \rightarrow 2: adiabatic reversible (isentropic) compression ($Q = 0$) from T_L to T_H ,
- 2 \rightarrow 3: isothermal reversible expansion at T_H ,
- 3 \rightarrow 4: adiabatic reversible (isentropic) expansion from T_H to T_L , and
- 4 \rightarrow 1: isothermal compression at T_L .

We always assume the same fluid is present within the Carnot engine, and ignore the effects of valves. We also ignore the effect of mixtures of combustible gases.

The Carnot cycle for a CPIG is such a foundational idealization for mechanical engineers that it is centrally incorporated in the logo of the international mechanical engineering academic honor society, Pi Tau Sigma ($\Pi\tau\sigma$). The logo is reproduced in Fig. 8.26.

Fig 8.26. Logo of the international mechanical engineering honor society, Pi Tau Sigma $\Pi\tau\sigma$ featuring the Carnot cycle for a CPIG in the $P - v$ plane as displayed on the campus of the University of Notre Dame



8.8.2 Otto

The Otto cycle approximates the gasoline engine using what is known as an *air standard* approximation. It is named for Nikolaus Otto, depicted in Fig. 8.28. Many details are

Fig 8.28. Nikolaus August Otto (1832-1891), German developer of the internal combustion engine



ignored (like inlet and exhaust), and all material properties are taken to be those of air modelled as a CPIG. It employs a *fixed mass* approach. Diagrams for $P - v$ and $T - s$ for the Otto cycle are shown in Fig. 8.29. One can outline the Otto cycle as follows:

- $1 \rightarrow 2$: isentropic compression in the compression stroke,
- $2 \rightarrow 3$: isochoric heating in the combustion stroke during spark ignition,
- $3 \rightarrow 4$: isentropic expansion in power stroke, and
- $4 \rightarrow 1$: isochoric rejection of heat to the surroundings.

Clearly, the cycle is not a Carnot cycle. The heat transfer during the combustion and exhaust strokes does not take place at constant temperature. Roughly speaking, *we might*

expect degradation of the thermal efficiency, relative to an equivalent Carnot engine operating between the same temperature bounds, because some of the heat transfer of the Otto cycle occurs at lower temperatures than other parts of the cycle. Recall that for maximum Carnot efficiency, we would like T_H as high as possible. Just past state 2, the heat transferred at T_2 is at a lower temperature than the heat transferred at T_3 .

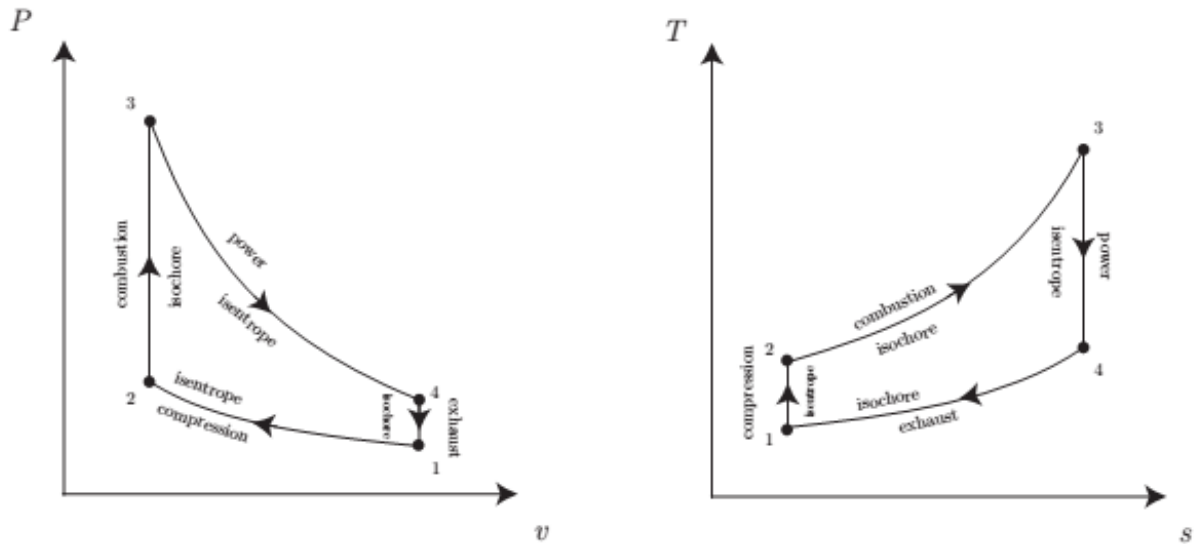


Fig 8.29. P – v and T – s diagrams for the Otto cycle

Note for isochoric heating, such as $2 \rightarrow 3$, in a fixed mass environment, the first law gives

$$u_3 - u_2 = 2q_3 - 2w_3, \quad (8.377)$$

$$u_3 - u_2 = 2q_3 - \int_{v_2}^{v_3} P \, dv, \quad \text{but } v_2 = v_3, \quad (8.378)$$

$$u_3 - u_2 = 2q_3 - \underbrace{\int_{v_2}^{v_2} P \, dv}_{=0}, \quad (8.379)$$

$$2q_3 = u_3 - u_2, \quad (8.380)$$

$$2q_3 = c_v(T_3 - T_2), \quad \text{if CFIG.} \quad (8.381)$$

The thermal efficiency is found as follows:

$$\eta = \frac{W_{net}}{Q_H}, \quad (8.382)$$

$$= \frac{Q_H - Q_L}{Q_H}, \quad (8.383)$$

$$= 1 - \frac{Q_L}{Q_H}, \quad (8.384)$$

$$= 1 - \frac{mc_v(T_4 - T_1)}{mc_v(T_3 - T_2)}, \quad (8.385)$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2}, \quad (8.386)$$

$$= 1 - \frac{T_1 \left(\frac{T_4}{T_1} - 1 \right)}{T_2 \left(\frac{T_3}{T_2} - 1 \right)}. \quad (8.387)$$

Now, one also has the isentropic relations:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{k-1}, \quad (8.388)$$

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3} \right)^{k-1}. \quad (8.389)$$

But $V_4 = V_1$ and $V_2 = V_3$, so

$$\frac{T_3}{T_4} = \left(\frac{V_1}{V_2} \right)^{k-1} = \frac{T_2}{T_1}. \quad (8.390)$$

Cross multiplying the temperatures, one finds

$$\frac{T_3}{T_2} = \frac{T_4}{T_1}. \quad (8.391)$$

Thus, the thermal efficiency reduces to

$$\eta = 1 - \frac{T_1}{T_2}. \quad (8.392)$$

This looks a lot like the Carnot efficiency. But for a Carnot engine operating between the same temperature bounds, we would have found $\eta = 1 - T_1/T_3$. Since $T_3 > T_2$, the Carnot engine is more efficient than the ideal Otto engine. This identifies an important

- **THERMAL ENGINE DESIGN PRINCIPLE:** To optimize the performance of a thermal engine, the $T - s$ diagram describing its behavior should be as close to a rectangle as possible, with the highest possible T_H and the lowest possible T_L .

One often finds commercial engines characterized by their compression ratios. Modern gasoline engines may have compression ratios of $r_v = 10$. In terms of the compression ratio $r_v = V_1/V_2$, one has

$$\eta = 1 - r_v^{1-k} = 1 - \frac{1}{r_v^{k-1}}. \quad (8.393)$$

Note if the compression ratio increases, the thermal efficiency increases, so this is desirable, in principle. However, high compression ratios introduces a variety of problems including 1) loss of material strength of hot metals in the engine, 2) higher incidence of detonation or knock in the combustion process, 3) greater tendency to form harmful pollutants such as NO_x .

Some deviations of actual performance from that of the air-standard Otto cycle are as follows:

- specific heats actually vary with temperature,
- combustion may be incomplete (induces pollution and lowers fuel efficiency),
- work of inlet and exhaust is ignored, and
- losses of heat transfer to engine walls are ignored.

8.9. Entropy of thermo-mechanical mixing

We believe from experience that mixing is most likely a process which is entropy-generating. For instance, it is easy to mix water and ink together, but hard to separate them into their original components. Separation can be accomplished, but it takes energy. Now, we can also mix the energy of components. We might imagine two gases at different states. This is a structured arrangement. When the two gases mix, they come to a new equilibrium without external impetus. There is consequently less structure in the universe, and the entropy should go up. Moreover, it would require an external action to return the system to its original state. Let us demonstrate this with a simple example thermo-mechanically mixing two CPIGs initially at different temperatures and pressures, but with otherwise identical properties. We will enforce thermal equilibrium via temperature equilibration and mechanical equilibrium via pressure equilibration.

We note

- The entropy of the universe increased, and we were able to quantify it.
- The adiabatic mixing process we described is irreversible. That is to say, once mixed, we do not expect to see a spontaneous return to the initial state.
- The entropy of the universe will increase whenever two systems, initially not in equilibrium, come to an equilibrium.

8.10. Probabilistic approach to entropy

One of the more difficult concepts regarding entropy is how it relates to the randomness of a system. In fact what constitutes randomness *vis-à-vis* structure may be open to question.

Consider the diagram of Fig. [8.31](#). Here, we take the level of the grey scale to be proportional to the local temperature. The blocks on the left are held at a variety of temperatures, hot, intermediate, and cold. The blocks on the right are held at the same intermediate temperature. Let us restrict attention to the case where the hot and cold temperature blocks

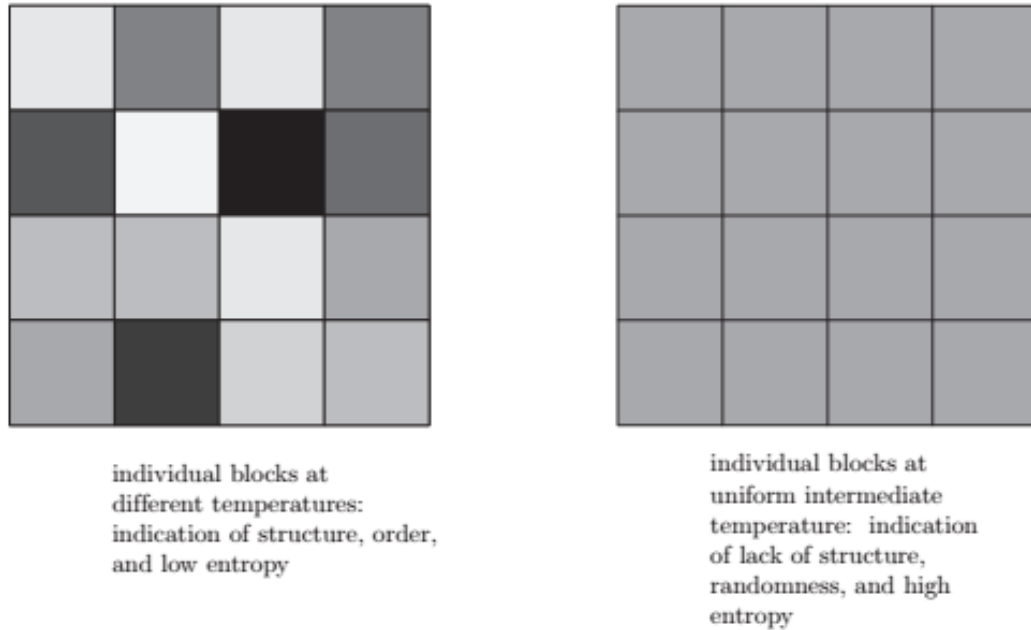


Fig 8.31. Two scenarios for the temperature field with the grey scale proportional to the temperature

on the left just balance, so that when the net temperature of all the blocks on the left is calculated, it is precisely the intermediate temperature of the blocks on the right. For such a case, the total thermal energy of the left and right configurations is equal. Energy being equal, which configuration has the higher entropy? One is tempted to say that on the left because it looks to be more random. But in fact it is the configuration on the right, which is equivalent to that on the left having come to equilibrium, while conserving energy. The configuration on the left has each block at a different temperature. This is properly considered, in the sense of thermodynamics, to be a structure. Left to itself, the thermal energy would diffuse, giving rise to the configuration on the right. Now, the grey-level of each block on the left is representative of that block's average kinetic energy. Within each block, there will be a distribution of kinetic energy for each individual molecule. For the blocks on the right, there is an overall distribution of randomness, the same for each block. That randomness is not represented by the uniform grey shade, which only captures the average kinetic energy.

It may be possible to better understand the relationship between entropy and randomness, such as that depicted in Fig. 8.31, by the following discussion. Let us consider a radically different approach to entropy, first advocated by Boltzmann in the late nineteenth century. Boltzmann, depicted at two disparate stages in his life in Fig. 8.32, had to struggle mightily

for his theories to gain acceptance in a time when the atomic theory of matter was not widely understood. His arguments have become accepted over time relative to those of his many detractors. Let us define a set of N possible states, each with a probability of p_n . By the nature of probability, we must have

$$\sum_{n=1}^N p_n = 1. \quad (8.448)$$

Fig 8.32. Ludwig Boltzmann (1844-1906), Austrian physicist whose statistical approach to thermodynamics laid the foundation for quantum mechanics



Because of the nature of probability, we will demand that

$$p_n \in [0, 1]. \quad (8.449)$$

That is to say neither negative probability or probability greater than unity has any meaning. Let us define the entropy of the system as

$$S = -k_B \sum_{n=1}^N p_n \ln p_n. \quad (8.450)$$

where we take k_B to be the *Boltzmann constant*. Boltzmann's tomb has a variant of this equation cut into its stone, as shown in Fig. 8.32. As an aside, we note that operating on Eq. (8.450) yields an alternative expression relating S to p_n :

$$-\frac{S}{k_B} = \sum_{n=1}^N p_n \ln p_n, \quad (8.451)$$

$$-\frac{S}{k_B} = \sum_{n=1}^N \ln p_n^{p_n}, \quad (8.452)$$

$$-\frac{S}{k_B} = \ln \prod_{n=1}^N p_n^{p_n}, \quad (8.453)$$

$$\exp\left(-\frac{S}{k_B}\right) = \prod_{n=1}^N p_n^{p_n}. \quad (8.454)$$

Boltzmann defined k_B such that

$$k_B \equiv \frac{\bar{R}}{N}, \quad (8.455)$$

where N is Avogadro's number, $N = 6.02214179 \times 10^{23}$ *molecule/mole*. So

$$k_B = \frac{8.314472 \frac{J}{K \text{ mole}}}{6.02214179 \times 10^{23} \frac{\text{molecule}}{\text{mole}}} = 1.380650 \times 10^{-23} \frac{J}{K \text{ molecule}}. \quad (8.456)$$

Unaware of Boltzmann's theory, electrical engineer and mathematician Claude Shannon published in 1948 what amounts to precisely the same theory in the context of data communication. When applied in such context, Boltzmann's theory is known as *information theory*. Information theory was constructed to quantify data lost in telephone line signals. The theory and its author has had a seminal effect on modern computer and communication technologies.¹¹¹² Shannon is depicted in Fig. 8.35.

¹¹C. E. Shannon, 1948, "A mathematical theory of communication," *Bell System Technical Journal*, 27(3): 379-423.

¹²C. E. Shannon, 1948, "A mathematical theory of communication," *Bell System Technical Journal*, 27(4): 623-656.

8.11. Summary statement of thermodynamics

We have now covered the major ideas of the natural philosophy that is thermodynamics. We can summarize for an *isolated* universe by stating

- THE ENERGY OF THE UNIVERSE IS CONSTANT, AND ITS ENTROPY IS INCREASING.

This is a loose translation of the statement of Clausius.¹³

¹³R. Clausius, 1865, "Ueber verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie," *Annalen der Physik und Chemie*, 125(7): 353-390.

Fig 8.35. Claude Elwood Shannon (1916-2001), American electrical engineer and mathematician whose "information entropy" mathematically identical to Boltzmann's statistical definition of entropy



- *Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.*

It is a pessimistic set of principles! Thinking cosmologically, these laws would suggest that a large concentrated mass-energy complex, initially in a highly structured state, would ultimately deteriorate into spatially homogeneous space dust at a state of final equilibrium, the so-called *heat death* scenario posed initially in the nineteenth century by Kelvin and others. Present non-equilibrium thermodynamic theory would admit local structures to self-organize into ordered units such as a solar system or living beings. Such structures could potentially draw the energy necessary for self-organization from residual energy from the initial state.

Though some disagree, it is claimed here that the science of thermodynamics is incapable of definitively answering theological questions which often arise regarding the origin of the

universe, its ultimate fate, and the evolution of structures within it. It simply gives a framework for what is admissible with a given set of assumptions. In that it can illuminate some aspects of theology by identifying those parts of it that are in and out of agreement with empirical observations and their consequences, it may be of some use to such disciplines that are outside its realm. More generally, many scientists follow the train of thought popularized by the Austrian philosopher of science Karl Popper (1902-1994) who restricted scientific theories to those that are empirically testable, or more specifically, “falsifiable.” Statements need not be falsifiable to be true, which thus admits the possibility of theological fact; they simply are not science.

So, *if* our universe is formally isolated, we can look forward to “heat death” and the ultimate equilibrium, first suggested by Thomson¹⁴. *If* it is not isolated, there is more

¹⁴W. Thomson, 1852, “On a universal tendency in nature to the dissipation of mechanical energy,” *Transactions of the Royal Society of Edinburgh*, 20(3): 139-142.

uncertainty, and perhaps less reason for pessimism. The so-called laws of thermodynamics are simply an efficient reflection of present-day empirical data. Science is in that sense radically pragmatic; if unimpeachable data is found which contradict our present axioms of thermodynamics, science resorts to new and improved axioms.

NOTES

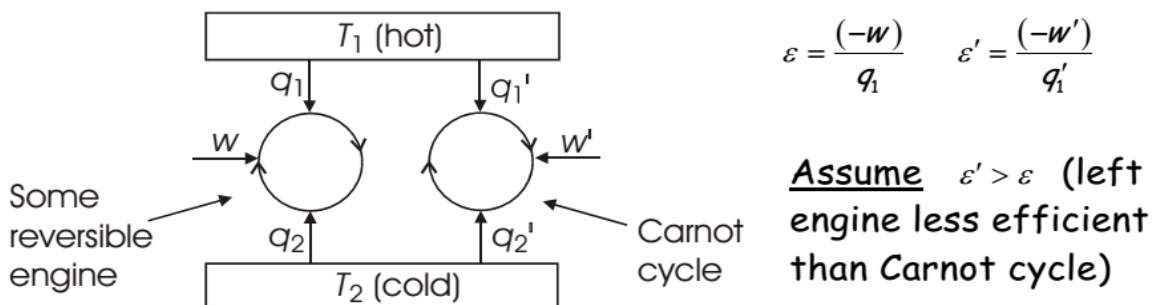
Entropy

- For a reversible ideal gas Carnot cycle:

$$\text{Efficiency} \quad \varepsilon = \frac{-w}{q_{rev}} = 1 + \frac{q_2^{rev}}{q_1^{rev}} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq_{rev}}{T} = 0$$

- The efficiency of any reversible engine has to be the same as the Carnot cycle:



Since the engine is reversible, we can run it backwards. Use the work $(-w')$ out of the Carnot engine as work input (w) to run the left engine backwards.

$$\therefore \text{Total work out} = 0 \quad (-w' = w > 0)$$

$$\text{But } \varepsilon' > \varepsilon \Rightarrow \frac{-w'}{q_1'} > \frac{-w}{q_1} \Rightarrow \frac{w}{q_1'} > \frac{-w}{q_1} = \frac{w}{-q_1} \Rightarrow q_1 < -q_1' \text{ since } q_1 < 0, q_1' > 0 \\ \Rightarrow -(q_1' + q_1) > 0$$

This contradicts the 2nd law (Clausius). This says that we have a net flow of heat into the hot reservoir, but no work is being done!

\therefore The efficiency of any reversible engine is $\varepsilon = 1 - \frac{T_2}{T_1}$

- We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

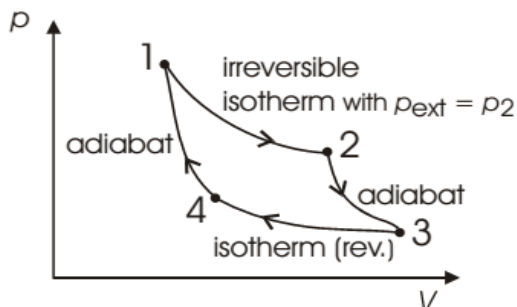
\therefore For any reversible cycle $\oint \frac{dq_{rev}}{T} = 0$

- This defines Entropy, a function of state

$$dS = \frac{dq_{rev}}{T} \Rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{rev}}{T}$$

Note: Entropy is a state function, but to calculate ΔS requires a reversible path.

- An irreversible Carnot (or any other) cycle is less efficient than a reversible one.



$1 \rightarrow 2$

$$(-w)_{irrev} < (-w)_{rev} \Rightarrow w_{irrev} > w_{rev}$$

$$\Delta U = q_{irrev} + w_{irrev} = q_{rev} + w_{rev}$$

$$\therefore q_{irrev} < q_{rev}$$

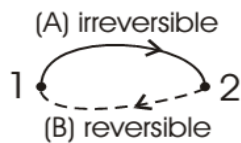
**** An irreversible isothermal expansion requires less heat than a reversible one. ****

$$\varepsilon_{irrev} = 1 + \frac{q_2^{rev}}{q_1^{irrev}} < 1 + \frac{q_2^{rev}}{q_1^{rev}} = \varepsilon_{rev} \quad (q_2 < 0)$$

also $\frac{\dot{d}q_{irrev}}{T} < \frac{\dot{d}q_{rev}}{T} \Rightarrow \oint \frac{\dot{d}q_{irrev}}{T} < 0$

• Leads to Clausius inequality $\oint \frac{\dot{d}q}{T} \leq 0$ contains $\begin{cases} \oint \frac{\dot{d}q_{rev}}{T} = 0 \\ \oint \frac{\dot{d}q_{irrev}}{T} < 0 \end{cases}$

The entropy of an isolated system never decreases



(A): The system is isolated and irreversibly (spontaneously) changes from [1] to [2]

(B): The system is brought into contact with a heat reservoir and reversibly brought back from [2] to [1]

Path (A): $q_{irrev} = 0$ (isolated)

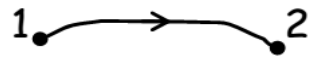
Clausius $\oint \frac{\dot{d}q}{T} \leq 0 \Rightarrow \int_1^2 \frac{\dot{d}q_{irrev}}{T} \stackrel{=0!}{=} + \int_2^1 \frac{\dot{d}q_{rev}}{T} \leq 0$

$$\Rightarrow \int_2^1 \frac{\dot{d}q_{rev}}{T} = S_1 - S_2 = -\Delta S \leq 0$$

$$\therefore \Delta S = S_2 - S_1 \geq 0$$

This gives the direction of spontaneous change!

For isolated systems	{	$\Delta S > 0$ Spontaneous, irreversible process
		$\Delta S = 0$ Reversible process
		$\Delta S < 0$ Impossible



$$\Delta S = S_2 - S_1$$

independent of path

But!

$$\Delta S_{\text{surroundings}}$$

depends on whether the process is
reversible or irreversible

- (a) Irreversible: Consider the universe as an isolated system containing our initial system and its surroundings.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

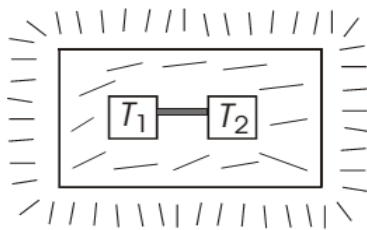
$$\therefore \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$$

- (b) Reversible:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S'_{\text{surr}} = 0$$

$$\therefore \Delta S'_{\text{surr}} = -\Delta S_{\text{sys}}$$

Examples of a spontaneous process



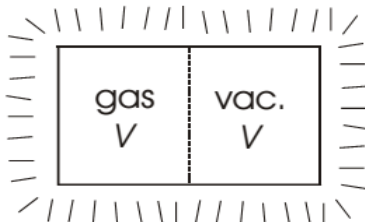
Connect two metal blocks thermally in an isolated system ($\Delta U = 0$)

Initially $T_1 \neq T_2$

$$dS = dS_1 + dS_2 = \frac{\dot{d}q_1}{T_1} - \frac{\dot{d}q_2}{T_2} = \dot{d}q_1 \frac{(T_2 - T_1)}{T_1 T_2} \quad (\dot{d}q_1 = -\dot{d}q_2)$$

$dS > 0$ for spontaneous process

\Rightarrow if $T_2 > T_1 \Rightarrow \dot{d}q_1 > 0$ } in both cases heat flows
 $T_2 < T_1 \Rightarrow \dot{d}q_1 < 0$ } from hot to cold as expected



Joule expansion with an ideal gas

$$1 \text{ mol gas } (V, T) \stackrel{\text{adiabatic}}{=} 1 \text{ mol gas } (2V, T)$$

$$\Delta U = 0 \quad q = 0 \quad w = 0$$

$\Delta S = -\Delta S_{\text{backwards}}$ Compress back isothermally and reversibly

$$q_{\text{rev}} \neq 0$$

$$1 \text{ mol gas } (2V, T) = 1 \text{ mol gas } (V, T)$$

$$\Delta S_{\text{backwards}} = \int \frac{dq_{\text{rev}}}{T} = -\int \frac{dw}{T} = \int_{2V}^V \frac{RdV}{V} = R \ln \frac{1}{2}$$

$$\therefore \boxed{\Delta S = R \ln 2 > 0} \quad \text{spontaneous}$$

Note that to calculate ΔS for the *irreversible* process, we needed to find a reversible path so we could determine dq_{rev} and $\int \frac{dq_{\text{rev}}}{T}$.

Clausius's theorem

In *any* cyclic transformation throughout which the temperature is defined, the following inequality holds:

$$\oint \frac{dQ}{T} \leq 0$$

where the integral extends over one cycle of the transformation. The equality holds if the cyclic transformation is reversible.

Proof Let the cyclic transformation in question be denoted by \mathcal{O} . Divide the cyclic into n infinitesimal steps for which the temperature may be considered to be constant in each step. The system is imagined to be brought successively into contact with heat reservoirs at temperatures T_1, T_2, \dots, T_n . Let Q_i be the amount of heat absorbed by the system during the i th step from the heat reservoir of temperature T_i . We shall prove that

$$\sum_{i=1}^n \left(\frac{Q_i}{T_i} \right) \leq 0$$

The theorem is obtained as we let $n \rightarrow \infty$. Construct a set of n Carnot engines $\{C_1, C_2, \dots, C_n\}$ such that C_i

- (a) operates between T_i and T_o ($T_o \geq T_i$, all i),
- (b) absorbs amount of heat $Q_i^{(o)}$ from T_o ,
- (c) rejects amount of heat Q_i to T_i .

We have, by definition of the temperature scale.

$$\frac{Q_i^{(o)}}{Q_i} = \frac{T_o}{T_i}$$

Consider one cycle of the combined operation $\theta + \{C_1 + \dots + C_n\}$. The net result of this cycle is that an amount of heat

$$Q_o = \sum_{i=1}^n Q_i^{(o)} = T_o \sum_{i=1}^n \left(\frac{Q_i}{T_i} \right)$$

is absorbed from the reservoir T_o and converted entirely into work, with no other effect. According to the second law this is impossible unless $Q_o \leq 0$. Therefore

$$\sum_{i=1}^n \left(\frac{Q_i}{T_i} \right) \leq 0$$

This proves the first part of the theorem.

If θ is reversible, we reverse it. Going through the same arguments, we arrive at the same inequality except that the signs of Q_i are reversed:

$$- \sum_{i=1}^n \left(\frac{Q_i}{T_i} \right) \leq 0$$

Combining this with the previous inequality (which of course still holds for a reversible θ) we obtain

$$\sum_{i=1}^n \left(\frac{Q_i}{T_i} \right) = 0 \quad \blacksquare$$

COROLLARY

For a reversible transformation, the integral

$$\int \frac{dQ}{T}$$

is independent of the path and depends only on the initial and final states of the transformation.

Proof Let the initial state be A and the final state be B . Let I, II denote two arbitrary reversible paths joining A to B , and let II' be the reverse of II. Clausius' theorem implies that

$$\int_I \frac{dQ}{T} + \int_{II'} \frac{dQ}{T} = 0$$

But

$$\int_{II'} \frac{dQ}{T} = - \int_{II} \frac{dQ}{T}$$

Hence,

$$\int_I \frac{dQ}{T} = \int_{II} \frac{dQ}{T} \quad \blacksquare$$

Entropy

The second law of thermodynamics enables us to define a state function S , the entropy, which we shall find useful. We owe this possibility to the Clausius's theorem

The corollary in above mentioned section enables us to define a state function, the entropy. It is defined as follows.

Choose an arbitrary fixed state O as reference state. The entropy $S(A)$ for any state A is defined by

$$S(A) \equiv \int_O^A \frac{dQ}{T}$$

where the path of integration is any reversible path joining O to A . Thus the entropy is defined only up to an arbitrary additive constant.* The difference in the entropy of two states, however, is completely defined:

$$S(A) - S(B) = \int_B^A \frac{dQ}{T}$$

where the path of integration is any reversible path jointing B to A . It follows from this formula that in any infinitesimal *reversible* transformation the change in S is given by

$$dS = \frac{dQ}{T}$$

which is an exact differential.

We note the following properties of the entropy:

(a) For an arbitrary transformation,

$$\int_A^B \frac{dQ}{T} \leq S(B) - S(A)$$

The equality holds if the transformation is reversible.

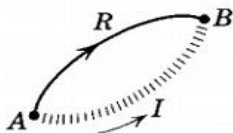


Fig. 1.7 Reversible path R and irreversible path I connecting states A and B .

Proof Let R and I denote respectively any reversible and any irreversible path joining A to B , as shown in Fig. 1.7. For path R the assertion holds by definition of S . Now consider the cyclic transformation made up of I plus the reverse of R . From Clausius' theorem we have

$$\int_I \frac{dQ}{T} - \int_R \frac{dQ}{T} \leq 0$$

or

$$\int_I \frac{dQ}{T} \leq \int_R \frac{dQ}{T} \equiv S(B) - S(A) \quad \blacksquare$$

(b) The entropy of a thermally isolated system never decreases.

Proof A thermally isolated system cannot exchange heat with the external world. Therefore $dQ = 0$ for any transformation. By the previous property we immediately have

$$S(B) - S(A) \geq 0$$

The equality holds if the transformation is reversible. ■

That is, the entropy of an isolated system never decreases and it remains constant during a reversible transformation.

We emphasize the following points:

- The principle that the entropy never decreases applies to the “universe” consisting of a system and its environments. It does not apply to a nonisolated system, whose entropy may increase or decrease.
- Since the entropy is a state function, the entropy change of the system in going from state A to state B is $S_B - S_A$ regardless of the path, which may be reversible or irreversible. For an irreversible path, the entropy of the environment changes, whereas for a reversible path it does not change.
- The entropy difference $S_B - S_A$ is not necessarily equal to the integral $\int_A^B dQ/T$. It is equal to the integral only if the path from A to B is reversible. Otherwise, it is generally *larger* than the integral.

Entropy - a new state variable

Consider a system performing a reversible cycle from initial state i to an intermediate state f then back to i , as shown in the indicator diagram (think of it as a sample of gas). Since the cycle is reversible the equality sign in the Clausius inequality applies giving,

$$\int \frac{\delta q_R}{T} = \int_i^f \frac{\delta q_R}{T} + \int_f^i \frac{\delta q_R}{T} = 0$$

from which

$$\int_{i|\text{path 1}}^f \frac{\delta q_R}{T} = \int_{i|\text{path 2}}^f \frac{\delta q_R}{T}.$$

Because the value of the integral is path-independent, $\frac{\delta q_R}{T}$ is an exact differential of some state function, we call it entropy S :

$$\int_i^f \frac{\delta q_R}{T} = \int_i^f dS = S_f - S_i = \Delta S$$

The Principle of Increasing Entropy

Now reconsider the existence proof for entropy if one part (i to f) is irreversible.

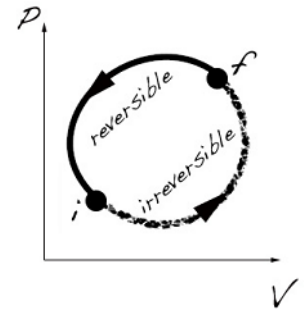
The Clausius inequality leads to $\int_i^f \frac{\delta q}{T} + \int_f^i \frac{\delta q_R}{T} \leq 0$

from which $\int_i^f \frac{\delta q}{T} \leq \int_i^f \frac{\delta q_R}{T} = S_f - S_i$

(note the change in sign when inverting the limits on the integral).

This means that in an irreversible process, the change in entropy, $S_f - S_i$, is greater than the integration of infinitesimal contributions:

$$\begin{aligned} & \text{("heat supplied from the surroundings")} / \\ & \text{("temperature of the contributing part of the surroundings")}. \end{aligned}$$



Changes of entropy of thermally isolated systems in adiabatic processes

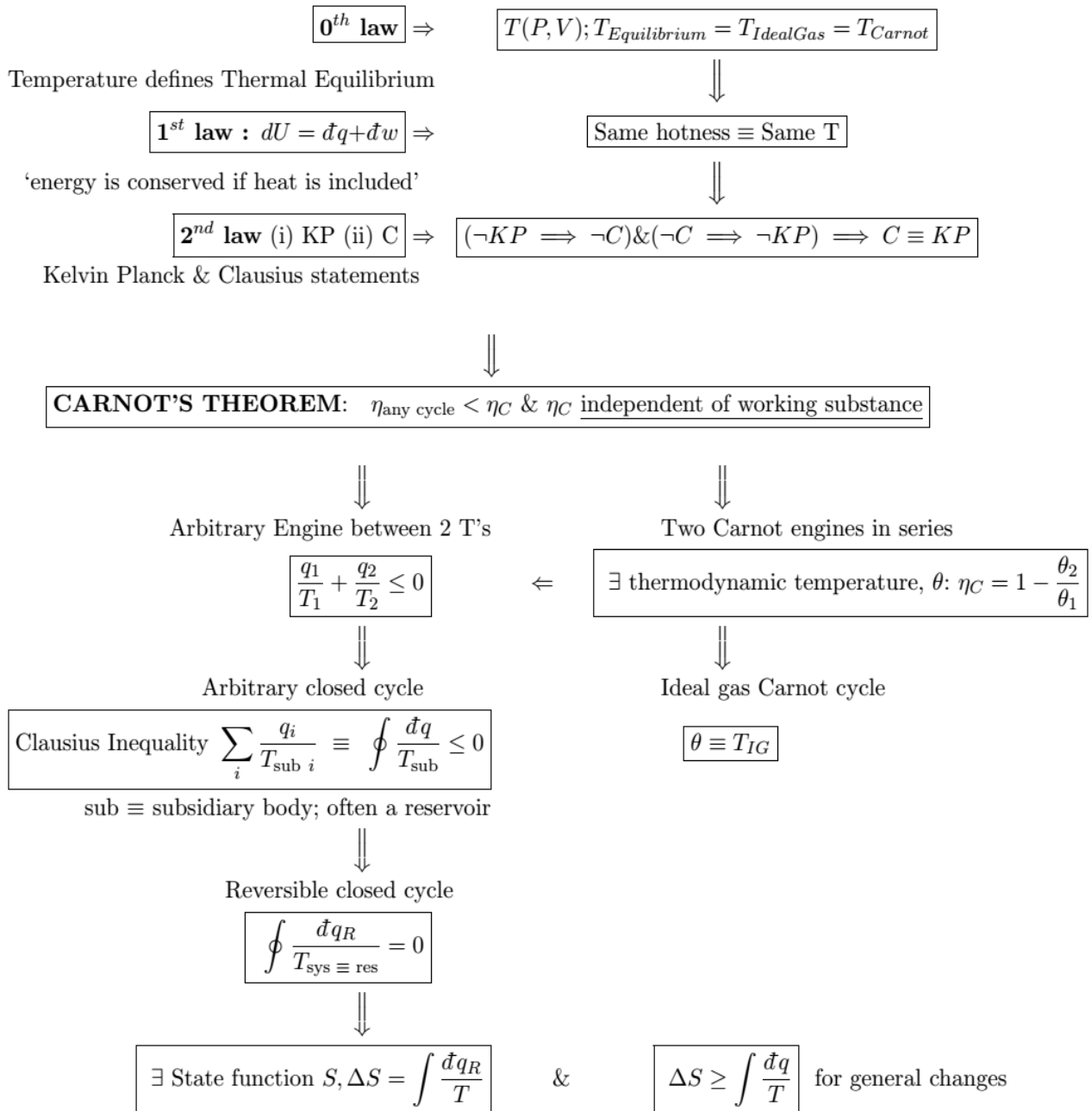
When a system is thermally isolated no heat is exchanged with the surroundings. Then for an irreversible process undergone by a thermally isolated system

$$dS > 0 \quad (\rightarrow S_f - S_i = \Delta S > 0 \text{ for a finite process})$$

It also follows that for a finite **reversible** adiabatic process $\Delta S = 0$.

The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process. This is the principle of increasing entropy.

Summary of 0th, 1st, 2nd Law



An example, "heating water on a stove"

Calculate the change in entropy of water heated from 20°C to 100°C on a stove.

method 1 (lecture 7): Create equivalent reversible process.

$$\Delta S = \int_{T_i}^{T_f} \frac{\delta q_R}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

The change of entropy of the water is the same as in the irreversible process that actually occurs since entropy is a state function and the initial and final equilibrium states match.

method 2: Integrate the central equation:

$$\Delta S = \int_i^f \frac{dU}{T} + \int_i^f \frac{p}{T} dV$$

Need to expand dU and dV in terms of {p,T}.

$$\Delta S = \int_i^f \frac{\left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp}{T} + \int_i^f \frac{p}{T} \left[\left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \right]$$

stove is open to atmosphere so p is constant and dp = 0.

$$\Delta S = \int_{T_i}^{T_f} \frac{\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial(U+pV)}{\partial T}\right)_p}{T} dT = \int_{T_i}^{T_f} \frac{\left(\frac{\partial H}{\partial T}\right)_p}{T} dT$$

method 3: Use enthalpy for constant pressure process:

$$dH = dU + pdV + Vdp = (TdS - pdV) + pdV + Vdp = TdS + Vdp$$

$$\Rightarrow \boxed{dH = TdS + Vdp}$$

and integrate with p = const to get

$$\int_{p=\text{const}} dS = \int_{p=\text{const}} \frac{dH}{T}$$

Writing $H = H(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp.$$

Along the path p = const, dp = 0 and $dH|_p = C_p dT$

$$\Rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT \quad \text{as found previously.}$$

Entropy change in the universe: a hint of the Third Law

For heating water from T to $T + \Delta T$

$$\Delta S_{water} = C_P \ln\left(\frac{T + \Delta T}{T}\right)$$

$$\Delta S_{surr} = C_P \frac{\Delta T}{T}$$

Defining $x = \frac{\Delta T}{T}$, the entropy change of the universe is:

$$\Delta S_{total} = [x - \ln(1 + x)] C_P$$

The function $f(x) = x - \ln(1 + x)$ is ALWAYS positive for $x > -1$. Entropy always increases for positive T .

Another example, "electrical work"

Consider emf \mathcal{E} driving current I through resistor R in an adiabatic box. The power delivered is $\mathcal{E}I = I^2R$. No heat or mechanical work input.

$$1^{st} \text{ law: } \quad \Delta U = I^2R\Delta t$$

Electrical work is dissipated irreversibly as heat: $\Delta U = C_V\Delta T|_V$
The change in temperature is then:

$$I^2R\Delta t = \int_{T_i}^{T_f} C_V dT = C_V\Delta T \quad \Rightarrow \quad \Delta T = I^2R\Delta t / C_V$$

What is the change of entropy?

The change in temperature:

$$\Delta T = I^2R\Delta t / C_V$$

Use method 2 Central Equation for constant V process $dV = 0$

$$dS = dU/T \Rightarrow dS = C_V dT/T \Rightarrow \Delta S = \int_{T_i}^{T_i+\Delta T} \frac{C_V}{T} dT$$

Use method 1 Equivalent Reversible Process.

$$\Delta S = \int_{T_i}^{T_i+\Delta T} dq_R/T = \int_{T_i}^{T_i+\Delta T} C_v dT/T$$

$$\Delta S = C_v \ln \left[1 + \frac{I^2 R \Delta t}{T_i C_v} \right]$$

again, that nagging problem of infinite negative entropy at T=0.

Romantic Poets on Entropy and Measurement

*How do I love thee? Let me count the ways.
I love thee to the depth and breadth and height*

...
Elizabeth Barrett Browning (1806 - 1861)



c/f Wordsworth

"I've measured it from side to side: 'Tis three feet long, and two feet wide."

Entropy is Counting things

Planck, "The logarithmic connection between entropy and probability was first stated by Ludwig Boltzmann in his kinetic theory of gases"



"The calculus of probabilities teaches us precisely this: any non-uniform distribution, unlikely as it may be, is not strictly speaking impossible."

Thermodynamics and Statistical Mechanics

- Thermodynamics: total entropy of an isolated system must increase.
- Statistical Physics: transform to more probable state.
- This suggests there is a relationship between probability and entropy.

$$S = k \ln \Omega$$

(Use Ω to avoid confusion with work)

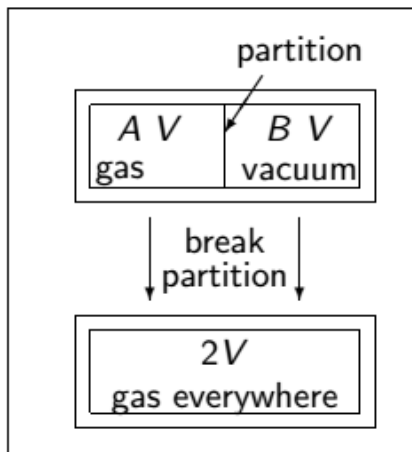
e.g. Maxwell-Boltzmann distribution,

e.g. Quantum wavefunction,

High entropy states of matter exist because of the existence of arrangements of atoms which have never, and will never occur.

Entropy, Counting, and Probability

Consider the Joule (free) expansion of N gas atoms.



When the partition is removed, all gas in A

Prob. that one atom is in A: $\frac{1}{2}$.

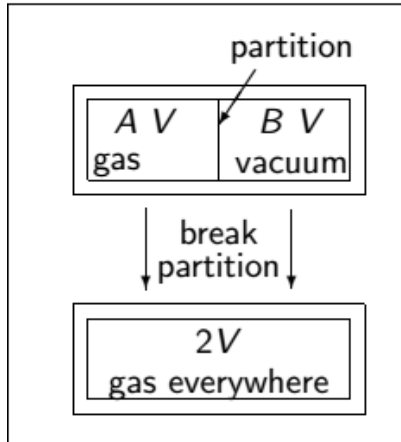
Prob. that all atoms are in A: $\frac{1}{2^N}$.

Prob. that 50% atoms are in A: ${}^N C_{N/2} \times \frac{1}{2^N}$.

We observe the state with most options.

We observe the state with highest entropy?

A hint of where the log comes from



Number of possible states with all particles

...

in A: $\Omega(N, V, E)$.

in A or B: $\Omega(N, 2V, E)$.

If all the accessible microstates are equally likely.

$$\frac{\Omega_A}{\Omega_{A+B}} = \frac{\Omega(N, V, E)}{\Omega(N, 2V, E)} = \left(\frac{1}{2}\right)^N$$

Suppose that there is a relationship between the entropy and Ω . $S = f(\Omega)$.

Entropy is additive $S = S_1 + S_2$, but permutations grow as product $\Omega = \Omega_1 \Omega_2$.

$$f(\Omega_1 \Omega_2) = f(\Omega_1) + f(\Omega_2)$$

Thus f must be a logarithm,

Statistical entropy

Definition of statistical entropy for fixed E

$$S = k_B \ln(\Omega)$$

k_B , Boltzmann's Constant, relates micro- and macro- worlds.

Caveat: Lots of subtle assumptions sneaked in here: We'll do it properly in Stat.Mech..

LECTURE 9: CYCLES

Content of Lecture 9

9.1. Rankine

9.2. Brayton

9.3. Refrigeration

9.1. Rankine

Large electric power plants typically utilize a vapor power cycle. Regardless of the heat source, be it nuclear or combustion of coal, oil, natural gas, wood chips, etc., the remaining details of these plants are similar. Typically a pure working fluid, usually water, is circulated through a cycle, and that fluid trades heat and work with its surroundings. We sketch a typical power plant cycle for electricity generation in Fig. 9.1. The ideal Rankine cycle was first described in 1859 by William John Macquorn Rankine long after the steam engine was in wide usage. This cycle has the following steps

- 1 → 2: isentropic compression in a pump,
- 2 → 3: isobaric heating in a boiler,
- 3 → 4: isentropic expansion in a turbine, and
- 4 → 1: isobaric cooling in a condenser.

Two variants of the $T - s$ diagram are given in Fig 9.2. The first is more efficient as it has the appearance of a Carnot cycle. However, it is impractical. As it induces liquid water in the turbine, which can damage its blades. So the second is more common.

The thermal efficiency is

$$\eta = \frac{\dot{W}_{net}}{\dot{Q}_H} = \frac{\dot{W}_{turbine} + \dot{W}_{pump}}{\dot{Q}_{boiler}} \quad (9.1)$$

This reduces to

$$\eta = \frac{\dot{m} [h_3 - h_4 + h_1 - h_2]}{\dot{m} h_3 - h_2} = 1 - \frac{h_4 - h_1}{h_3 - h_2} = 1 - \frac{q_{out,condenser}}{q_{in,boiler}} \quad (9.2)$$

Note that because the Rankine cycle is *not* a Carnot cycle, we have $q_{out,condenser}/q_{in,boiler} \neq T_1/T_3$.

Power plants are sometimes characterized by their

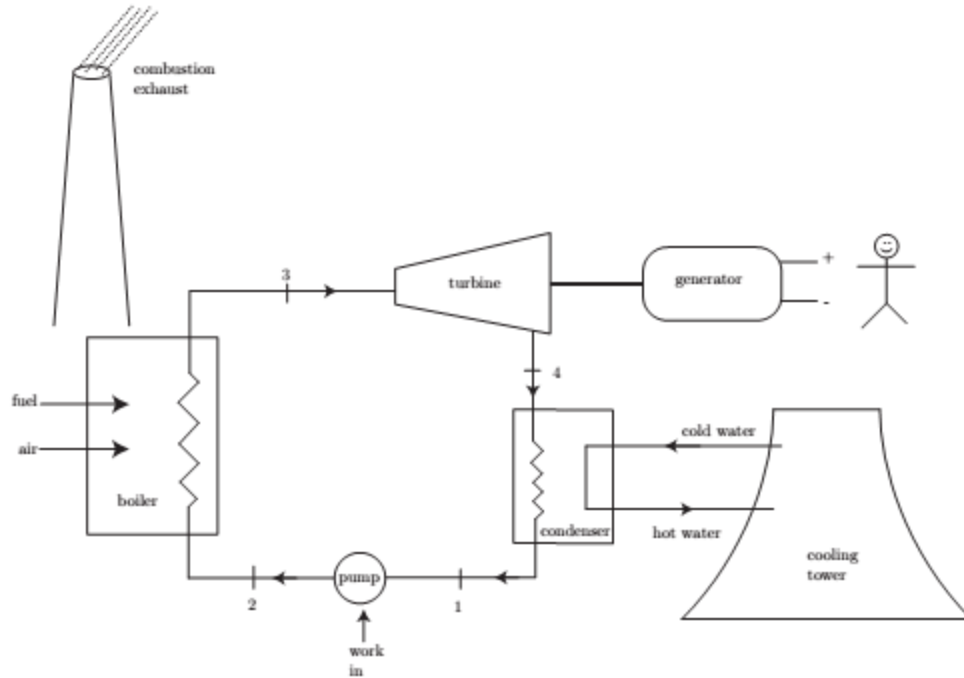


Fig 9.1. Rankine cycle schematic

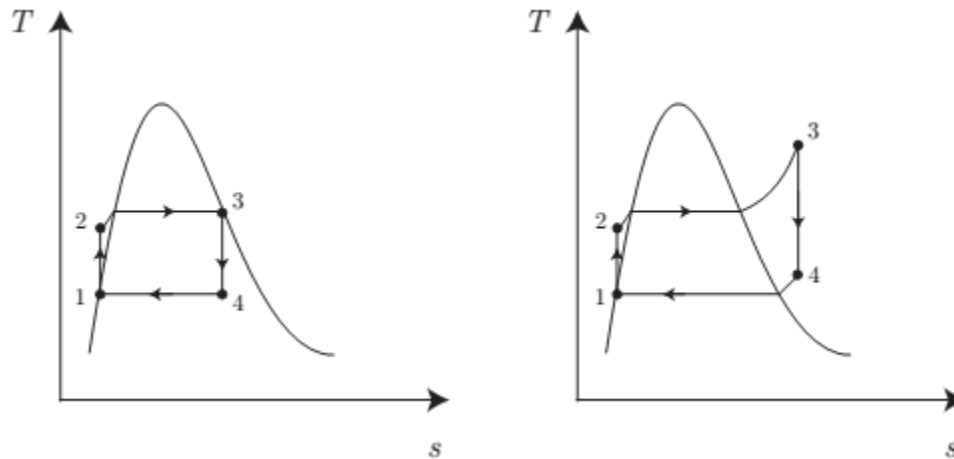


Fig 9.2. T – s for two Rankine cycles

- BACK WORK RATIO: *bwr*, the ratio of pump work to turbine work.

Here,

$$bwr = \frac{|\text{pump work}|}{|\text{turbine work}|} = \frac{h_2 - h_1}{h_3 - h_4} \quad (9.3)$$

We model the pump work as an isentropic process. The Gibbs equation gives

$$Tds = dh - vdP.$$

If $ds = 0$, we have

$$dh = vdP \quad (9.4)$$

Thus, for the pump

$$h_2 - h_1 = v (P_2 - P_1) , \quad (9.5)$$

since v is nearly constant, so the integration is simple.

It might be tempting to make the Rankine cycle into a Carnot cycle as sketched in Fig 9.3. However, it is practically difficult to build a pump to handle two-phase mixtures.

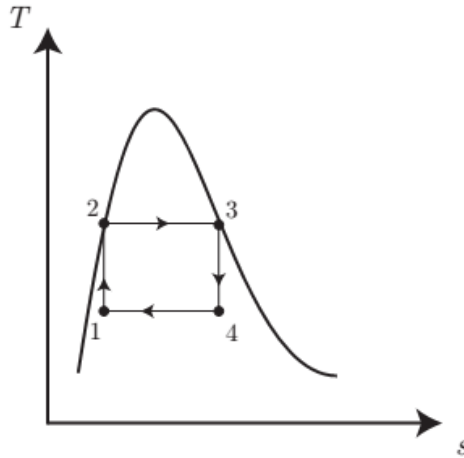


Fig 9.3. Rankine-Carnot cycle

The gas phase can seriously damage the pump. Some features which could be desirable for a Rankine cycle include

- high power output: One can enhance this by raising the fluid to a high temperature during the combustion process or by pumping the fluid to a high pressure. Both strategies soon run into material limits; turbine blades melt and pipes burst. Another strategy is to lower the condenser pressure, which means that one must maintain a vacuum, which can be difficult.
- high thermal efficiency: The key design strategy here lies in 1) increasing component efficiencies, and 2) rendering the overall cycle as much like a Carnot cycle as is feasible. Modern power plants have had revolutionary increases in overall thermal efficiency because of enhancements which make the process more Carnot-like.

There are some important loss mechanisms in the Rankine cycle which inhibit efficiency. They include

- Turbine losses: These are the major losses. To avoid these losses requires detailed consideration of fluid mechanics, material science, and heat transfer and is beyond the scope of classical thermodynamics. Thermodynamics develops broad measures of turbine efficiency such as $\eta_{turbine} = (h_3 - h_4)/(h_3 - h_{4s})$.
- Pump losses: Again, fluid mechanics, machine design, and material science are required to analyze how to actually avoid these losses. Thermodynamics characterizes them by pump efficiency, $\eta_{pump} = (h_{2s} - h_1)/(h_2 - h_1)$.

- Heat transfer losses from components.
- Pressure drop in pipes.
- Incomplete fuel combustion.
- Pollution removal devices.
- Loss of heat to surroundings in the condenser.

One simple design strategy to make the system more Carnot-like is to use

- REHEAT: a design strategy in which steam is extracted from the turbine before it is fully expanded, then sent to the boiler again, and re-expanded through the remainder of the turbine.

This has the effect of making the system more like a Carnot cycle. A schematic and $T - s$ diagram for the Rankine cycle with reheat is given in Fig 9.4

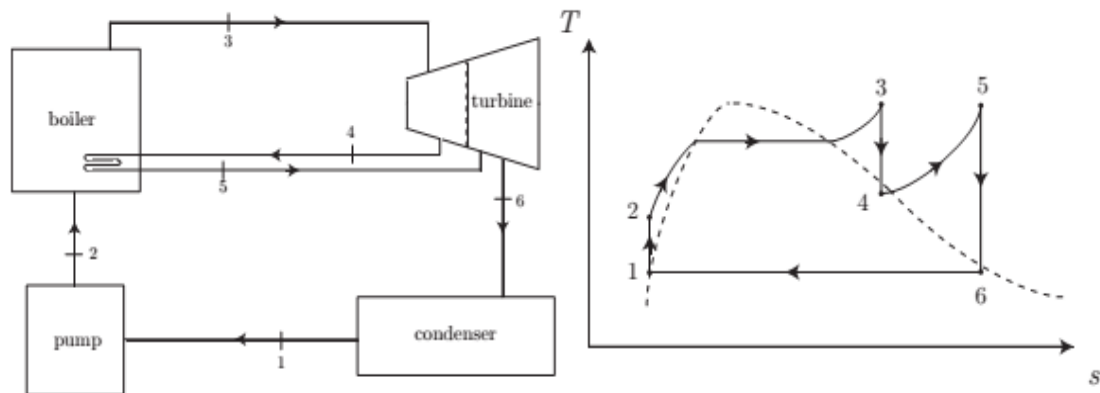


Fig 9.4. Rankine cycle with reheat schematic and $T - s$ diagram.

9.2. Brayton

Gas turbine power plants, both stationary and those for jet engines operate on the Brayton cycle. The cycle is named after George Brayton, an American mechanical engineer. Brayton is depicted in Fig 9.5. It has many similarities to the Rankine cycle. A schematic and $T - s$ and $P - v$ diagrams for the Brayton cycle for a power plant is illustrated in Fig 9.6.

The Brayton cycle is outlined as follows:

- $1 \rightarrow 2$: isentropic compression (W added),
- $2 \rightarrow 3$: isobaric heat addition (Q added),

Fig 9.5. George Brayton (1830-1892), American mechanical engineer from Exeter.

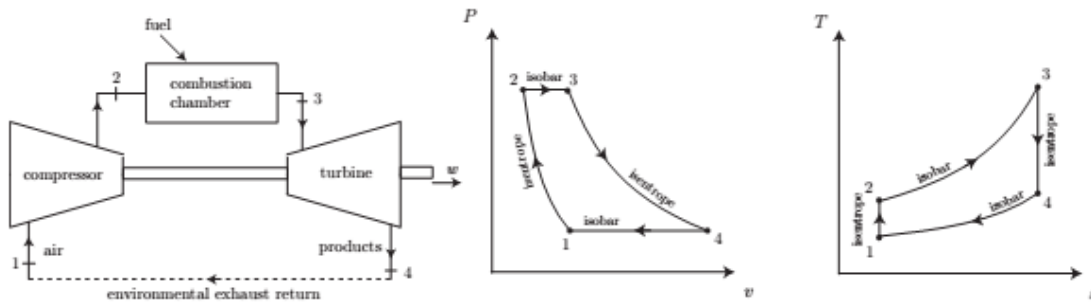


Fig 9.6. Schematic of Brayton cycle along with $P-v$ and $T-s$ diagrams

- 3 → 4: isentropic expansion (W extracted), and
- 4 → 1: isobaric heat rejection (passive exhaust).

Note, the work extracted is greater than the work added, i.e.

$$|h_3 - h_4| > |h_2 - h_1| \quad (9.6)$$

Often we will be dealing with a CPIG, in which case $\Delta h = c_p \Delta T$. If so, then we can say

$$|T_3 - T_4| > |T_2 - T_1| \quad (9.7)$$

Another reason for this is that

- *isobars diverge in $T-s$ space as s increases.*

This is easy to understand when we recall the Gibbs equation, $Tds = dh - vdP$. On an isobar, we have $dP = 0$, so

$$Tds = dh, \quad \text{on isobar,} \quad (9.8)$$

$$Tds = c_p dT, \quad \text{if IG,} \quad (9.9)$$

$$\left(\frac{\partial T}{\partial s} \right)_p = \frac{T}{c_p} \quad (9.10)$$

Since at a given s , a high T isobar sits above a low T isobar, and the slope of the isobar is proportional to T , it is easily seen how they must diverge. This is illustrated in Fig 9.7.

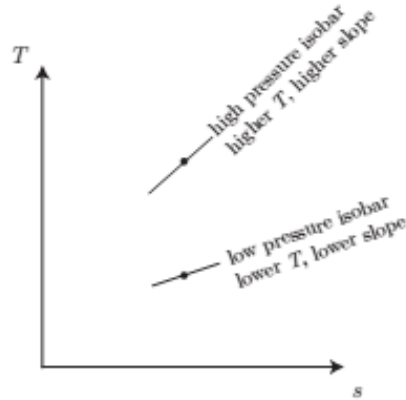


Fig 9.7. Sketch of diverging isobars for CPIG in $T - s$ plane

There are other classes of Brayton cycle plants. Schematics are shown next.

- *Turbojet.* In the turbojet, the kinetic energy of the fluid becomes important at two points in the cycle. In the compression, the freestream fluid, entering the compressor at the flight speed, has its pressure increased by the so-called “ram effect” where the fluid decelerates. Second, the point of the turbojet is to produce thrust, which requires a significant exit velocity. The turbine work is used solely to power the compressor.

See Fig 9.8

- *Turbojet with afterburners.* We are limited in an ordinary turbojet by how much heat can be added to the flow in combustion because such flow typically must pass through the turbine blades, which suffer material degradation if the fluid is too hot. However, we can add heat *after* the turbine in so-called *afterburners*. This releases chemical energy, turns it into fluid potential energy in the form of high P/ρ , and then converts to kinetic energy in the nozzle. This can enhance the thrust, though it can be shown it is not particularly efficient. A sketch is given in Fig 9.9.
- *Ramjet.* A ramjet is much simpler. The compressor and turbine are removed. We rely on the ram compression effect alone for compression and convert as much of the thermal energy as possible into mechanical energy used to generate thrust force. A sketch is given in Fig 9.10

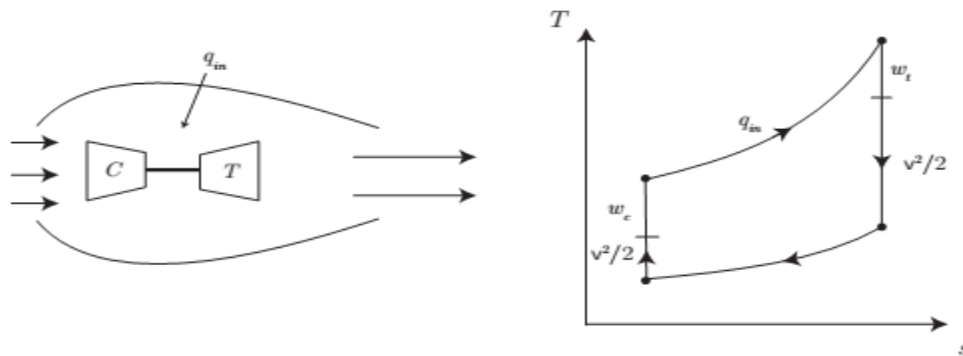


Fig 9.8. Sketch of turbojet schematic and associated $T - s$ plane

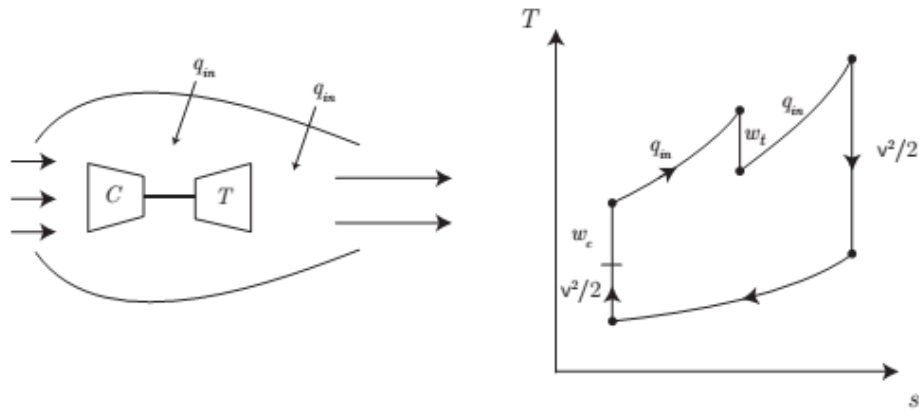


Fig 9.9. Sketch of turbojet with afterburners schematic and associated $T - s$ plane

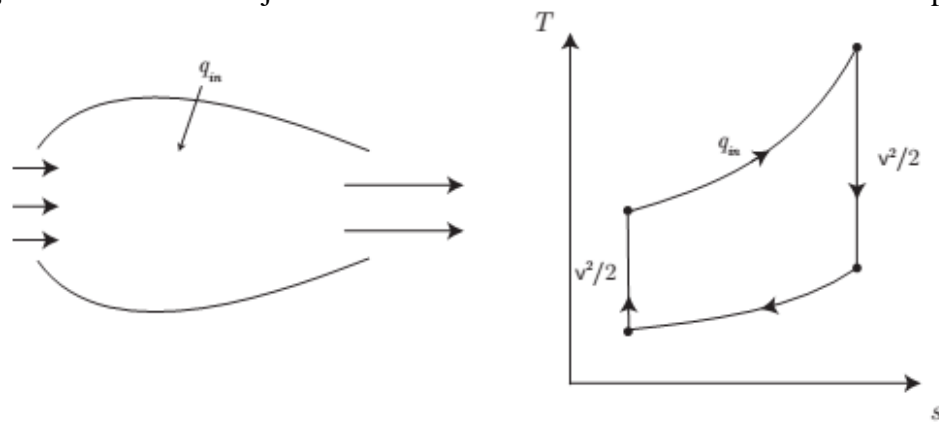


Fig 9.10. Sketch of ramjet schematic and associated $T - s$ plane

Let us consider an

- **AIR STANDARD ANALYSIS:** a common set of assumptions used for idealized cyclic devices.

The air standard make many compromises in order to admit some simple analysis tools to be used to make simple estimates for the performance of a variety of devices. Actual design calculations would have to remedy the many shortcomings. But it is useful for a framework of understanding. We take the air standard to entail

- The working fluid is air. This ignores any effect of the properties of the fuel or any other fluid which is mixed with the air.
- The working fluid is an ideal gas. We will often assume it is a CPIG, but sometimes not.
- We will ignore all details of the combustion process and treat it as a simple heat addition.

Often in cycle analysis, the formal sign convention is ignored. We take the following

- Turbine work: $w_t = h_3 - h_4$. Here, the sign convention is maintained.
- Compressor work: $w_c = h_2 - h_1$. Here, the sign convention is ignored.
- Heat addition: $q_{in} = h_3 - h_2$. Here, the sign convention is maintained.
- Heat rejection: $q_{out} = h_4 - h_1$. Here, the sign convention is ignored.

The cycle efficiency is

$$\eta = \frac{\underbrace{h_3 - h_4}_{\text{turbine}} - \underbrace{h_2 - h_1}_{\text{compressor}}}{\underbrace{h_3 - h_2}_{\text{combustor}}} \quad (9.11)$$

Rearranging (9.11), we can also say

$$\eta = 1 - \frac{\underbrace{h_4 - h_1}_{\text{heat rejected}}}{\underbrace{h_3 - h_2}_{\text{heat added}}} \quad (9.12)$$

The back work ratio, bwr , is

$$bwr = \frac{w_c}{w_t} = \frac{h_2 - h_1}{h_3 - h_4} \quad (9.13)$$

Note the back work ratio will be seen to be much larger for gas phase power cycles than it was for vapor cycles. For Brayton cycles, we may see $bwr \sim 0.4$. For Rankine cycles, we usually see $bwr \sim 0.01$

Now, if we have a CPIG, we get $\Delta h = \int c_p dT$ to reduce to $\Delta h = c_p \Delta T$. So Eq. (9.11) reduces to

$$\eta = \frac{c_p \frac{T_3 - T_4}{T_3 - T_2} - c_p \frac{T_2 - T_1}{T_3 - T_2}}{c_p \frac{T_3 - T_4}{T_3 - T_2} - c_p \frac{T_2 - T_1}{T_3 - T_2}} = \frac{T_3 - T_4 - T_2 + T_1}{T_3 - T_2} = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_1}{T_2} \left(\frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1} \right) \quad (9.14)$$

Now, $1 \rightarrow 2$ is isentropic. Recall for a CPIG which is isentropic that $T_2/T_1 = (P_2/P_1)^{(k-1)/k}$. We also have $3 \rightarrow 4$ to be isentropic, so $T_3/T_4 = (P_3/P_4)^{(k-1)/k}$. But $P_2 = P_3$ and $P_1 = P_4$. So

$$\frac{T_2}{T_1} = \frac{T_3}{T_4}, \quad (9.15)$$

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \quad (9.16)$$

So

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}}} \quad (9.17)$$

A plot of η versus the pressure ratio P_2/P_1 for $k = 7/5$ is plotted in Fig 9.11. As the pressure ratio P_2/P_1 rises, the thermal efficiency increases for the Brayton cycle. It still is much less than unity for $P_2/P_1 = 20$. To approach unity, high pressure ratios are needed; $\eta = 0.9$ requires $P_2/P_1 \sim 3200$. Note in terms of temperature, the efficiency looks like that for a Carnot cycle, but it is not. The highest temperature in the Brayton cycle is T_3 , so the equivalent Carnot efficiency would be $1 - T_1/T_3$.

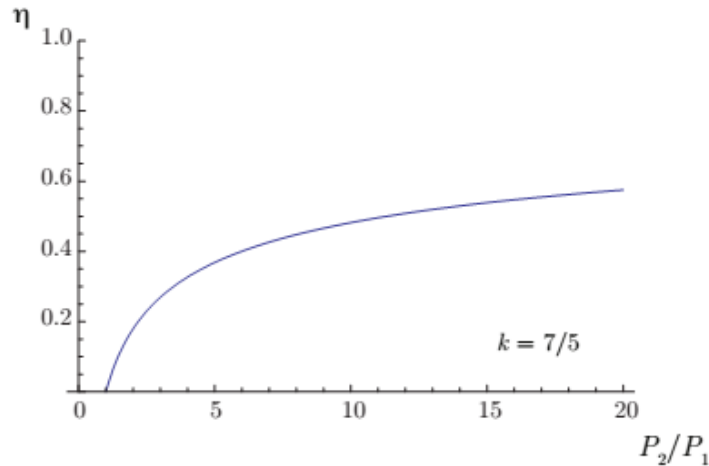


Fig 9.11. Thermal efficiency versus pressure ratio for air standard Brayton cycle, $k = 7/5$

9.3. Refrigeration

A simple way to think of a refrigerator is a cyclic heat engine operating in reverse. Rather than extracting work from heat transfer from a high temperature source and rejecting heat to a low temperature source, the refrigerator takes a work input to move heat from a low temperature source to a high temperature source.

A common refrigerator is based on a vapor-compression cycle. This is a Rankine cycle in reverse. While one could employ a turbine to extract some work, it is often impractical. Instead the high pressure gas is simply irreversibly throttled down to low pressure.

One can outline the vapor-compression refrigeration cycle as follows:

- 1 \rightarrow 2: isentropic compression
- 2 \rightarrow 3: isobaric heat transfer to high temperature reservoir in condenser,
- 3 \rightarrow 4: adiabatic expansion in throttling valve, and
- 4 \rightarrow 1: isobaric (and often isothermal) heat transfer from a low temperature reservoir to an evaporator.

A schematic and associated $T - s$ diagram for the vapor-compression refrigeration cycle is shown in Fig 9.12. One goal in design of refrigerators is low work input. There are two main strategies in this:

- Design the best refrigerator to minimize \dot{Q}_{in} . This really means reducing the conductive heat flux through the refrigerator walls. One can use a highly insulating material. One

can also use thick walls. Thick walls will reduce available space for storage however. This is an example of a design trade-off.

- For a given \dot{Q}_{in} , design the optimal thermodynamic cycle to minimize the work necessary to achieve the goal. In practice, this means making the topology of the cycle as much as possible resemble that of a Carnot refrigerator. Our vapor compression refrigeration cycle is actually close to a Carnot cycle.

The efficiency does not make sense for a refrigerator as $0 \leq \eta \leq 1$. Instead, much as our earlier analysis for Carnot refrigerators, a coefficient of performance, β , is defined as

$$\beta = \frac{\text{what one wants}}{\text{what one pays for}} = \frac{q_L}{w_c} \quad (9.18)$$

Note that a heat pump is effectively the same as a refrigerator, except one desires q_H rather than q_L . So for a heat pump, the coefficient of performance, β' , is defined as

$$\beta' = \frac{q_H}{w_c} \quad (9.19)$$

The University of Notre Dame Power Plant also serves as a generator of chilled water for air conditioning campus buildings. This is effectively a refrigerator on a grand scale, though we omit details of the actual system here. A photograph of one of the campus chillers is shown in Fig. 9.12



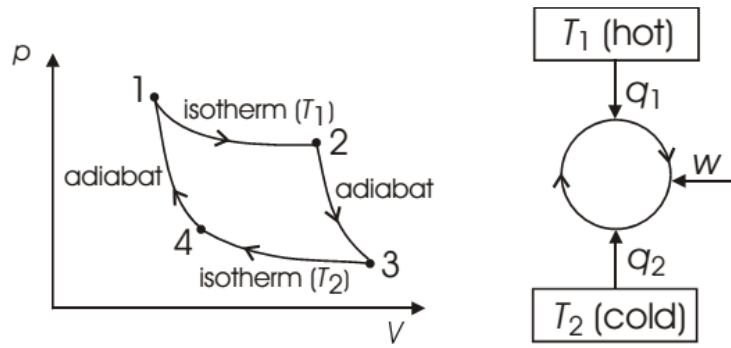
Fig 9.12. Chiller in the University of Notre Dame power plant, 14 June 2010

NOTES

The Carnot Cycle

- a typical heat engine

All paths are reversible



- 1 → 2 isothermal expansion at T_1 (hot) $\Delta U = q_1 + w_1$
- 2 → 3 adiabatic expansion ($q = 0$) $\Delta U = w'_1$
- 3 → 4 isothermal compression at T_2 (cold) $\Delta U = q_2 + w_2$
- 4 → 1 adiabatic compression ($q = 0$) $\Delta U = w'_2$

$$\text{Efficiency} = \frac{\text{work output to surroundings}}{\text{heat in at } T_1 \text{ (hot)}} = \frac{-(w_1 + w'_1 + w_2 + w'_2)}{q_1}$$

$$1^{\text{st}} \text{ Law} \Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -(w_1 + w'_1 + w_2 + w'_2)$$

$$\therefore \text{Efficiency} \equiv \varepsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

$$\text{Kelvin: } q_2 < 0 \rightarrow \text{Efficiency} \equiv \varepsilon < 1 \text{ (< 100\%)}$$

$$-w = q_1 \varepsilon = \text{work output}$$

Note: if cycle were run in reverse, then $q_1 < 0$, $q_2 > 0$, $w > 0$.
It's a refrigerator!

Carnot cycle for an ideal gas

$$1 \rightarrow 2 \quad \Delta U = 0; \quad q_1 = -w_1 = \int_1^2 p dV = RT_1 \ln \left(\frac{V_2}{V_1} \right)$$

$$2 \rightarrow 3 \quad q = 0; \quad w'_1 = C_V (T_2 - T_1)$$

$$\text{Rev. adiabat} \quad \Rightarrow \quad \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$3 \rightarrow 4 \quad \Delta U = 0; \quad q_2 = -w_2 = \int_3^4 p dV = R T_2 \ln\left(\frac{V_4}{V_3}\right)$$

$$4 \rightarrow 1 \quad q = 0; \quad w'_2 = C_V (T_1 - T_2)$$

$$\text{Rev. adiabat} \quad \Rightarrow \quad \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1}$$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)}$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \Rightarrow \frac{q_2}{q_1} = -\frac{T_2}{T_1}$$

$$\text{or} \quad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq_{\text{rev}}}{T} = 0$$

links heat engines to mathematical statement

$$\text{Efficiency} \quad \boxed{\varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}} \quad \rightarrow 100\% \text{ as } T_2 \rightarrow 0 \text{ K}$$

For a heat engine (Kelvin): $q_1 > 0, w < 0, T_2 < T_1$

$$\text{Total work out} = -w = \varepsilon q_1 = \left(\frac{T_1 - T_2}{T_1}\right) q_1 \Rightarrow (-w) < q_1$$

Note: In the limit $T_2 \rightarrow 0 \text{ K}$, $(-w) \rightarrow q_1$, and $\varepsilon \rightarrow 100\%$ conversion of heat into work. 3rd law will state that we can't reach this limit!

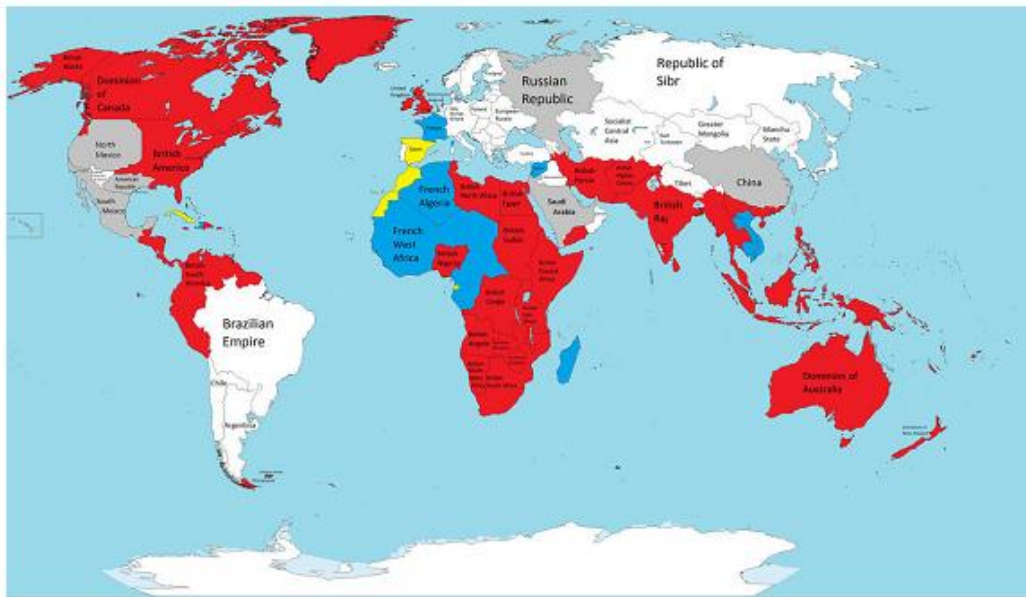
For a refrigerator (Clausius): $q_2 > 0, w > 0, T_2 < T_1$

$$\text{Total work in} = w = \left(\frac{T_2 - T_1}{T_1}\right) q_1$$

$$\text{But } \frac{q_1}{T_1} = -\frac{q_2}{T_2} \Rightarrow w = \left(\frac{T_1 - T_2}{T_2} \right) q_2$$

Note: In the limit $T_2 \rightarrow 0 \text{ K}$, $w \rightarrow \infty$. This means it takes an infinite amount of work to extract heat from a reservoir at $0 \text{ K} \Rightarrow 0 \text{ K}$ cannot be reached (3rd law).

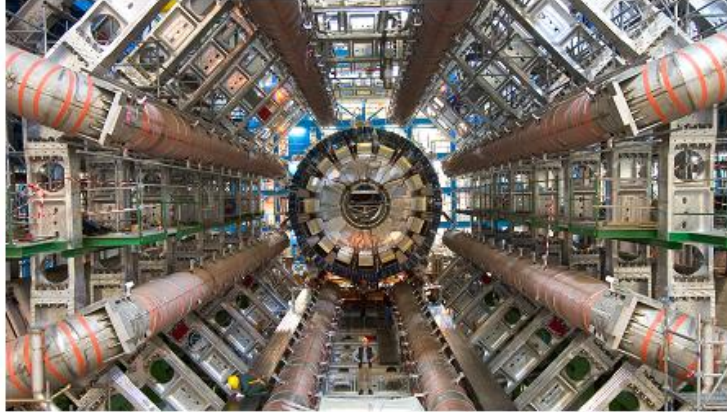
British Empire - built by thermodynamics



Can define ideal efficiency via of the temperatures of the reservoirs. Efficiency is always *defined* by (what you want out)/(what you put in). So

- For an *Engine* you put heat in and get work out.
- For a *Refrigerator*, put work in, take heat out (from the cold region).
- For a *Heat Pump* put work in, get heat out (into the warm region).

World's biggest Fridge Magnet?



CERN uses about 1/3rd as much energy as Geneva. Of which..

LHC cryogenics 27.5 MW

LHC experiments 22 MW

Heat Pump and Refrigerator: same device, different purpose.

Refrigerator, coefficient of performance η^R :

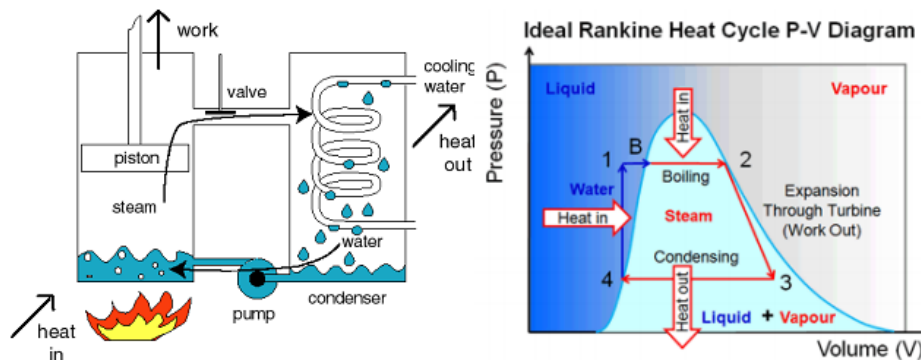
$$\eta^R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} \quad \eta_C^R = \frac{T_2}{T_1 - T_2}$$

Heat pump, heat pump efficiency η^{HP} :

$$\eta^{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} \quad \eta_C^{HP} = \frac{T_1}{T_1 - T_2}$$

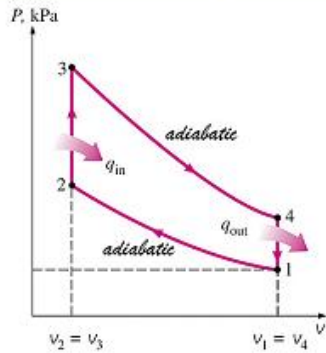
QUESTION : Explain (using the engineering definition of the efficiency of a heat pump) why heat pumps are best used to produce domestic **background** heating.

Steam Engine

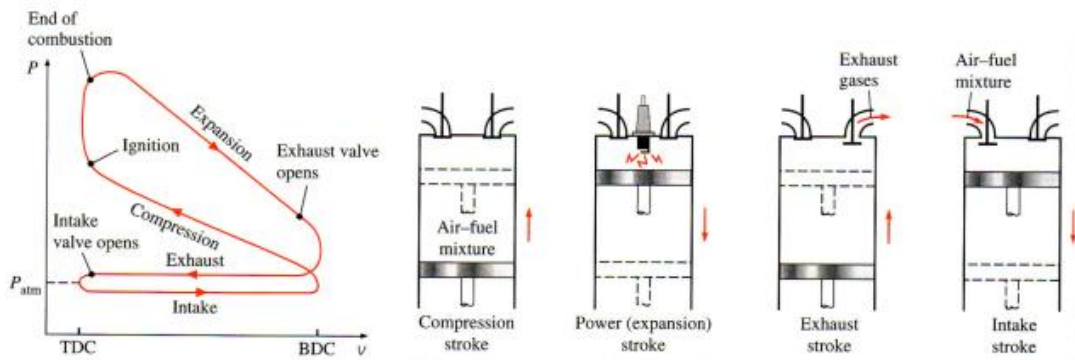


Steam engine works with a liquid+vapour mixture, which combines big volume expansion (steam) and easy to pump/heat (water)

The Otto cycle: a “nearly real” engine



- Simplified two-stroke petrol engine.
- Assume single working substance with “external” heating
- Two adiabats and two isochores.
- Heat exchange takes place in the isochoric processes (i.e. not isothermal)



- 1 a – b: reversible adiabatic compression (Piston moves in)

$$T_a V_1^{\gamma-1} = T_b V_2^{\gamma-1}$$

- 2 b – c: heat added (actually, combustion) at constant volume.

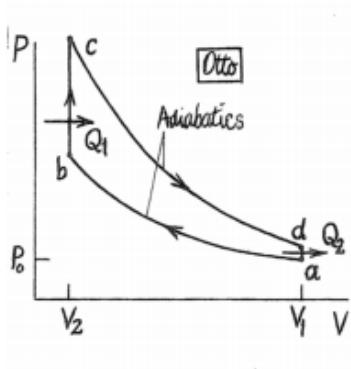
$$Q_1 = C_V(T_c - T_b)$$

- 3 c – d: reversible adiabatic expansion (the “power stroke”: piston moves out)

$$T_d V_1^{\gamma-1} = T_c V_2^{\gamma-1}$$

- 4 d – a: heat rejected (actually exhaust) at constant volume.

$$Q_2 = C_V(T_d - T_a)$$



Otto efficiency

The efficiency η for the engine has to be specified in terms of Q_1 and Q_2 . From (4) and (2):

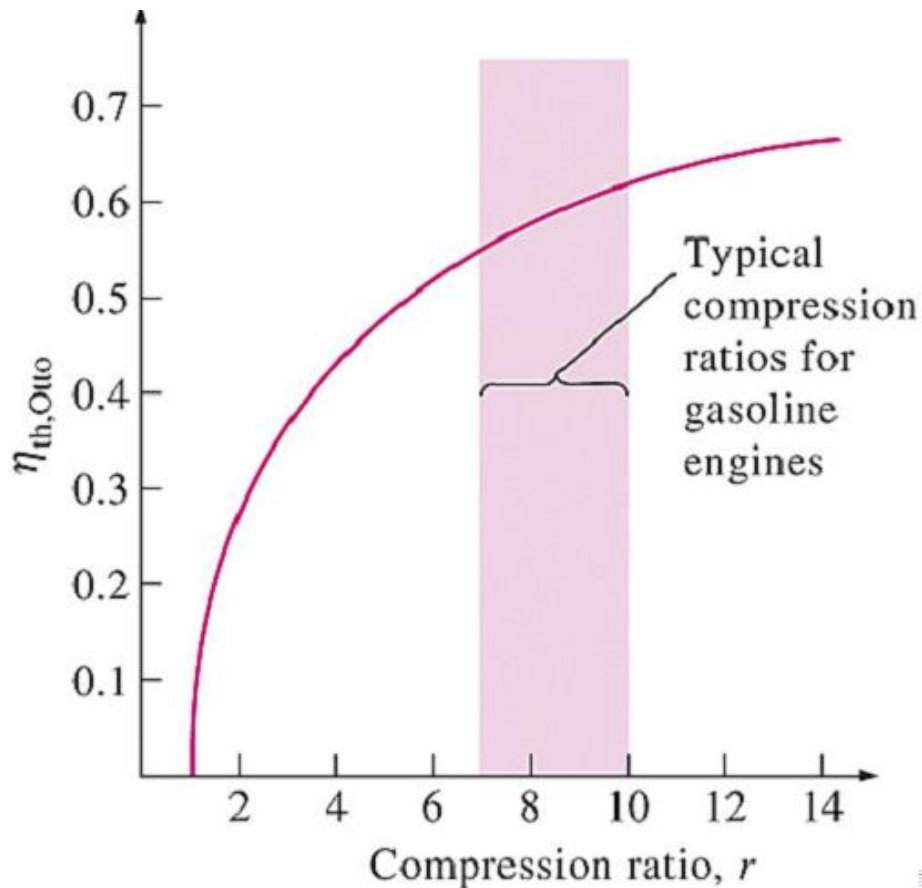
$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_d - T_a}{T_c - T_b}$$

To get more insight into the factors controlling efficiency use (1) and (3) to give:

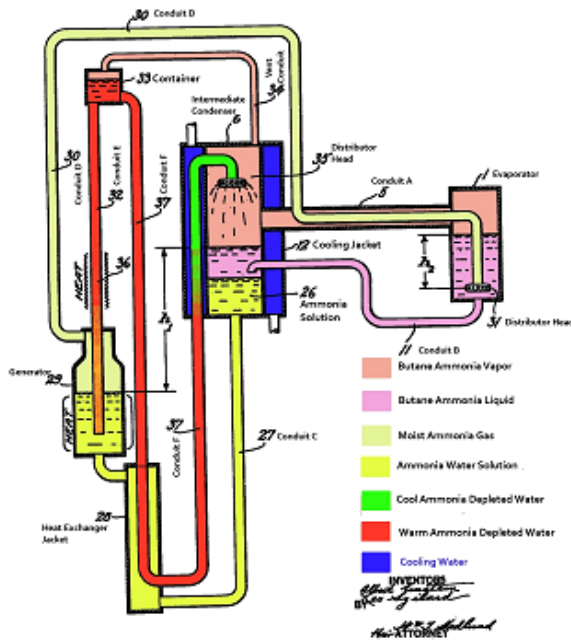
$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r_c^{\gamma-1}}$$

where $r_c = V_1/V_2$ is called the compression ratio. If r_c is ~ 5 , $\eta \sim 50\%$. Other considerations mean real engines are well below this.

Four-stroke engines have exhaust and intake stages between da and ab .



Fridge without electricity



1930

Courtesy UCSD

Einstein and Szilard patent a fridge.
 No moving parts.
 No work input.
 Butane as working fluid.
 Ammonia/water mixture pump.
 Energy supplied as heat to
 Ammonia/water

<https://www.youtube.com/watch?v=aeW76Jequag>

<http://www.bbc.co.uk/newsbeat/article/37306334/this-invention-by-a-british-student-could-save-millions-of-lives-across-the-world>

LECTURE 10: MATHEMATICAL FOUNDATIONS

Content of Lecture 10

- 10.1. Maxwell relations
- 10.2. Functions of two independent variables
- 10.3. Legendre transformations
- 10.4. Specific heat capacity
- 10.5. The first law and coordinate transformations
- 10.6. The van der Waals gas
- 10.7. Adiabatic sound speed
- 10.8. Introduction to compressible flow
 - 10.8.1. Acoustics
 - 10.8.2. Steady flow with area change

This lecture will serve as an introduction to some of the mathematical underpinning of the thermodynamics. Though the practicality is not immediately obvious to all, this analysis is a necessary precursor for building many useful and standard theories. Important among those are theories to describe chemical reactions, which have widespread application in a variety of engineering scenarios, including combustion, materials processing, and pollution control.

10.1. Maxwell relations

We begin with a discussion of the so-called Maxwell¹ relations, named after the great nineteenth century physicist, Jame Clerk Maxwell, shown in Fig 10.1.

¹J. C. Maxwell, 1871, *Theory of Heat*, reprinted 2001, Dover, Mineola, New York, p. 169.



Fig 10.1. Jame Clerk Maxwell (1831-1879), Scottish physicist

Recall that if $z = z(x, y)$, we have

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \quad (10.1)$$

Recall if $dz = M(x, y)dx + N(x, y)dy$, the requirement for an exact differential is

$$\left(\frac{\partial z}{\partial x} \right)_y = M, \quad \left(\frac{\partial z}{\partial y} \right)_x = N, \quad (10.2)$$

$$\frac{\partial^2 z}{\partial y \partial x} = \left(\frac{\partial M}{\partial y} \right)_x, \quad \frac{\partial^2 z}{\partial x \partial y} = \left(\frac{\partial N}{\partial x} \right)_y \quad (10.3)$$

Because order of differentiation does not matter for functions which are continuous and differentiable, we must have for exact differentials

$$\left(\frac{\partial N}{\partial x} \right)_y = \left(\frac{\partial M}{\partial y} \right)_x \quad (10.4)$$

Compare the Gibbs equation to our equation for dz

$$du = -Pdv + Tds, \quad (10.5)$$

$$dz = Mdx + Ndy \quad (10.6)$$

We see the equivalences

$$z \rightarrow u, \quad x \rightarrow v, \quad y \rightarrow s, \quad M \rightarrow -P, \quad N \rightarrow T \quad (10.7)$$

and just as one expects $z = z(x, y)$, one then expects the natural, or *canonical* form of

$$u = u(v, s) \quad (10.8)$$

Application of Eq.(10.4) to the Gibbs equation gives then

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v \quad (10.9)$$

Equation (10.9) is known as a *Maxwell relation*. Moreover, specialization of Eq. (10.2) to the Gibbs equation gives

$$\left(\frac{\partial u}{\partial v} \right)_s = -P, \quad \left(\frac{\partial u}{\partial s} \right)_v = T \quad (10.10)$$

10.2. Functions of two independent variables

Consider a general implicit function linking three variables, x, y, z :

$$f(x, y, z) = 0 \quad (10.11)$$

In $x - y - z$ space, this will represent a surface. If the function can be inverted, it will be possible to write the explicit forms

$$x = x(y, z), \quad y = y(x, z), \quad z = z(x, y) \quad (10.12)$$

Differentiating the first two of Eqs.(10.12) gives

$$dx = \left(\frac{\partial x}{\partial y} \right)_z dy + \left(\frac{\partial x}{\partial z} \right)_y dz, \quad (10.13)$$

$$dy = \left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \quad (10.14)$$

Now, use Eq.(10.14) to eliminate dy in Eq.(11.13)

$$dx = \left(\frac{\partial x}{\partial y} \right)_z \left[\left(\frac{\partial y}{\partial x} \right)_z dx + \left(\frac{\partial y}{\partial z} \right)_x dz \right] + \left(\frac{\partial x}{\partial z} \right)_y dz, \quad (10.15)$$

$$\left[1 - \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z \right] dx = \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] dz, \quad (10.16)$$

$$0dx + 0dz = \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z - 1 \right] dx + \left[\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y \right] dz \quad (10.17)$$

Since x and z are independent, so are dx and dz , and the coefficients on each in Eq. (10.17) must be zero. Therefore, from the coefficient on dx in Eq. (10.17), we have

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z - 1 = 0, \quad (10.18)$$

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial x} \right)_z = 1, \quad (10.19)$$

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z} \quad (10.20)$$

and also from the coefficient on dz in Eq. (10.17), we have

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x + \left(\frac{\partial x}{\partial z} \right)_y = 0, \quad (10.21)$$

$$\left(\frac{\partial x}{\partial z} \right)_y = - \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x, \quad (10.22)$$

$$\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z = -1 \quad (10.23)$$

If one now divides Eq.(11.13) by a fourth differential, dw , one gets

$$\frac{dx}{dw} = \left(\frac{\partial x}{\partial y} \right)_z \frac{dy}{dw} + \left(\frac{\partial x}{\partial z} \right)_y \frac{dz}{dw} \quad (10.24)$$

Demanding that z be held constant in Eq.(11.24) gives

$$\left(\frac{\partial x}{\partial w} \right)_z = \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial w} \right)_z \quad (10.25)$$

$$\frac{\left(\frac{\partial x}{\partial w} \right)_z}{\left(\frac{\partial y}{\partial w} \right)_z} = \left(\frac{\partial x}{\partial y} \right)_z, \quad (10.26)$$

$$\left(\frac{\partial x}{\partial w} \right)_z \left(\frac{\partial w}{\partial y} \right)_z = \left(\frac{\partial x}{\partial y} \right)_z \quad (10.27)$$

If $x = x(y, w)$, one then gets

$$dx = \left(\frac{\partial x}{\partial y} \right)_w dy + \left(\frac{\partial x}{\partial w} \right)_y dw \quad (10.28)$$

Divide now by dy while holding z constant so

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z \quad (10.29)$$

These general operations can be applied to a wide variety of thermodynamic operations.

10.3. Legendre transformations

The Gibbs equation, Eq. (8.59): $du = -Pdv + Tds$, is the fundamental equation of classical thermodynamics. It is a canonical form which suggests the most natural set of variables in which to express internal energy u are v and s :

$$u = u(v, s) \quad (10.30)$$

However, v and s may not be convenient for a particular problem. There may be other combinations of variables whose canonical form gives a more convenient set of independent variables for a particular problem. An example is the enthalpy, Eq. (5.52):

$$h = u + Pv \quad (10.31)$$

Differentiating the enthalpy gives

$$dh = du + Pdv + vdP \quad (10.32)$$

We repeat the analysis used to obtain Eq.(8.66) earlier. Use Eq.(10.32) to eliminate du in the Gibbs equation, Eq.(8.59), to give

$$dh - Pdv - vdP = du = -Pdv + Tds, \quad (10.33)$$

$$dh = Tds + vdP \quad (10.34)$$

So the canonical variables for h are s and P . One then expects

$$h = h(s, P) \quad (10.35)$$

This exercise can be systematized with the Legendre transformation, details of which we will omit. The interested student can consult Zia, *et al.*² or Abbott and van Ness.³ The transformation is named after Adrien-Marie Legendre, whose work was not motivated by thermodynamic concerns, but has found application in thermodynamics. The only known image of Legendre is shown in Fig 10.2

²R. K. P. Zia, E. F. Redish, and S. R. McKay, 2009. "Making sense of the Legendre transform," *American Journal of Physics*, 77(7): 614-622.

³M. M. Abbott and H. C. van Ness, 1972, *Thermodynamics*, Schaum's Outline Series in Engineering, McGraw-Hill, New York.

The basic outline of the Legendre transformation is as follows. The form $du = -Pdv + Tds$, suggests u is the fundamental dependent variable, v and s are the canonical independent variables, with $-P$ and T serving as so-called conjugate variables. We seek transformations which can render conjugate variables to be canonical variables. We can achieve this by defining new dependent variables as the difference between the original dependent variable and simple second order combinations of the canonical and conjugate variables. For the

Fig 10.2. Adrien-Marie Legendre (1752-1833), French mathematician.



Gibbs equation, there are only three combinations, $-Pv$, Ts , and $-Pv + Ts$, which are dimensionally consistent with u . We subtract each of these from u to define new dependent variables as follows: They are

$$h = h(P, s) = u - (-Pv) = u + Pv, \text{ enthalpy,} \quad (10.36)$$

$$a = a(v, T) = u - Ts, \text{ Helmholtz free energy,} \quad (10.37)$$

$$g = g(P, T) = u - (-Pv + Ts) = u + Pv - Ts, \text{ Gibbs free energy} \quad (10.38)$$

The Helmholtz free energy was developed by Helmholtz.⁴ It is symbolized by a in recognition of the German word *arbeit*, or “work.” An image of the original appearance of the notion from Helmholtz’s 1882 work is shown in Fig 10.3. The notation \mathfrak{A} is our Helmholtz free energy a ; U is our u ; \mathfrak{J} is our mechanical equivalent of heat \mathcal{J} ; ϑ is our temperature T , and S is our entropy s .

The Gibbs free energy was introduced by Gibbs.⁵ An image of a somewhat roundabout appearance of the Gibbs from Gibbs’ 1873 work is shown in Fig 10.4. Here, ϵ is our u , E is our U , η is our s ; and H is our S

⁴H. Helmholtz, 1882, “Die Thermodynamik chemischer Vorgänge,” *Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin*, 1: 22-39.

⁵J. W. Gibbs, 1873, “A method of geometrical representation of the thermodynamic properties of substances by means of surfaces,” *Transactions of the Connecticut Academy of Arts and Sciences*, 2: 382-404.

It has already been shown for the enthalpy that $dh = Tds + vdP$, so that the canonical variables are s and P . One then also has

$$dh = \left(\frac{\partial h}{\partial s} \right)_P ds + \left(\frac{\partial h}{\partial P} \right)_s dP \quad (10.39)$$

from which one deduces that

$$T = \left(\frac{\partial h}{\partial s} \right)_P, \quad v = \left(\frac{\partial h}{\partial P} \right)_s \quad (10.40)$$

From Eq. (10.40), a second Maxwell relation can be deduced by differentiation of the first with respect to P and the second with respect to s

$$\left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P \quad (10.41)$$

The relations for Helmholtz and Gibbs free energies each supply additional useful relations including two new Maxwell relations. First consider the Helmholtz free energy

Körpers, d. h. von den Parametern p_i abhängigen Function ist, welche Hr. CLAUSIUS für einen Parameter »Entropie« genannt und mit S bezeichnet hat.

Also

$$\frac{1}{\mathfrak{S}} \cdot dQ = dS = \frac{\partial S}{\partial \mathfrak{S}} \cdot d\mathfrak{S} + \sum_i \left\{ \frac{\partial S}{\partial p_i} \cdot dp_i \right\} \dots \dots \dots \left. \right\} 1.$$

Aus 1 und 1₁ folgt:

$$\mathfrak{J} \cdot \frac{\partial S}{\partial \mathfrak{S}} = \frac{1}{\mathfrak{S}} \cdot \frac{\partial U}{\partial \mathfrak{S}}$$

$$\mathfrak{J} \cdot \frac{\partial S}{\partial p_i} = \frac{1}{\mathfrak{S}} \left[\frac{\partial U}{\partial p_i} + P_i \right]$$

Daraus folgt:

$$P_i = \frac{\partial}{\partial p_i} [\mathfrak{J} \cdot \mathfrak{S} \cdot S - U] \dots \dots \dots \left. \right\} 1.$$

Ferner

$$\mathfrak{J} \cdot \frac{\partial^2 S}{\partial \mathfrak{S} \cdot \partial p_i} = \frac{1}{\mathfrak{S}} \cdot \frac{\partial^2 U}{\partial \mathfrak{S} \cdot \partial p_i} = \frac{1}{\mathfrak{S}} \left[\frac{\partial^2 U}{\partial \mathfrak{S} \cdot \partial p_i} + \frac{\partial P_i}{\partial \mathfrak{S}} \right] - \frac{1}{\mathfrak{S}^2} \left[\frac{\partial U}{\partial p_i} + P_i \right] \dots \dots \dots \left. \right\} 1.$$

Aus der letzten Gleichung folgt wiederum:

$$\mathfrak{S} \cdot \frac{\partial P_i}{\partial \mathfrak{S}} = \frac{\partial U}{\partial p_i} + P_i \dots \dots \dots \left. \right\} 1.$$

Wenn wir setzen

$$\mathfrak{F} = U - \mathfrak{J} \cdot \mathfrak{S} \cdot S \dots \dots \dots \left. \right\} 1.$$

so ist \mathfrak{F} , wie U und S es sind, eine eindeutige Function der Grössen p_i und \mathfrak{S} . Die Functionen U und S , welche nur durch die Grössen ihrer Differentialquotienten definirt sind, enthalten jede eine willkürliche additive Constante. Wenn wir diese mit α und β bezeichnen,

Fig. 10.3. Image of the original 1882 appearance of the Helmholtz free energy

$$a = u - Ts, \tag{10.42}$$

$$da = du - Tds - sdT = -Pdv + Tds - Tds - sdT = -Pdv - sdT \tag{10.43}$$

So the canonical variables for a are v and T . The conjugate variables are $-P$ and $-s$. Thus

$$da = \left(\frac{\partial a}{\partial v} \right)_T dv + \left(\frac{\partial a}{\partial T} \right)_v dT \tag{10.44}$$

So one gets

$$-P = \left(\frac{\partial a}{\partial v} \right)_T, \quad -s = \left(\frac{\partial a}{\partial T} \right)_v \tag{10.45}$$

and the consequent Maxwell relation

$$\left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \tag{10.46}$$

For the Gibbs free energy

$$g = \underbrace{u + Pv}_h - Ts = h - Ts, \tag{10.47}$$

$$dg = \underbrace{dh + v dP}_{dh} - Tds - sdT = vdP - sdT \tag{10.48}$$

Many find some of these equations to have sufficient appeal to cast them in concrete. The extensive version of Eq.(10.48), unfortunately restricted to the isothermal limit, is depicted in the floor of University of Notre Dame's Jordan Hall of Science atrium, see Fig. 10.5.

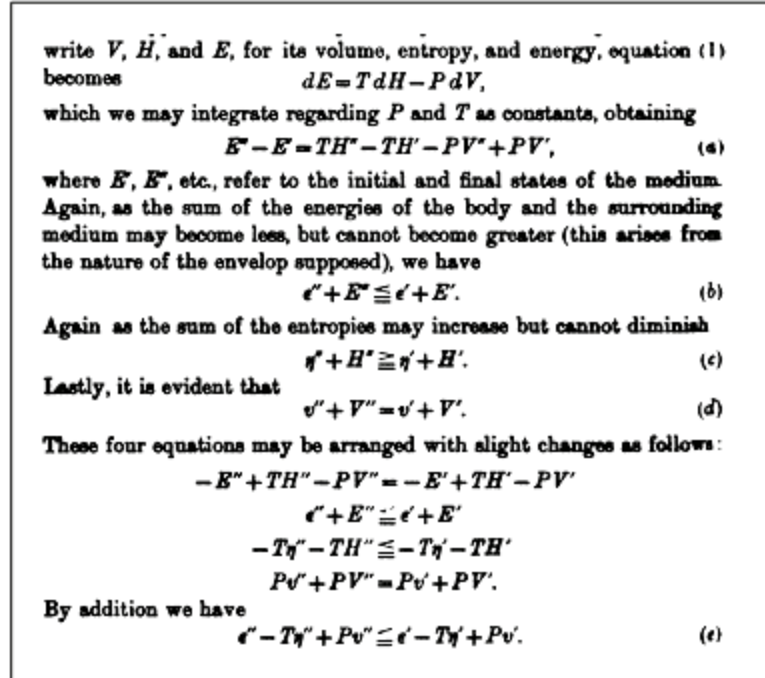


Fig 10.4. Image of the original 1873 appearance of a combination of terms which is now known as the Gibbs free energy



Fig 10.5. Figure cast in the atrium floor of the University of Notre Dame's Jordan Hall of Science containing an isothermal extensive version of Eq.(10.48), among other things

So for Gibbs free energy, the canonical variables are P and T , while the conjugate variables are v and $-s$. One then has $g = g(P, T)$, which gives

$$dg = \left(\frac{\partial g}{\partial P} \right)_T dP + \left(\frac{\partial g}{\partial T} \right)_P dT \quad (10.49)$$

So one finds

$$v = \left(\frac{\partial g}{\partial P} \right)_T, \quad -s = \left(\frac{\partial g}{\partial T} \right)_P \quad (10.50)$$

The resulting Maxwell relation is then

$$\left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T \quad (10.51)$$

Table 10.1 gives a summary of the Maxwell relations and their generators. An image showing the first published appearance of the Maxwell relations is given in Fig 10.6. In Fig 10.the “thermodynamic function“ ϕ is our s , and θ is our T . Note that typography for partial derivatives was non-existent in most texts of the nineteenth century.

Table 10.1. Summary of Maxwell relations and their generators

$u = u$	$h = u + Pv$	$a = u - Ts$	$g = u + Pv - Ts$
$du = -Pdv + Tds$	$dh = Tds + vdP$	$da = -Pdv - sdT$	$dg = vdP - sdT$
$u = u(v, s)$	$h = h(s, P)$	$a = a(v, T)$	$g = g(P, T)$
$-\frac{\partial P}{\partial s} \Big _v = \frac{\partial T}{\partial v} \Big _s$	$\frac{\partial T}{\partial P} \Big _s = \frac{\partial v}{\partial s} \Big _P$	$\frac{\partial P}{\partial T} \Big _v = \frac{\partial s}{\partial v} \Big _T$	$\frac{\partial v}{\partial T} \Big _P = - \frac{\partial s}{\partial P} \Big _T$

10.4. Specific heat capacity

specific heat capacities are defined as

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v, \quad (10.52)$$

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P \quad (10.53)$$

Then perform operations on the Gibbs equation, Eq. (8.59):

$$du = Tds - Pdv, \quad (10.54)$$

$$\left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial s}{\partial T} \right)_v, \quad (10.55)$$

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad (10.56)$$

Likewise, operating on Eq. (8.66), we get,

$$dh = Tds + vdP, \quad (10.57)$$

$$\left(\frac{\partial h}{\partial T} \right)_P = T \left(\frac{\partial s}{\partial T} \right)_P, \quad (10.58)$$

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_P \quad (10.59)$$

One finds further useful relations by operating on the Gibbs equation, Eq. (8.59):

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_v - P \quad (10.60)$$

So one can then say

$$u = u(T, v), \quad (10.61)$$

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv = c_v dT + T\left[\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv \quad (10.62)$$

For an ideal gas, one has

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P = T\frac{R}{v} - \frac{RT}{v} = 0 \quad (10.63)$$

Consequently, u is not a function of v for an ideal gas, so $u = u(T)$ alone. Since $h = u + Pv$, h for an ideal gas reduces to $h = u + RT$. Thus,

$$h = u(T) + RT = h(T) \quad (10.64)$$

Now, return to general equations of state. With $s = s(T, v)$ or $s = s(T, P)$, one gets

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv, \quad (10.65)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP, \quad (10.66)$$

Therefore,

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv, \quad (10.67)$$

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP \quad (10.68)$$

Subtracting Eq.(10.69) from Eq.(10.67), one finds

$$0 = \frac{c_v - c_p}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv + \left(\frac{\partial v}{\partial T}\right)_P dP, \quad (10.69)$$

$$c_p - c_v dT = T\left(\frac{\partial P}{\partial T}\right)_v dv + T\left(\frac{\partial v}{\partial T}\right)_P dP \quad (10.70)$$

Now, divide both sides by dT and hold *either* P or v constant. In either case, one gets

$$c_p - c_v = T\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_P \quad (10.71)$$

Since $\left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P$, (10.71) can be rewritten as

$$c_p - c_v = -T\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2 \quad (10.72)$$

Now, since $T > 0$, $(\partial v/\partial T|_P)^2 > 0$, and for all known materials $\partial P/\partial v|_T < 0$, we must have

$$c_p > c_v \quad (10.73)$$

10.5. The first law and coordinate transformations

One can apply standard notions from the mathematics of coordinate transformations to the first law of thermodynamics. Recall the primitive form of the first law Eq. (5.3): $\oint \delta Q = \oint \delta W$. In intensive form, this becomes

$$\oint \delta q = \oint \delta w \quad (10.74)$$

We also know that $\delta q = Tds$ and $\delta w = Pdv$, so that

$$\oint Tds = \oint Pdv \quad (10.75)$$

Geometrically, one could say that an area in the $T-s$ plane has the same value in the $P-v$ plane. Moreover, because the cyclic integral is direction-dependent, one must insist that an area in the $T-s$ plane maintain its orientation in the $P-v$ plane. As an example, a rotation of a two-dimensional geometric entity preserves area and orientation, while a reflection of the same entity preserves area, but not orientation.

Now we can consider equations of state to be coordinate mappings; for example, consider the general equations of state

$$T = T(P, v), \quad (10.76)$$

$$s = s(P, v) \quad (10.77)$$

These are mappings which take points in the $P-v$ plane into the $T-s$ plane. The differentials of Eqs.(10.76),(10.77) are

$$dT = \left(\frac{\partial T}{\partial P} \right)_v dP + \left(\frac{\partial T}{\partial v} \right)_P dv, \quad (10.78)$$

$$ds = \left(\frac{\partial s}{\partial P} \right)_v dP + \left(\frac{\partial s}{\partial v} \right)_P dv \quad (10.79)$$

In matrix form, we could say

$$\begin{pmatrix} dT \\ ds \end{pmatrix} = \underbrace{\begin{pmatrix} \left(\frac{\partial T}{\partial P} \right)_v & \left(\frac{\partial T}{\partial v} \right)_P \\ \left(\frac{\partial s}{\partial P} \right)_v & \left(\frac{\partial s}{\partial v} \right)_P \end{pmatrix}}_{\mathfrak{J}} \cdot \begin{pmatrix} dP \\ dv \end{pmatrix}, \quad \mathfrak{J} = \begin{pmatrix} \left(\frac{\partial T}{\partial P} \right)_v & \left(\frac{\partial T}{\partial v} \right)_P \\ \left(\frac{\partial s}{\partial P} \right)_v & \left(\frac{\partial s}{\partial v} \right)_P \end{pmatrix} \quad (10.80)$$

\mathfrak{J} is the *Jacobian matrix* of the mapping from the standard mathematics of coordinate transformations

In a standard result from mathematics, for a coordinate transformation to be area- and orientation-preserving, its *Jacobian determinant*, J must have a value of unity:

$$J \equiv \det \mathfrak{J} = 1 \quad (10.81)$$

Expanding the Jacobian determinant, we require

$$J = \left(\frac{\partial T}{\partial P} \right)_v \left(\frac{\partial s}{\partial v} \right)_P - \left(\frac{\partial T}{\partial v} \right)_P \left(\frac{\partial s}{\partial P} \right)_v = 1 \quad (10.82)$$

For general mathematical background of Jacobians and coordinate transformations, the interested reader can consult a variety of sources, for example, Kaplan⁶

⁶W. Kaplan, 2003, *Advanced Calculus*, Fifth Edition, Addison-Wesley, Boston, pp. 90-95, pp. 331-336.

10.6. The van der Waals gas

A van der Waals gas is a common model for a non-ideal gas, introduced earlier in Sec. 3.4.2.1. It can capture some of the behavior of a gas as it approaches the vapor dome. Its form is

$$P_{T,v} = \frac{RT}{v-b} - \frac{a}{v^2} \quad (10.83)$$

where b accounts for the finite volume of the molecules, and a accounts for intermolecular forces.

If we select

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}, \quad b = \frac{RT_c}{P_c} \quad (10.84)$$

where T_c and P_c are the critical point temperature and pressure, respectively, we approximate some physical behavior well, namely

- at the critical point $\partial P / \partial v|_T = 0$; that is an isotherm has a zero slope in the $P - v$ plane at the critical point, and
- at the critical point $\partial^2 P / \partial v^2|_T = 0$; that is an isotherm has a point of inflection in the $P - v$ plane at the critical point.

It is also easy to show that at the critical point, we have

$$v_c = 3b = \frac{3}{8} \frac{RT_c}{P_c} \quad (10.85)$$

10.7. Adiabatic sound speed

With help from the mass, linear momentum, and energy equations, along with validation from experiment, it can be shown that the speed of sound waves, c , is given by the formula

$$c = \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_s} \quad (10.86)$$

As the entropy is constant for such a calculation, this is sometimes called the adiabatic sound speed.

Let us calculate c . From the Gibbs equation, Eq. (8.60), we have

$$Tds = du + Pdv \quad (10.87)$$

Now, since $v = 1/\rho$, we get $dv = -(1/\rho^2)d\rho$, and Eq. (10.87) can be rewritten as

$$Tds = du - \frac{P}{\rho^2} d\rho \quad (10.88)$$

Now, for simple compressible substances, we can always form $u = u(P, \rho)$. Thus, we also have

$$du = \left(\frac{\partial u}{\partial P} \right)_\rho dP + \left(\frac{\partial u}{\partial \rho} \right)_P d\rho \quad (10.89)$$

Now, use Eq. (10.89) to eliminate du in Eq. (10.88) so to get

$$\begin{aligned} Tds = du - \frac{P}{\rho^2} d\rho &= \left(\frac{\partial u}{\partial P} \right)_\rho dP + \left(\frac{\partial u}{\partial \rho} \right)_P d\rho - \frac{P}{\rho^2} d\rho \\ &= \left(\frac{\partial u}{\partial P} \right)_\rho dP + \left[\left(\frac{\partial u}{\partial \rho} \right)_P - \frac{P}{\rho^2} \right] d\rho \end{aligned} \quad (10.90)$$

Now, to find $c = \sqrt{\partial P / \partial \rho|_s}$, take $ds = 0$, divide both sides by $d\rho$, and solve for $\partial P / \partial \rho|_s$ in Eq.(10.90) so as to get

$$\left(\frac{\partial P}{\partial \rho} \right)_s = \frac{-\left(\frac{\partial u}{\partial \rho} \right)_P + \frac{P}{\rho^2}}{\left(\frac{\partial u}{\partial P} \right)_\rho} \quad (10.91)$$

Now, Eq. (10.91) is valid for a general equation of state. Let us specialize it for a CPIG.

For the CPIG, we have

$$\begin{aligned} u = c_v T + \text{const} &= c_v \frac{P}{\rho R} + \text{const} = \frac{c_v}{c_p - c_v} \frac{P}{\rho} + \text{const} \\ &= \frac{1}{\frac{c_p}{c_v} - 1} \frac{P}{\rho} + \text{const} = \frac{1}{k - 1} \frac{P}{\rho} + \text{const} \end{aligned} \quad (10.92)$$

Thus, we have for the CPIG

$$\left(\frac{\partial u}{\partial P} \right)_\rho = \frac{1}{k - 1} \frac{1}{\rho}, \quad (10.93)$$

$$\left(\frac{\partial u}{\partial \rho} \right)_P = \frac{-1}{k - 1} \frac{P}{\rho^2} \quad (10.94)$$

Now, substitute Eqs. (10.93), (10.94) into (10.91) so to get

$$\left(\frac{\partial P}{\partial \rho} \right)_s = \frac{\frac{1}{k - 1} \frac{P}{\rho^2} + \frac{P}{\rho^2}}{\frac{1}{k - 1} \frac{1}{\rho}} = \frac{P}{\rho} + k - 1 \frac{P}{\rho} = k \frac{P}{\rho} = kRT \quad (10.95)$$

Thus,

$$c^2 = \left(\frac{\partial P}{\partial \rho} \right)_s = kRT, \quad (10.96)$$

$$c = \sqrt{kRT} = \sqrt{k \frac{P}{\rho}} \quad (10.97)$$

Compare this to the isothermal sound speed:

$$c_T = \sqrt{\left(\frac{\partial P}{\partial \rho} \right)_T} = \sqrt{RT} \quad (10.98)$$

By use of the ideal gas law, one can also say

$$c_T = \sqrt{\frac{P}{\rho}} \quad (10.99)$$

This is the form Newton used in 1687 to estimate the sound speed; however, he probably used an approach different from assuming Boyle's law and taking derivatives. Newton's approach was corrected by Laplace in 1816 who generated what amounts to our adiabatic prediction, long before notions of thermodynamics were settled. Laplace is depicted in Fig 10.6 Laplace's notions rested on an uncertain theoretical foundation; he in fact adjusted

Fig 10.6. Pierre-Simon Laplace (1749-1827), French mathematician and physicist who improved Newton's sound speed estimates



his theory often, and it was not until thermodynamics was well established several decades later that our understanding of sound waves clarified. The interested reader can consult Finn⁷

⁷B. S. Finn, 1964, "Laplace and the speed of sound," *Isis*, 55(1): 7-19.

10.8. Introduction to compressible flow

We close these course notes with an opening to later coursework in which thermodynamics and the adiabatic sound speed plays a critical role: compressible fluid mechanics. We only sketch two critical results here and leave the details for another semester.

To see the importance of the sound speed for compressible flows, let us consider briefly the equations of motion for a one-dimensional flow in a duct with area change. We ignore effects of momentum and energy diffusion as embodied in viscosity and heat conduction. The conservation laws of mass, linear momentum, and energy can be shown to be

$$\frac{\partial}{\partial t} \rho A + \frac{\partial}{\partial x} \rho |\vec{v}| A = 0, \quad (10.100)$$

$$\rho \left(\frac{\partial |\bar{v}|}{\partial t} + |\bar{v}| \frac{\partial |\bar{v}|}{\partial x} \right) = -\frac{\partial P}{\partial x}, \quad (10.101)$$

$$\frac{\partial u}{\partial t} + |\bar{v}| \frac{\partial u}{\partial x} = -P \left(\frac{\partial v}{\partial t} + |\bar{v}| \frac{\partial v}{\partial x} \right) \quad (10.102)$$

Note, we have not specified any equation of state. It can be shown that viscosity and heat conduction, which we have neglected, are the only mechanisms to generate entropy in a flow without shock waves. Since we have neglected these mechanisms, our equations are isentropic as long as there are no shock waves. Note that Eq.(10.102) can be rewritten as $du/dt = -Pdv/dt$ when we define the material derivative as $d/dt = \partial/\partial t + v\partial/\partial x$. Thus, Eq.(10.102) also says $du = -Pdv$. Comparing this to the Gibbs equation, Eq.(8.59), $du = Tds - Pdv$, we see that our energy equation, Eq.(10.102), is isentropic, $du = 0$. We can thus replace Eq.(10.102) by $ds/dt = \partial s/\partial t + |\bar{v}|\partial s/\partial x = 0$. We also take a general equation of state $P = P(\rho, s)$. So our governing equations, Eqs.(10.100)-(10.102) supplemented by the general equation of state become

$$\frac{\partial}{\partial t} \rho A + \frac{\partial}{\partial x} \rho |\bar{v}| A = 0, \quad (10.103)$$

$$\rho \left(\frac{\partial |\bar{v}|}{\partial t} + |\bar{v}| \frac{\partial |\bar{v}|}{\partial x} \right) = -\frac{\partial P}{\partial x}, \quad (10.104)$$

$$\frac{\partial s}{\partial t} + |\bar{v}| \frac{\partial s}{\partial x} = 0, \quad (10.105)$$

$$P = P(\rho, s) \quad (10.106)$$

10.8.1. Acoustics

Let us first explore the acoustic limit in which disturbances to an otherwise stationary material are small but non-zero. We restrict attention to purely isentropic flows, so $s = \text{constant}$, and all its derivatives are zero. We first consider the state equation, Eq.

(10.106) so as to remove P from our analysis.

$$dP = \left(\frac{\partial P}{\partial \rho} \right)_s d\rho + \left(\frac{\partial P}{\partial s} \right)_\rho ds, \quad (10.107)$$

$$\frac{\partial P}{\partial x} = \underbrace{\left(\frac{\partial P}{\partial \rho} \right)_s}_{0} \frac{\partial \rho}{\partial x} + \underbrace{\left(\frac{\partial P}{\partial s} \right)_\rho}_{0} \frac{\partial s}{\partial x}, \quad (10.108)$$

$$\frac{\partial P}{\partial x} = c^2 \frac{\partial \rho}{\partial x} \quad (10.109)$$

We next consider Eq. (10.103) in the limit where A is a constant and Eq.(10.104) where $\partial P/\partial x$ is replaced in favor of $\partial \rho/\partial x$ via Eq. (10.109)

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x} \rho |\bar{v}| = 0, \quad (10.110)$$

$$\rho \left(\frac{\partial |\bar{v}|}{\partial t} + |\bar{v}| \frac{\partial |\bar{v}|}{\partial x} \right) = -c^2 \frac{\partial \rho}{\partial x} \quad (10.111)$$

We next assume that the state variables ρ and \mathbf{v} are the sum of a constant state and a small perturbation:

$$\rho = \rho_0 + \tilde{\rho}, \quad (10.112)$$

$$|\tilde{\mathbf{v}}| = 0 + |\tilde{v}| \quad (10.113)$$

The velocity is assumed to be perturbed about zero, the stationary state. We substitute Eqs.(10.112)-(10.113) into Eqs.(10-108)-(10.109) to get

$$\frac{\partial \rho_0 + \tilde{\rho}}{\partial t} + \frac{\partial}{\partial x} \rho_0 + \tilde{\rho} |\tilde{v}| = 0, \quad (10.114)$$

$$\rho_0 + \tilde{\rho} \left(\frac{\partial |\tilde{v}|}{\partial t} + |\tilde{v}| \frac{\partial |\tilde{v}|}{\partial x} \right) = -c^2 \frac{\partial}{\partial x} \rho_0 + \tilde{\rho} \quad (10.115)$$

We expand to get

$$\frac{\partial \rho_0}{\partial t} + \frac{\partial \tilde{\rho}}{\partial t} + \rho_0 \frac{\partial |\tilde{v}|}{\partial x} + \underbrace{\frac{\partial}{\partial x} \tilde{\rho} |\tilde{v}|}_{\sim 0} = 0, \quad (10.116)$$

$$\rho_0 \left(\frac{\partial |\tilde{v}|}{\partial t} + \underbrace{|\tilde{v}| \frac{\partial |\tilde{v}|}{\partial x}}_{\sim 0} \right) + \tilde{\rho} \left(\underbrace{\frac{\partial |\tilde{v}|}{\partial t} + |\tilde{v}| \frac{\partial |\tilde{v}|}{\partial x}}_{\sim 0} \right) = -c^2 \frac{\partial \rho_0}{\partial x} - c^2 \frac{\partial \tilde{\rho}}{\partial x} \quad (10.117)$$

Neglecting small terms, we remain only with

$$\frac{\partial \tilde{\rho}}{\partial t} + \rho_0 \frac{\partial |\tilde{v}|}{\partial x} = 0, \quad (10.118)$$

$$\rho_0 \frac{\partial |\tilde{v}|}{\partial t} = -c^2 \frac{\partial \tilde{\rho}}{\partial x} \quad (10.119)$$

Now, take the time derivative of Eq. (10.118) and the space derivative of Eq.(10.119) and get

$$\frac{\partial^2 \tilde{\rho}}{\partial t^2} + \rho_0 \frac{\partial^2 |\tilde{v}|}{\partial t \partial x} = 0, \quad (10.120)$$

$$\rho_0 \frac{\partial^2 |\tilde{v}|}{\partial x \partial t} = -c^2 \frac{\partial^2 \tilde{\rho}}{\partial x^2} \quad (10.121)$$

Next, realizing the order of the mixed second partial derivatives does not matter for functions which are continuous and differentiable, we eliminate $\partial^2 |\tilde{v}| / \partial t \partial x$ and get

$$\frac{\partial^2 \tilde{\rho}}{\partial t^2} = c^2 \frac{\partial^2 \tilde{\rho}}{\partial x^2} \quad (10.122)$$

Taking $P = P_0 + \tilde{P}$, we have

$$\begin{aligned}
c^2 &= k \frac{P}{\rho} = k \frac{P_0 + \tilde{P}}{\rho_0 + \tilde{\rho}} = k \frac{P_0 \left(1 + \frac{\tilde{P}}{P_0}\right)}{\rho_0 \left(1 + \frac{\tilde{\rho}}{\rho_0}\right)} = k \frac{P_0}{\rho_0} \left(1 + \frac{\tilde{P}}{P_0}\right) \left(1 - \frac{\tilde{\rho}}{\rho_0} + \dots\right) \\
&= k \frac{P_0}{\rho_0} \left(1 + \frac{\tilde{P}}{P_0} - \frac{\tilde{\rho}}{\rho_0} + \dots\right)
\end{aligned} \tag{10.123}$$

We retain only the most important term and take then

$$c^2 = c_0^2 + \dots \text{ with } c_0^2 = k \frac{P_0}{\rho_0} \tag{10.124}$$

So we get

$$\frac{\partial^2 \tilde{\rho}}{\partial t^2} = c_0^2 \frac{\partial^2 \tilde{\rho}}{\partial x^2} \tag{10.125}$$

This is the well known wave equation which is satisfied by the well known D'Alembert solution:

$$\tilde{\rho}(x,t) = f(x + c_0 t) + g(x - c_0 t) \tag{10.126}$$

Here, f and g are arbitrary functions. In a physical problem, they are determined by the actual initial and boundary conditions which are appropriate for the particular problem. The so-called "phase" ϕ of f is $\phi = x + c_0 t$. We can find the speed of a point with constant phase by considering ϕ to be a constant, and taking appropriate derivatives:

$$\phi = \text{const} = x + c_0 t, \tag{10.127}$$

$$\frac{d\phi}{dt} = 0 = \frac{dx}{dt} + c_0, \tag{10.128}$$

$$\frac{dx}{dt} = -c_0 \tag{10.129}$$

Thus, waves described by $\tilde{\rho}(x,t) = f(x + c_0 t)$ are traveling to the left (negative x direction) with speed c_0 . Similarly the waves given by $g(x - c_0 t)$ are traveling to the right (positive x direction) with speed c_0 .

10.8.2. Steady flow with area change

Let us now return to the full equations, (10.103)-(10.106). In particular, we will now consider potentially large fluid velocities, \mathbf{v} ; more specifically, the kinetic energy changes of the flow may be as important as the internal energy changes. Let us also consider only steady flows; thus, $\partial/\partial t = 0$. Our governing equations. Eqs.(10.103)-(10.106), reduce to

$$\frac{d}{dx} \rho |\vec{v}| A = 0, \tag{10.130}$$

$$\rho |\vec{v}| \frac{d|\vec{v}|}{dx} = -\frac{dP}{dx}, \tag{10.131}$$

$$\frac{ds}{dx} = 0, \tag{10.132}$$

$$P = P(\rho, s) \quad (10.133)$$

Specializing Eq.(10.109) for steady flows, we have

$$\frac{dP}{dx} = c^2 \frac{d\rho}{dx} \quad (10.134)$$

Using Eq. (10.134), in the linear momentum equation, Eq.(10.131), and expanding the mass equation, Eq.(10.130), our mass and linear momentum equations become

$$\rho|\bar{v}|\frac{dA}{dx} + \rho A \frac{d|\bar{v}|}{dx} + |\bar{v}|A \frac{d\rho}{dx} = 0, \quad (10.135)$$

$$\rho|\bar{v}|\frac{d|\bar{v}|}{dx} = -c^2 \frac{d\rho}{dx} \quad (10.136)$$

We next use Eq.(10.136) to eliminate $d\rho/dx$ in the mass equation, Eq.(10.135), to get

$$\rho|\bar{v}|\frac{dA}{dx} + \rho A \frac{d|\bar{v}|}{dx} + |\bar{v}|A \left(-\frac{\rho|\bar{v}|}{c^2} \frac{d|\bar{v}|}{dx} \right) = 0, \quad (10.137)$$

$$\frac{1}{A} \frac{dA}{dx} + \frac{1}{|\bar{v}|} \frac{d|\bar{v}|}{dx} - \frac{|\bar{v}|}{c^2} \frac{d|\bar{v}|}{dx} = 0, \quad (10.138)$$

$$\frac{1}{|\bar{v}|} \frac{d|\bar{v}|}{dx} \left(1 - \frac{|\bar{v}|^2}{c^2} \right) = -\frac{1}{A} \frac{dA}{dx}, \quad (10.139)$$

$$\frac{d|\bar{v}|}{dx} = \frac{\frac{|\bar{v}|}{A} \frac{dA}{dx}}{\frac{|\bar{v}|^2}{c^2} - 1} \quad (10.140)$$

We define the Mach number, M as the ratio of the local fluid velocity to the local adiabatic sound speed:

$$M \equiv \frac{|\bar{v}|}{c} \quad (10.141)$$

So we can restate Eq.(10.140) as

$$\frac{d|\bar{v}|}{dx} = \frac{\frac{|\bar{v}|}{A} \frac{dA}{dx}}{M^2 - 1} \quad (10.142)$$

Notice when the Mach number is unity, there is a potential singularity in dv/dx . This caused great concern in the design of early supersonic vehicles. The only way to prevent the singular behavior is to require at a sonic point, where $M = 1$, for dA/dx to be simultaneously zero. Remarkably, this is precisely how nature behaves and is the reason why supersonic nozzles are first converging, then diverging. At the point where $dA/dx = 0$, the flow becomes locally sonic and can undergo a transition from subsonic to supersonic.

In terms of differentials,, we can restate Eq. (10.142) as

$$\frac{d|\bar{v}|}{|\bar{v}|} = \frac{1}{M^2 - 1} \frac{dA}{A} \quad (10.143)$$

Note, if the flow is subsonic, $M < 1$, with $v > 0$ and area increasing $dA > 0$, then $dv < 0$: *area increase in a subsonic nozzle generates velocity decrease*. For supersonic flow, the opposite is true: *area increase in a supersonic nozzle generates velocity increase*. One can see a converging-diverging nozzle as well as its use in generating supersonic flow at its exit plane in an image of a 2010 space shuttle launch depicted in Fig 10.7.



a)



b)

Fig 10.7. a) Diverging section of a nozzle for the space shuttle main engine; b) Launch Space Shuttle Atlantis, STS-132, 14 May 2010, with a crew including astronaut Michael T. Good, BSAE 1984, MSAE 1986, University of Notre Dame

NOTES

The Legendre transformation

Let us first restrict ourselves to functions of one variable. The results are then readily generalized to functions of several variables. Assume $f(x)$ to be a function of the variable x , with the total differential

$$df = \frac{\partial f}{\partial x} dx = p(x) dx$$

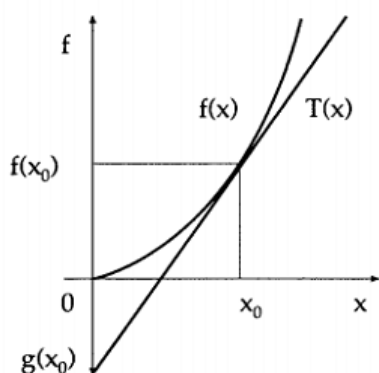


Figure 4.2. Concerning the Legendre transformation.

The function $p(x) = f'(x)$ gives the slope of the curve $f(x)$ for every value of the variable x (let us assume that $f(x)$ is differentiable for all x). The task of the Legendre transformation is to find a function $g(p)$ of the new variable $p = f'(x)$, which is equivalent to the function $f(x)$, i.e., which contains the same information. Thus, one must be able to calculate $g(p)$ unambiguously from the function $f(x)$ and vice versa. The new function $g(p)$ can be readily obtained using the illustrative interpretation in Figure 4.2 of the variable p as slope of the function $f(x)$. To this end, we consider the intersection of the tangent to f at the point $(x_0, f(x_0))$ with the y -axis. The tangent has the following equation:

$$T(x) = f(x_0) + f'(x_0)(x - x_0)$$

The intersection with the y -axis $g = T(0)$ therefore is

$$g(x_0) = f(x_0) - x_0 f'(x_0)$$

and depends, of course, on the point x_0 under consideration. One calls the function $g(x)$ for an arbitrary point x the *Legendre transform* of $f(x)$; it is

$$g = f - xp \quad \text{with} \quad p = \frac{\partial f}{\partial x}$$

(+)

In other words, $g(x)$ is the corresponding value of the intersection of the tangent to f at point $(x, f(x))$ with the y -axis.

We now want to show that g depends solely on the slope $p = f'(x)$. To this end we differentiate Equation (4.20):

$$dg = df - p dx - x dp$$

one has

$$dg = -x dp$$

(++)

Thus, g can depend only on the variable p . To calculate $g(p)$ explicitly, we have to eliminate x in Equation (4.20),

$$g(x) = f(x) - x f'(x) \quad (*)$$

with the help of the equation

$$p = f'(x) \quad (**)$$

This, however, is only possible, if Equation (4.24) can be uniquely solved for x , i.e., if there exists the inverse f'^{-1} to f' . Then one can insert

$$x = f'^{-1}(p)$$

(***)

into Eq. (*) and one obtains explicitly the function

$$g(p) = f(f'^{-1}(p)) - f'^{-1}(p)p$$

It is therefore evident that a unique Legendre transform exists only if Equation

(**)

represents a bijective mapping, i.e., if every value of the variable x is uniquely mapped onto a certain value of the slope p and vice versa. From mathematics it is known that the function $f'(x)$ has to be strictly monotonic for Equation (**)

to be invertible. Thus, only if $f'(x)$ is strictly monotonic does the Legendre transform $g(p)$ exist. If the slope $f'(x)$ is not strictly monotonic, there may be several values of x belonging to a value of the slope p , and the transformation is no longer unique.

Next we show that one can reconstruct the original function $f(x)$ from the Legendre transform in a unique way. According to Equation (+), it holds that

$$f(p) = g(p) + xp \tag{****}$$

In this equation we can uniquely replace p by x . According to Equation (++) we have

$$x = -g'(p) \tag{*****}$$

Since $f'(x)$ is strictly monotonous, the inverse function is also

strictly monotonous. Therefore Equation (*****)

can be uniquely solved

for $p(x)$. This can be inserted into Equation (****)

and we uniquely

reobtain the function $f(x)$.

Helmholtz free energy

In the laboratory it is difficult to manipulate S , V , but far easier to change T , V . It is thus natural to ask, "What is the equilibrium condition at constant T , V ?" To answer this question, we go back to the inequality $\Delta U \leq T \Delta S - \Delta W$. If T is kept constant, we can rewrite it in the form

$$\Delta W \leq -\Delta(U - TS)$$

If $\Delta W = 0$, then $(U - TS) \leq 0$. This motivates us to define a new thermodynamic function, the *Helmholtz free energy* (or simply *free energy*):

$$A \equiv U - TS$$

The earlier inequality now reads

$$\Delta A \leq -\Delta W$$

If $\Delta W = 0$, then $\Delta A \leq 0$. The equilibrium condition for a mechanically isolated body at constant temperature is that the free energy be minimum.

For infinitesimal reversible transformations we have $dA = dU - TdS - SdT$. Using the first law, we can reduce this to

$$dA = -PdV - SdT$$

If we know the function $A(T, V)$, then all thermodynamic properties can be obtained through the Maxwell relations

$$P = - \left(\frac{\partial A}{\partial V} \right)_T$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

The first of these reduces to the intuitive relation $P = -\partial U/\partial V$ at absolute zero.

Gibbs potential

We have seen that the thermodynamic properties of a system can be obtained from the function $U(S, V)$, or from $A(V, T)$, depending on the choice of independent variables. The replacement of U by $A = U - TS$ was motivated by the fact that $dU = TdS - PdV$, and we want to replace the term TdS by SdT . This is an example of a *Legendre transformation*.

Let us now consider P, T as independent variables. We introduce the Gibbs potential G , by making a Legendre transformation on A :

$$G \equiv A + PV$$

Then, $dG = dA + PdV + VdP = -SdT - PdV + PdV + VdP$, or

$$dG = -SdT + VdP$$

The condition for equilibrium at constant T , P is that G be at a minimum. We now have further Maxwell relations

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

The Gibbs potential is useful in describing chemical processes, which usually take place under constant atmospheric pressure.

Maxwell relations

Above obtained Maxwell relations are

$$P = - \left(\frac{\partial A}{\partial V} \right)_T$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

Still two more Maxwell relations may be obtained by considering the differential changes of the enthalpy:

$$H = U + PV$$

$$dH = TdS + VdP$$

from which follow

$$V = \left(\frac{\partial H}{\partial P} \right)_S$$

$$T = \left(\frac{\partial H}{\partial S} \right)_P$$

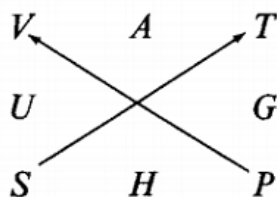
Further Maxwell relations are

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S$$

which follow from the first law, $dU = -P dV + T dS$.

The eight Maxwell relations may be conveniently summarized by the following diagram:



The functions A, G, H, U are flanked by their respective natural arguments, for example, $A = A(V, T)$. The derivative with respect to one argument, with the other held fixed, may be found by going along a diagonal line, either with or against the direction of the arrow. Going against the arrow yields a minus sign; for example, $(\partial A / \partial T)_V = -S$, $(\partial A / \partial V)_T = -P$.

Chemical potential

So far we have kept the number of particles N constant in thermodynamic transformations. When N does change, the first law is generalized to the form

$$dU = dQ - dW + \mu dN$$

where μ is called the *chemical potential*, the energy needed to add one particle to a thermally and mechanically isolated system. For a gas-liquid system we have

$$dU = TdS - PdV + \mu dN$$

The change in free energy is given by

$$dA = -SdT - PdV + \mu dN$$

which gives the Maxwell relation

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

Similarly, for processes at constant P and T , we consider the change in the Gibbs potential:

$$dG = -SdT - VdP + \mu dN$$

and obtain

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{P,T}$$

LECTURE 11: SOME OTHER PROBLEMS OF THERMODYNAMICS

Content of Lecture 11

- 11.1. Third law of thermodynamics
- 11.2. Euler's equation and the Gibbs-Duhem relation
- 11.3. Jacobi transformation
- 11.4. Gibbs's phase rule
- 11.5. Phase equilibrium and Maxwell construction
- 11.6. The law of mass action
- 11.7. The Joule-Thomson effect
- 11.8. Phase transition

11.1. Third law of thermodynamics

The second law of thermodynamics enables us to define the entropy of a substance up to an arbitrary additive constant. The definition of the entropy depends on the existence of a reversible transformation connecting an arbitrarily chosen reference state O to the state A under consideration. Such a reversible transformation always exists if both O and A lie on one sheet of the equation of state surface. If we consider two different substances, or metastable phases of the same substance, the equation of state surface may consist of more than one disjoint sheets. In such cases the kind of reversible path we have mentioned may not exist. Therefore the second law does not uniquely determine the difference in entropy of two states A and B , if A refers to one substance and B to another. In 1905 Nernst supplied a rule for such a determination. This rule has since been called the *third law of thermodynamics*. It states:

The entropy of a system at absolute zero is a universal constant, which may be taken to be zero.

The generality of this statement rests in the facts that (a) it refers to any system, and that (b) it states that $S = 0$ at $T = 0$, regardless of the values of any other parameter of which S may be a function. It is obvious that the third law renders the entropy of any state of any system unique.

The third law immediately implies that any heat capacity of a system must vanish at absolute zero. Let R be any reversible path connecting a state of the system at absolute zero to the state A , whose entropy is to be calculated. Let $C_R(T)$ be the heat capacity of the system along the path R . Then, by the second law,

$$S(A) = \int_0^{T_A} C_R(T) \frac{dT}{T} \quad (11.1)$$

But according to the third law

$$S(A) \xrightarrow{T_A \rightarrow 0} 0 \quad (11.2)$$

Hence we must have

$$C_R(T) \xrightarrow{T \rightarrow 0} 0 \quad (11.3)$$

In particular, C_R may be C_V or C_P . The statement (11.3) is experimentally verified for all substances so far examined.

A less obvious consequence of the third law is that at absolute zero the coefficient of thermal expansion of any substance vanishes. This may be shown as follows. From the TdS equations we can deduce the equalities

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \right)_P &= \frac{C_P}{T} \\ \left(\frac{\partial S}{\partial P} \right)_T &= - \left(\frac{\partial V}{\partial T} \right)_P \end{aligned} \quad (11.4)$$

Combining these we arrive at

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P \quad (11.5)$$

we have, for the coefficient of thermal expansion α , the expression

$$V\alpha \equiv \left(\frac{\partial V}{\partial T} \right)_P = - \left(\frac{\partial S}{\partial P} \right)_T = - \frac{\partial}{\partial P} \int_0^T C_P \frac{dT}{T} = - \int_0^T \left(\frac{\partial C_P}{\partial P} \right)_T \frac{dT}{T} \quad (11.6)$$

where the integrations proceed along a path of constant P .
we rewrite this as

$$V\alpha = \int_0^T \left(\frac{\partial^2 V}{\partial T^2} \right)_P dT = \left(\frac{\partial V}{\partial T} \right)_P - \left[\left(\frac{\partial V}{\partial T} \right)_P \right]_{T=0} \quad (11.7)$$

Therefore

$$\alpha \xrightarrow{T \rightarrow 0} 0 \quad (11.8)$$

In a similar fashion we can show that

$$\left(\frac{\partial P}{\partial T} \right)_V \xrightarrow{T \rightarrow 0} 0 \quad (11.9)$$

this implies that on the P - T diagram the melting curve has zero tangent at $T = 0$.

It is experimentally found that C_p can be represented by the following series expansion at low temperatures:

$$C_p = T^x (a + bT + cT^2 + \dots) \quad (11.10)$$

where x is a positive constant, and a, b, c, \dots are functions of P . Differentiating this expression with respect to P , we find that

$$\left(\frac{\partial C_p}{\partial P} \right)_T = T^x (a' + b'T + c'T^2 + \dots) \quad (11.11)$$

Therefore

$$V\alpha = - \int_0^T dT (a'T^{x-1} + b'T^x + \dots) = -T^x \left(\frac{a'}{x} + \frac{b'T}{x+1} + \frac{c'T^2}{x+2} + \dots \right) \quad (11.12)$$

Hence

$$\frac{V\alpha}{C_p} \xrightarrow{T \rightarrow 0} \text{finite constant} \quad (11.13)$$

This has the consequence that a system cannot be cooled to absolute zero by a finite change of the thermodynamic parameters. For example, from one of the

TdS equations we find that through an adiabatic change dP of the pressure, the temperature changes by

$$dT = \left(\frac{V\alpha}{C_P} \right) T dP \quad (11.14)$$

the change of P required to produce a finite change in the temperature is unbounded as $T \rightarrow 0$.

The unattainability of absolute zero is sometimes stated as an alternative formulation of the third law. This statement is independent of the second law, for the latter only implies that there exists no Carnot engine whose lower reservoir is at absolute zero.* Whether it is possible to make a system approach absolute zero from a higher temperature is an independent question. According to (11.14) it depends on the behavior of the specific heat, of which the second law says nothing.

Before experimental techniques were well developed for low temperatures, it was generally believed that heat capacities of substances remain constant down to absolute zero, as classical kinetic theory predicts (i.e., $x = 0$ in (11.10)). If this were so, we see directly from (11.14) that the unattainability of absolute zero would be automatic. This is why the question did not receive attention until the turn of the century, when it was discovered that heat capacities tend to vanish at low temperatures. We now see that even if the heat capacities vanish at absolute zero, the absolute zero is still unattainable.

We see, when we come to quantum statistical mechanics, that the third law of thermodynamics is a macroscopic manifestation of quantum effects

The foregoing discussions, which are somewhat abstract, become concrete and physical when they are presented in the context of quantum statistical mechanics. The importance of the third law of thermodynamics, therefore, does not lie in these abstract considerations, but in its practical usefulness. We end our discussion of the third law with one of its applications.

The free energy of a system is defined as

$$A = U - TS \quad (11.15)$$

which, according to the third law, can be written in the form

$$A = U - T \int_0^T \frac{C_V}{T'} dT' \quad (11.16)$$

where the integral in the second term extends over a path of constant volume. There is no arbitrary additive constant except the one already contained in U . This formula, together with

$$U = \int_0^T C_V dT' + \text{constant} \quad (11.17)$$

enables us to determine both U and A up to the same arbitrary additive constant from measurements of C_V .

To illustrate the practical use of these formulas we consider the melting point of solid quartz. The stable phase of quartz at low temperatures is a crystalline solid. The liquid phase (glass), however, can be supercooled and can exist in metastable equilibrium far below the melting point. Hence a direct measurement of the melting point is difficult. It can, however, be determined indirectly through the use of (11.16). Let the specific heat c_V of both solid and liquid quartz be measured through a range of temperatures at a fixed volume V . Let Δc_V denote their difference, which is a function of temperature. Then the difference in internal energy per unit mass of the two phases is obtained by numerically integrating Δc_V at constant V :

$$\Delta u = \int \Delta c_V dT' \quad (11.18)$$

Using (11.17) we have, for the difference in free energy per unit mass of the two phases,

$$\Delta a = \Delta u - T \int_0^T \frac{\Delta c_V}{T'} dT' \quad (11.19)$$

Plotting Δu and Δa as a function of T at a fixed V , we should obtain a graph that looks qualitatively like that shown in Fig. 11.1. The melting point is the temperature at which $\Delta a = 0$, since the condition of phase equilibrium at fixed T and V is the equality of the free energies per unit mass. In practice the point at which $\Delta a = 0$ may be obtained either by direct integration up to that point, or by extrapolation.

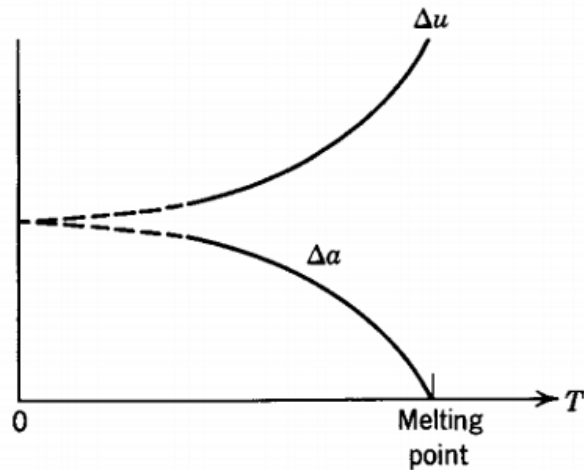


Fig. 11.1. Determination of the melting point through use of the third law

11.2. Euler's equation and the Gibbs-Duhem relation

We start from the first law for reversible changes of states for a system which is as general as possible. We assume that the system contains K particle species (chemical components), each of which has, of course, a separate particle number and chemical potential. Then we have

$$dU = T dS - p dV + \sum_{i=1}^K \mu_i dN_i \quad (11.20)$$

If in addition further forms of work can be exchanged, for instance, electric or magnetic work, other terms have to be added which have, however, quite analogous forms. Thus, the extensive internal energy U has to be interpreted as a function of the extensive state variables S, V, N_1, \dots, N_K . Now in general, an extensive state variable is proportional to the absolute size of the system. In other words, if one doubles all extensive state variables, all other extensive quantities also become twice as large. Especially for the internal energy this means that

$$U(\alpha S, \alpha V, \alpha N_1, \dots, \alpha N_K) = \alpha U(S, V, N_1, \dots, N_K) \quad (11.21)$$

if α is the enlargement factor. One calls functions which have this property *homogeneous functions of first order*. All extensive variables are homogeneous functions of first order of the other extensive variables. On the other hand, the intensive variables are homogeneous functions of *zeroth* order of the extensive variables,

$$T(\alpha S, \alpha V, \alpha N_1, \dots, \alpha N_k) = T(S, V, N_1, \dots, N_k) \quad (11.22)$$

i.e., they do *not* change if we divide or duplicate the system.

Equation (11.21) has far-reaching consequences. For if we consider an infinitesimal increase of the system ($\alpha = 1 + \epsilon$ with $\epsilon \ll 1$), we can expand the left-hand side in a Taylor series:

$$U((1 + \epsilon)S, \dots) = U + \frac{\partial U}{\partial S} \epsilon S + \frac{\partial U}{\partial V} \epsilon V + \dots + \frac{\partial U}{\partial N_K} \epsilon N_K \quad (11.23)$$

If we insert this into Equation (11.21) and consider that according to Equation (11.20)

$$\frac{\partial U}{\partial S} = T, \quad \frac{\partial U}{\partial V} = -p, \quad \frac{\partial U}{\partial N_1} = \mu_1, \quad \dots, \quad \frac{\partial U}{\partial N_K} = \mu_K \quad (11.24)$$

it follows that

$$U((1 + \epsilon)S, \dots) = U + \epsilon U = U + \epsilon \left(TS - pV + \sum_i \mu_i N_i \right) \quad (11.25)$$

i.e., Euler's equation is valid,

$$U = TS - pV + \sum_i \mu_i N_i \quad (11.26)$$

In other words, from Eq (11.21) it follows that Eq (11.20) may be trivially integrated. This is by no means obvious since according to Eq (11.24) T , p and μ_i are functions of S , V and N_i . If we calculate the total differential of Euler's equation, it holds that

$$dU = T dS - p dV + \sum_i \mu_i dN_i + S dT - V dp + \sum_i N_i d\mu_i \quad (11.27)$$

If we compare this with Eq (11.20), obviously the condition

must always be fulfilled (plus additional terms, if other state variables are necessary). One calls Eq (11.27) the *Gibbs-Duhem relation*. It means that the intensive variables

T , p , μ_1, \dots, μ_K which are conjugate to the extensive variables S , V , N_1, \dots, N_K are not all independent of each other. In principle this can be readily understood, since from three extensive state variables, e.g., S , V and N , one can derive only two independent intensive state variables, e.g., S/N and V/N . All other combinations can be expressed by these. In Eq (11.27) of course S , V , N_1, \dots, N_K are now functions of the variables

T , p , μ_1, \dots, μ_K , and this equation provides the possibility to eliminate one of these variables.

11.3. Jacobi transformations

A frequently occurring problem in thermodynamics is the transformation of variables in state functions. Such transformations must not be confused with the Legendre transformation. For the latter we have not simply replaced one variable in the internal energy by another, but have defined a new physical quantity, which is especially convenient for a certain system. In the following we want to investigate pure transformations of variables in the same physical quantity.

In general, the Jacobi determinant for the transformation from the variables (x_1, x_2, \dots, x_n) to the new variables (u_1, u_2, \dots, u_n) is defined by

$$J(x_1, \dots, x_n) = \begin{vmatrix} \frac{\partial u_1}{\partial x_1} & \frac{\partial u_1}{\partial x_2} & \dots & \frac{\partial u_1}{\partial x_n} \\ \frac{\partial u_2}{\partial x_1} & \frac{\partial u_2}{\partial x_2} & \dots & \frac{\partial u_2}{\partial x_n} \\ \vdots & \vdots & \vdots & \vdots \\ \frac{\partial u_n}{\partial x_1} & \frac{\partial u_n}{\partial x_2} & \dots & \frac{\partial u_n}{\partial x_n} \end{vmatrix} \quad (11.28)$$

It is also denoted as

$$J(x_1, \dots, x_n) = \frac{\partial(u_1, \dots, u_n)}{\partial(x_1, \dots, x_n)} \quad (11.29)$$

According to the rules for multiplication of determinants

$$\frac{\partial(u_1, \dots, u_n)}{\partial(w_1, \dots, w_n)} \frac{\partial(w_1, \dots, w_n)}{\partial(x_1, \dots, x_n)} = \frac{\partial(u_1, \dots, u_n)}{\partial(x_1, \dots, x_n)} \quad (11.30)$$

This is nothing but a generalized chain rule. For $n = 1$ Eq. (11.30) simply reads

$$\frac{du}{dw} \frac{dw}{dx} = \frac{du}{dx} \quad (11.31)$$

Exchange of columns or rows in the Jacobi determinant yields a minus sign. Because of Eq. (11.30) the Jacobi determinant of the reverse transformation

$$\frac{\partial(x_1, \dots, x_n)}{\partial(u_1, \dots, u_n)} = \left(\frac{\partial(u_1, \dots, u_n)}{\partial(x_1, \dots, x_n)} \right)^{-1} \quad (11.32)$$

is just the inverse of the original transformation.

Especially useful is the denotation of a derivative as a Jacobi determinant,

$$\frac{\partial u}{\partial x_1} \Big|_{x_2, x_3, \dots, x_n} = \frac{\partial(u, x_2, \dots, x_n)}{\partial(x_1, x_2, \dots, x_n)} = \begin{vmatrix} \frac{\partial u}{\partial x_1} & & 0 \\ & 1 & \\ & & \ddots \\ 0 & & & 1 \end{vmatrix} \quad (11.33)$$

since u can only depend on x_1 .

11.4. Gibbs's phase rule

We now want to return to the important problem of how many state variables are actually necessary to uniquely determine the state of a system. To this end, we start from an isolated system which contains K different particle species (chemical components) and P different phases (solid, liquid, gaseous, . . .). Each phase can be understood as a partial system of the total system and one can formulate the first law for each phase, where we denote quantities of the i^{th} phase by superscript $i = 1, \dots, P$. For reversible changes of state we have

$$dU^{(i)} = T^{(i)} dS^{(i)} - p^{(i)} dV^{(i)} + \sum_{l=1}^K \mu_l^{(i)} dN_l^{(i)}, \quad i = 1, 2, \dots, P \quad (11.34)$$

Other terms also may appear, if electric or magnetic effects play a role. However, since the corresponding terms have a quite analogous form, Eq (11.35) is sufficiently general. In this formulation of the first law, $U^{(i)}$ of phase i is a function of the extensive state variables $S^{(i)}, V^{(i)}, N_1^{(i)}, \dots, N_K^{(i)}$; i.e., it depends on $K + 2$ variables (if further terms appear in Eq.(11.34), the number of variables is larger). Altogether we therefore have $P(K + 2)$ extensive state variables. If the total system is in thermodynamic equilibrium, we have in addition the following conditions for the intensive state quantities

$$\begin{aligned} T^{(1)} &= T^{(2)} = \dots = T^{(P)} && \text{Thermal equilibrium} \\ p^{(1)} &= p^{(2)} = \dots = p^{(P)} && \text{Mechanical equilibrium} \\ \mu_l^{(1)} &= \mu_l^{(2)} = \dots = \mu_l^{(P)} \quad l = 1, \dots, K && \text{Chemical equilibrium} \end{aligned} \quad (11.35)$$

Each line contains $P - 1$ equations, so that Eq (11.35) is a system of $(P - 1)(K + 2)$

equations. Since $T^{(i)}$, $p^{(i)}$, and $\mu_i^{(i)}$ are functions of $S^{(i)}$, $V^{(i)}$, and $N_i^{(i)}$ we can eliminate one variable with each equation. Thus, we only require

$$(K + 2)P - (K + 2)(P - 1) = K + 2 \quad (11.36)$$

extensive variables to determine the equilibrium state of the total system. As we see, this number is *independent of the number of phases*. If we now consider that exactly P extensive variables (e.g., $V^{(i)}$, $i = 1, \dots, P$) determine the size of the phases (i.e., the volumes occupied by each), one needs

$$F = K + 2 - P \quad (11.37)$$

intensive variables. Eq (11.37) is named after J.W. Gibbs and is called *Gibbs' phase rule*. It is readily understood with the help of concrete examples. Let us for instance think of a closed pot containing a vapor. With $K = 1$ we need 3 ($= K + 2$) extensive variables for a complete description of the system, e.g., S , V , and N . One of these (e.g., V), however, determines only the size of the system. The intensive properties are completely described by $F = 1 + 2 - 1 = 2$ intensive variables, for instance by the pressure and the temperature. Then also U/V , S/V , N/V , etc. are fixed and by additionally specifying V one can also obtain all extensive quantities.

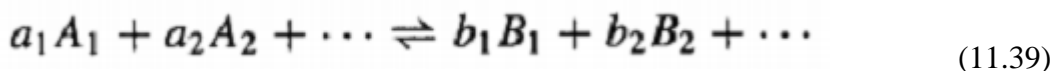
If both vapor and liquid are in the pot and if they are in equilibrium, we can only specify one intensive variable, $F = 1 + 2 - 2 = 1$, e.g., the temperature. *The vapor pressure assumes automatically its equilibrium value*. All other intensive properties of the phases are also determined. If one wants in addition to describe the extensive properties, one has to specify for instance V^{li} and V^v , i.e., one extensive variable for each phase, which determines the size of the phase (of course, one can also take N^{li} and N^v , etc.).

Finally, if there are vapor, liquid, and ice in equilibrium in the pot, we have $F = 1 + 2 - 3 = 0$. This means that all intensive properties are fixed: pressure and temperature have definite values. Only the size of the phases can be varied by specifying V^{li} , V^s , and V^v . This point is also called *triple point* of the system. If we have various chemical components (e.g., air and water) or further terms in Eq (11.34), all assertions hold with a correspondingly larger value of K .

If a system consists of various particle species (chemical components), reactions between particles are often possible, which transform one species into another. Then certain reaction equations, as are often used in chemistry, are valid, for example:



In general we can write such reaction equations as



where a_i particles of species A_i react with a_2 particles of species A_2 to form b_1 particles of species B_1 , etc. The numbers a_i and b_i are the *stoichiometric coefficients* from chemistry. Eq (11.40) is a condition for the particle numbers N_{A_1} , N_{A_2} , \dots and N_{B_1} , N_{B_2} , \dots ,

since the changes of these numbers are mutually related by the reaction equation. For instance, let dR be an arbitrary number of reactions of the type of eq(11.39). Then it must hold that

$$\begin{aligned}
 dN_{A_1} &= -a_1 dR \\
 dN_{A_2} &= -a_2 dR \\
 &\vdots \\
 dN_{B_1} &= b_1 dR \\
 dN_{B_2} &= b_2 dR \\
 &\vdots
 \end{aligned}
 \tag{11.40}$$

The signs are determined by the fact that in each reaction a_1 particles of species A_1 and a_2 particles of species A_2 , etc. vanish, while b_1 particles of species B_1 are created. As we already know, the equilibrium condition for an isolated system reads

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_i \mu_i dN_i = 0
 \tag{11.41}$$

However, if U and V are constant in such a system, we have from Eq (11.41) the condition

$$\sum_i \mu_i dN_i = 0
 \tag{11.42}$$

If we insert the dN_i from Eq(11.40) into Eq (11.42), we have after dividing by the common factor dR

$$\sum_i a_i \mu_i = \sum_j b_j \mu_j
 \tag{11.43}$$

This is a constraint for the chemical potentials, which depends on the reaction equation. With every reaction equation we are therefore able to eliminate another intensive variable. If we have, for instance, R reaction equations, we can formulate an *extended Gibbs' phase rule*:

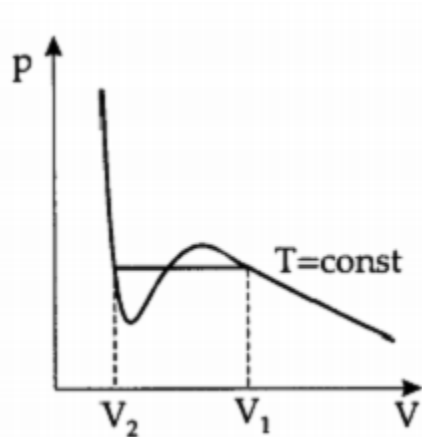
$$F = K + 2 - P - R
 \tag{11.44}$$

Also, the total number of extensive variables now becomes smaller ($K + 2 - R$). The reason is that for each phase only $K - R$ components have independent particle numbers; the other numbers can be calculated with the help of the reaction equations.

11.5. Phase equilibrium and Maxwell construction

When we introduced van der Waals' equation of state we already mentioned some inconsistencies of this equation. The isotherms of van der Waals' equation (Fig 11.2)

$$\left(p + \frac{N^2 a}{V^2} \right) (V - Nb) = NkT \quad (11.45)$$



show regions of negative pressure as well as mechanically unstable regions having $\partial p/\partial V > 0$, where the gas wants to compress itself. Both cases are certainly unphysical.

We now want to show that these contradictions can be resolved by considering the phase transition from gas to liquid. Most gases, if we compress them at constant temperature, start to liquefy below a critical temperature at a certain volume V_1 .

In equilibrium between vapor and liquid, however, a certain vapor pressure p_v is established, which we have already calculated for an ideal gas from the equilibrium conditions

$$p_{li} = p_v, \quad T_{li} = T_v, \quad \mu_{li}(p, T) = \mu_v(p, T) \quad (11.46)$$

Fig 11.2. Isotherms of the van der Waals

The vapor pressure $p_v(T)$ is solely a function of temperature and does not depend on the vapor volume V , so that one obtains a horizontal isotherm in the pV diagram. An isothermal compression beyond the point of liquefaction V_1 has the effect that more and more vapor is converted into liquid, until at point V_2 the whole amount of gas is liquefied. If we further compress the system the pressure increases strongly because of the small compressibility of the fluid.

It is remarkable that *neither the density of the liquid (given by N/V_2) nor the density of the vapor (given by N/V_1) changes during this phase transition*. The increase of the average density, which is enforced by the transition from V_1 to V_2 , is solely caused by the creation of more and more liquid and the simultaneous reduction of the partial volume of the vapor phase.

The pressure p_v can be calculated from Eq (11.46), **if the temperatures and chemical potentials of the vapor and liquid are known**. Now, however, we want to present a method known as the *Maxwell construction*: the internal energy $U(V, T)$ at fixed particle number is a state function, which depends only on the volume for a given temperature. For constant temperature we therefore have the energy difference

$$\Delta U = T(S_2 - S_1) - \int_{V_1}^{V_2} p(v) dV \quad (11.47)$$

between two volumes V_1 and V_2 with the entropies S_1 and S_2 for the purely gaseous and purely liquid phases, respectively. Since U has an exact differential, it cannot matter whether ΔU is calculated along the direct path of constant vapor pressure ($p(V) = p_{li} = p_v = \text{const.}$) or along the van der Waals isotherm, for which the following holds ($T = \text{const.}$):

$$p(V) = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2} \quad (11.48)$$

In the first case we simply have ($\Delta Q = T(S_2 - S_1)$ is the latent heat of the phase transition)

$$\Delta U_1 = \Delta Q - p_v(V_2 - V_1) \quad (11.49)$$

and in the case of the van der Waals isotherm we have

$$\Delta U_2 = \Delta Q - NkT \ln \frac{V_2 - Nb}{V_1 - Nb} - N^2a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \quad (11.50)$$

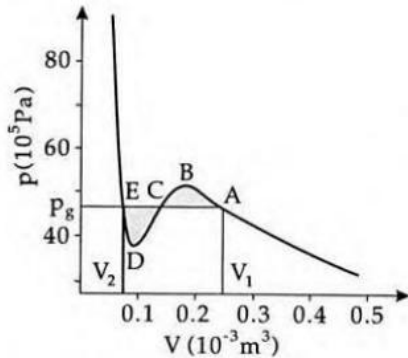


Fig 11.3. Maxwell construction

From the condition

$$\Delta U_1 = \Delta U_2$$

$$\Leftrightarrow -p_v(V_2 - V_1) = -NkT \ln \frac{V_2 - Nb}{V_1 - Nb}$$

$$- N^2a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \quad (11.51)$$

one can, in principle, determine the unknown pressure p_v as well as the also unknown volumes V_1 and V_2 , if one solves van der Waals' equation for $V_1(p_v, T)$ and $V_2(p_v, T)$. (Remark: For a given p_v and T the van der Waals isotherm has also a third (unstable) solution at C , Fig 11.3). However,

Eq.(11.51) can be understood far more easily. It tells us that the area $p_v(V_2 - V_1)$ of the rectangle between V_1 and V_2 below the unknown vapor pressure equals the area below the van der Waals isotherm.

Or, in other words: the area between the straight line of the vapor pressure and the van der Waals isotherm ABC has to equal the analogous area CDE . (See Fig 11.3). This is the well-known *Maxwell construction*. The explicit calculation following Eq (11.51) is equivalent to the Maxwell construction. If one draws the points A and E for a couple of isotherms in a diagram, one obtains the boundary of the phase coexistence region (Fig 11.4) In this region the van der Waals isotherms have to be replaced by straight lines for the vapor pressure. The maximum of the coexistence curve, the so-called *critical point* K , lies on the isotherm, which only has a saddle point (instead of the extrema D and B). Above the critical temperature the Maxwell construction is no longer possible; liquid and gas are no longer distinguishable.

With the help of Fig 11.5 one can also understand another phenomenon. If one isothermally compresses a real gas below the critical temperature until all of the gas is liquefied, then increases the temperature at constant volume V_2 to a point above the critical temperature, and then expands the gas to the initial volume V_1 at constant temperature, one can regain the initial (gaseous) state without a noticeable second phase transition (by a temperature decrease at constant volume).

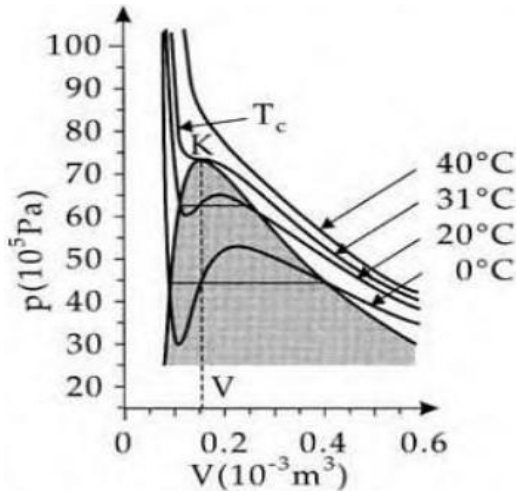


Fig 11.4. Critical point and critical isotherm

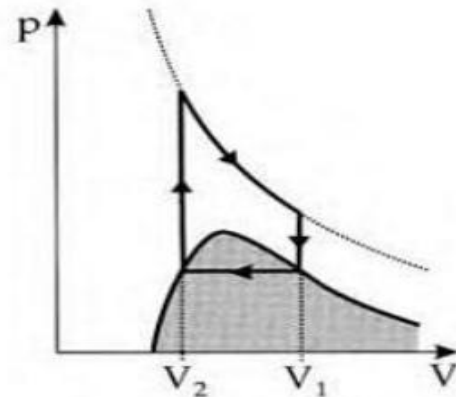


Fig 11.5. Scheme of considered process

This means that above the critical temperature (the critical isotherm) a distinction between the gaseous and liquid states is no longer reasonable! This distinction is only possible below the critical temperature, since liquids and gases have very different densities, and thus a *phase boundary surface* exists between the phases. At the critical point, however, the density of the liquid and the gas assume equal values, and a distinction between the phases is no longer possible above the critical temperature.

Because of the importance of the critical point we want to calculate the critical state quantities T_{cr} , p_{cr} , and V_{cr} from van der Waals' equation. The critical point is characterized by the fact that both derivatives vanish (saddle point):

$$\left. \frac{\partial p}{\partial V} \right|_{T_{cr}, V_{cr}} = 0, \quad \left. \frac{\partial^2 p}{\partial V^2} \right|_{T_{cr}, V_{cr}} = 0 \quad (11.52)$$

or

$$-\frac{NkT_{cr}}{(V_{cr} - Nb)^2} + \frac{2aN^2}{V_{cr}^3} = 0, \quad 2\frac{NkT_{cr}}{(V_{cr} - Nb)^3} - 6\frac{aN^2}{V_{cr}^4} = 0 \quad (11.53)$$

If one brings the negative terms to the other sides of the respective equations and divides one equation by the other, one obtains $V_{cr} - Nb = \frac{2}{3} V_{cr}$, and thus

$$V_{cr} = 3Nb \quad (11.54)$$

If one inserts this into Eq.(11.53), one gets

$$T_{cr} = \frac{2aN}{kV_{cr}^3} (V_{cr} - Nb)^2 = \frac{2aN}{kV_{cr}^3} \frac{4}{9} V_{cr}^2 = \frac{8a}{27kb} \quad (11.55)$$

from V_{cr} and T_{cr} it finally follows with van der Waals' equation that

$$p_{cr} = \frac{Nk8a}{2bN27kb} - \frac{aN^2}{9b^2N^2} = \frac{a}{27b^2} \quad (11.56)$$

The critical state quantities are therefore uniquely determined by the parameters a and b . Hence, for all gases one should have

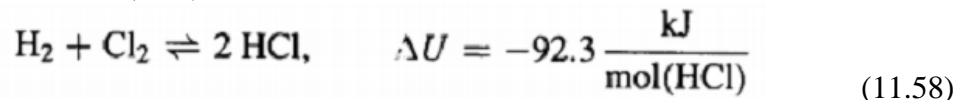
$$\frac{p_{cr} V_{cr}}{NkT_{cr}} = \frac{a3bN27kb}{27b^2Nk8a} = \frac{3}{8} = 0.375 \quad (11.57)$$

Experimentally one finds for Eq(11.57) numbers between 0.25 and 0.35, which once again confirms the qualitative usefulness of van der Waals' equation. On the other hand, a measurement of the critical data of a gas yields a comfortable method for determining the parameters a and b .

By the way, one can also experimentally find the (metastable) parts AB and DE of the van der Waals isotherm in nonequilibrium situations. If a gas is very carefully compressed at constant temperature (avoiding concussions and condensation nuclei), one may follow the isotherm beyond point A nearly up to point B . The same holds for the other side for an isothermal expansion beyond point E to point D . One speaks of *delayed condensation* or *delayed boiling*, respectively. The system is metastable in this region and switches over to the stable phase coexistence state even under small perturbations. The same phenomena can be observed for isochoric temperature changes. Here one speaks of superheated liquid or supercooled vapor, respectively. Analogous phenomena occur for the solid–liquid phase transition.

11.6. The law of mass action

Let us consider a vessel containing a mixture of ideal gases which mutually react, for instance according to Eq(11.6). To take a concrete example, let us take the reaction



where an energy of -92.3 kJ/mol is released in an isolated system per mole of hydrochloric acid. At first we have to extend our previous formula for the ideal gas. The purely thermal energy content of an ideal gas of N particles at temperature T was $U = 3NkT/2$. However, this energy does not take into account additional internal energies of different particle species due to their internal structures, different masses, etc. For instance, two molecules, H_2 and

Cl_2 , differ from two HCl molecules by the chemical binding energy which is released in the reaction. Thus, we have to consider these additional energies in the internal energy and write for each particle species i , with N_i particles at temperature T and pressure p_i :

$$U_i(N_i, T, p_i) = N_i \epsilon_i + \frac{3}{2} N_i kT, \quad p_i V = N_i kT \quad (11.59)$$

The energies ϵ_i define the different zero points of the energy scales of the respective particles. The difference $2\epsilon_{\text{HCl}} - \epsilon_{\text{H}_2} - \epsilon_{\text{Cl}_2}$, for instance, is the binding energy difference between two molecules of HCl and one molecule of H_2 and Cl_2 , respectively. Consequently, the constants ϵ_i appear also in the chemical potentials of the ideal gases since also the energy scales of the chemical potentials are shifted with respect to each other,

$$\mu_i(p_i, T) = \epsilon_i + kT \left(\frac{\mu_{i0}(p_0, T_0)}{kT_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p_i} \right) \right\} \right) \quad (11.60)$$

Of course, in the chemical potentials one must insert only the partial pressure of each component, since each component itself fulfills the thermodynamic relations for an ideal gas with N_i particles and pressure p_i at the temperature T common for all particles. Then, the total pressure of the system is $p = \sum_i p_i$ and fulfills $pV = NkT$ with $N = \sum_i N_i$. In particular, the ratio $p_i/p = N_i/N = X_i$ is the molar fraction of the component i and thus a measure for the concentration of particle species i . We can rewrite the equation for $\mu_i(p_i, T)$ using $p_0/p_i = (p_0/p) \cdot (p/p_i) = p_0/(pX_i)$,

$$\begin{aligned} \mu_i(p_i, T) &= \epsilon_i + kT \left(\frac{\mu_i(p_0, T_0)}{kT_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \frac{1}{X_i} \right) \right\} \right) \\ &= \epsilon_i + kT \left(\frac{\mu_i(p_0, T_0)}{kT_0} - \ln \left\{ \left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right\} \right) + kT \ln X_i \\ &= \mu_i(p, T) + kT \ln X_i \end{aligned} \quad (11.61)$$

This equation means that the chemical potential of component i with the partial pressure p_i in the total pressure p , or with the concentration X_i in the mixture, respectively, can be calculated from the chemical potential of a pure gas of particle species i with total pressure p , if one introduces an additional concentration dependence of the chemical potential. This has the advantage that now all chemical potentials refer to the same total pressure p , and the different partial pressures are taken into account via the concentration X_i . (Note that $\ln X_i = 0$ for $X_i = 1$, pure component i). By the way, this concentration dependence is valid not only for ideal gases, but also for dilute solutions of different components in a solvent. Such solutions are called *ideal* if the concentration dependence of the chemical potential of particle species i fulfills Eq (11.61). Now we can insert Eq (11.61) into the equilibrium condition, Eq (11.43), and we obtain in general

$$\sum_i a_i \mu_i(p_i, T) = \sum_j b_j \mu_j(p_j, T)$$

$$\sum_i a_i \mu_i(p, T) - \sum_j b_j \mu_j(p, T) = kT \left(\sum_i b_j \ln X_j - \sum_i a_i \ln X_i \right)$$

$$\exp \left\{ \frac{1}{kT} \left(\sum_i a_i \mu_i(p, T) - \sum_j b_j \mu_j(p, T) \right) \right\} = \frac{X_{B_1}^{b_1} X_{B_2}^{b_2} \dots}{X_{A_1}^{a_1} X_{A_2}^{a_2} \dots} \quad (11.62)$$

where we have divided by kT in the last step, exponentiated, and exploited the properties of the logarithm. Eq (11.62) is the *law of mass action*, which determines the equilibrium concentrations of products X_{B_1}, X_{B_2}, \dots and reactants X_{A_1}, X_{A_2}, \dots in a chemical reaction according to Eq (11.39). One often writes for the lefthand side in Eq (11.62)

$$K(p, T) = \exp \left\{ -\frac{1}{kT} \left(\sum_j b_j \mu_j(p, T) - \sum_i a_i \mu_i(p, T) \right) \right\} \quad (11.63)$$

This is the equilibrium constant of the reaction at the total pressure p and the temperature T . For ideal gases we can readily recalculate this constant for different pressures and temperatures, since we know the chemical potentials $\mu_i(p, T)$ for all pressures and temperatures, if we have determined them once for a standard pressure p_0 and a standard temperature T_0 —see Eq (11.60). To this end, we form the ratio of $K(p, T)$ to $K(p_0, T_0)$ and find, with Eq (11.60) that

$$K(p, T) = K(p_0, T_0) \exp \left\{ -\Delta\epsilon \left(\frac{1}{kT} - \frac{1}{kT_0} \right) \right\}$$

$$\times \left[\left(\frac{T}{T_0} \right)^{5/2} \left(\frac{p_0}{p} \right) \right]^{\sum_j b_j - \sum_i a_i} \quad (11.64)$$

with $\Delta\epsilon = \sum_j b_j \epsilon_j - \sum_i a_i \epsilon_i$, the energy gained or required per reaction (the binding energy difference between the products and the reactants). Let us first consider the pressure dependence of the equilibrium constant $K(p, T)$. This depends on whether $\sum_i b_j - \sum_i a_i$ is greater than, less than, or equal to zero. For our example in Eq (11.58), for instance, $a_{H_2} = a_{Cl_2} = 1$ and $b_{HCl} = 2$, i.e., $a_{H_2} + a_{Cl_2} - b_{HCl} = 0$. In the ideal case, such reactions do not show any dependence on the pressure, while for $N_2 + 3 H_2 \rightleftharpoons 2 NH_3$ we have $\sum_j b_j - \sum_i a_i = -2$. For the latter reaction $K(p, T_0) = K(p_0, T_0)(p/p_0)^2$. Hence, the equilibrium constant increases with increasing pressure. According to Equation (11.62) the concentration of the products has to increase with respect to that of the

reactants. The synthesis of ammonia from the elements is therefore more efficient at high pressure than at atmospheric pressure. For this reaction $\Delta\epsilon < 0$ and the equilibrium constant $K(p_0, T) = K(p_0, T_0) \exp\{-\Delta\epsilon(1/kT - 1/kT_0)\}(T_0/T)^5$ decreases with increasing temperature. To gain a high amount of ammonia one should therefore work at low temperatures. However, in practice the technically very important ammonia synthesis (fertilizer production) is performed at temperatures up to 500°C (and pressures up to 10⁸ Pa). This is, from a technical point of view, more convenient than synthesis at room temperature. Our equilibrium considerations namely do not tell us how fast a system assumes equilibrium. In general, the relaxation times needed to reach equilibrium are larger for lower temperatures. At low temperatures the reaction rate is also small. The gain of ammonia per unit time in a continuous reaction, where the reaction products are permanently removed from the system, may therefore be larger at high temperatures, although the equilibrium is actually shifted to disadvantageous values. We do not want to discuss these problems, which belong to the study of reaction dynamics, in more detail. Let us only mention that the reaction rate can be increased by catalytic agents which are not changed by the reaction. Here one exploits the fact that the chemical potential of the materials participating in the reaction is changed if they are absorbed on the surface of certain materials, i.e. if they cling to the surface of the catalyst. Thus, catalytic agents are mainly porous materials with a surface which is as large as possible.

In the following we want to use the concentration dependence of the chemical potential of component i

$$\mu_i(p, T, X_i) = \mu_i(p, T, X_i = 1) + kT \ln X_i \quad (11.65)$$

also for ideal solutions. Here $\mu_i(p, T, X_i)$ is the chemical potential of particle species i in a system at pressure p , temperature T , and with concentration X_i . This can be calculated according to Eq (11.65) from the chemical potential $\mu_i(p, T, 1)$ of the pure component i ($X_i = 1$) at the same p and T . This is a phenomenological equation of state like the ideal gas law and only experience can justify this ansatz. In nonideal solutions Equation (11.65) is not valid. However, one can retain the form of Eq (11.65) also for nonideal systems, if one transforms the term $kT \ln X_i$ to include the activities $kT \ln f_i X_i$, i.e., if one introduces effective concentrations. The f_i are phenomenological parameters which describe the deviations from the ideal case and may depend on the pressure, temperature, and concentration. The form of the law of mass action remains unchanged; one has only to replace the X_i by the effective concentrations $f_i X_i$.

11.7. The Joule-Thomson effect

From daily experience we know that a container filled with gas under large pressure cools down when the gas escapes (e.g., for sprays). Since no external work is performed in the expansion ($\delta A = 0$) and since the expansion happens very fast so that no heat is exchanged with the surroundings ($\delta Q = 0$), this process is an irreversible adiabatic expansion of a real

gas. Since $\delta A = 0$ and $\delta Q = 0$ we also have $dU = 0$. For an ideal gas or a van der Waals gas we can determine the change of the temperature. For the latter case we have already calculated the internal energy $U(V, T)$ as follows

$$U(V, T) = U_0(V_0, T_0) + C_V(T - T_0) - N^2 a \left(\frac{1}{V} - \frac{1}{V_0} \right) \quad (11.66)$$

For an ideal gas we simply put $a = 0$. With $\Delta U = 0$ it follows that

$$\Delta T = \frac{N^2 a}{C_V} \left(\frac{1}{V} - \frac{1}{V_0} \right). \quad (11.67)$$

The maximum change of temperature ΔT for the expansion into a very large volume ($V \rightarrow \infty$) is

$$\Delta T = - \frac{N^2 a}{C_V V_0} \quad (11.68)$$

For ideal gases we thus have $\Delta T = 0$, while for real van der Waals gases ($a > 0$) the temperature change is negative. The reason is that in the expansion internal work is performed against the molecular attractive forces, the strength of which is measured via the constant a . We want to investigate the irreversible expansion of an arbitrary real gas in somewhat more detail. To have definite thermodynamic conditions at every moment of the expansion one needs a device which slows down the spontaneous and thus irreversible expansion of the gas, so that one has a certain well-defined pressure at each moment. One achieves this via a porous plug (throttle), which permits only a small amount of gas to pass at each moment. Simultaneously the pressures on both sides of the throttle are continuously kept constant.

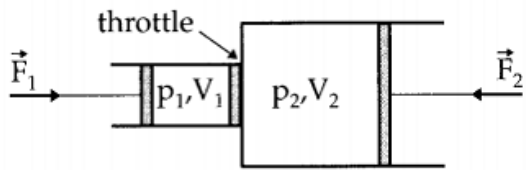


Fig 11.6. Joule-Thomson experiment

A possible practical set-up is shown in Fig 11.6. Pistons 1 and 2 (in practice the role of the pistons is assumed by a pump) provide at each moment a steady flood of gas from pressure p_1 to the smaller pressure p_2 , whereby the volume V_2 increases. We must now isolate the whole set-up well to provide adiabaticity ($\delta Q = 0$). We consider a certain amount of gas which has the volume V_1 at pressure p_1 and which is pumped to the other side of the throttle where it then takes the volume V_2 at pressure p_2 . The change of the internal energy of this amount of gas is given by the work done on the left side to expell the gas at constant pressure p_1 from volume V_1 , which is $p_1 V_1$ minus the work which is performed by the gas at constant pressure p_2 against piston 2, so that the gas takes the volume V_2 , which is $p_2 V_2$.

$$U_2 - U_1 = p_1 V_1 - p_2 V_2 \quad (11.69)$$

or

$$U_1 + p_1 V_1 = U_2 + p_2 V_2 \quad (11.70)$$

The enthalpy $U + pV$ remains constant on both sides; one says that the process happens isenthalpically. We now want to calculate for a given pressure change dp the change in temperature dT at constant enthalpy. To this end we assume H to be a function of T and p :

$$dH = \left. \frac{\partial H}{\partial T} \right|_p dT + \left. \frac{\partial H}{\partial p} \right|_T dp \quad (11.71)$$

For $H = \text{const.}$ we have $dH = 0$, and thus the temperature change under a change of pressure is

$$\left. \frac{\partial T}{\partial p} \right|_H = - \frac{\left. \frac{\partial H}{\partial p} \right|_T}{\left. \frac{\partial H}{\partial T} \right|_p} \quad (11.72)$$

Here we have simply $\partial H / \partial T|_p = C_p$. We also want to express $\partial H / \partial p|_T$ by simply measurable quantities. With ($N = \text{const.}$):

$$dH = T dS + V dp \quad (11.73)$$

we have

$$\left. \frac{\partial H}{\partial p} \right|_T = T \left. \frac{\partial S}{\partial p} \right|_T + V = V - T \left. \frac{\partial V}{\partial T} \right|_p \quad (11.74)$$

where we have used the Maxwell relation $\partial S / \partial p|_T = -\partial V / \partial T|_p$. Finally the Joule–Thomson coefficient δ is given by

$$\begin{aligned} \left. \frac{\partial T}{\partial p} \right|_H &= \delta = \frac{1}{C_p} \left(T \left. \frac{\partial V}{\partial T} \right|_p - V \right) \\ &= \frac{V}{C_p} (T\alpha - 1) \end{aligned} \quad (11.75)$$

where $\alpha V = \partial V / \partial T|_p$ is the isobaric expansion coefficient, which for an ideal gas has just the value $\alpha = 1/T$, so that (for an ideal gas) $\delta = 0$. We now want to evaluate Equation (11.75) for special equations of state of real gases. To this end, we use an approximation for

van der Waals' equation, since this equation is difficult to solve for V :

$$\left(p + \left(\frac{N}{V} \right)^2 a \right) (V - Nb) = NkT$$

$$\Leftrightarrow V = \frac{NkT}{p} - \frac{N^2 a}{pV} + Nb + \left(\frac{N}{V} \right)^2 \frac{Nab}{p} \quad (11.76)$$

Now we replace V in zeroth approximation by NkT/p on the righthand side. Moreover, we assume we have a fixed amount of gas (1 mole), i.e., $N = N_A$ and $Nk = R$. The constants a and b shall refer to 1 mole; i.e., we put $N_A^2 a \rightarrow a$ and $N_A b \rightarrow b$. Then V is equal to the molar volume v for which we obtain in a first successive approximation,

$$v = \frac{RT}{p} - \frac{a}{RT} + b + \frac{abp}{R^2 T^2} \quad (11.77)$$

From this we can calculate the required derivative,

$$T \left. \frac{\partial v}{\partial T} \right|_p = \frac{RT}{p} + \frac{a}{RT} - 2 \frac{abp}{R^2 T^2} \quad (11.78)$$

The difference $T \left. \frac{\partial v}{\partial T} \right|_p - v$ can thus be readily given in explicit terms, so that according to Eq.(11.75)

$$\delta = \left. \frac{\partial T}{\partial p} \right|_H = \frac{1}{C_p} \left(\frac{2a}{RT} - b - 3 \frac{abp}{R^2 T^2} \right) \quad (11.79)$$

For nitrogen, for instance, we have $a = 0.141 \text{ m}^6 \text{ Pa mol}^{-2}$ and $b = 0.03913 \cdot 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. At room temperature and a pressure $p = 10^7 \text{ Pa}$ Eq (11.79) yields $\delta_{\text{theo}} = 0.188^\circ\text{C}/10^5$

Pa, while the measured value is $\delta_{\text{exp}} = 0.141^\circ\text{C}/10^5 \text{ Pa}$.

Eq. (11.79) predicts not only cooling down under expansion ($\delta > 0$), but in certain regions also reheating. One calls the temperature–pressure curve at which δ just vanishes the *inversion curve*. In an expansion gases only cool down, if for a given pressure the initial temperature was smaller than the inversion temperature; in the other case they even heat up.

From Eq (11.79) we can calculate the inversion curve:

$$\delta = 0 \Leftrightarrow T_i^2 - \frac{2a}{Rb} T_i + \frac{3ap}{R^2} = 0 \quad (11.80)$$

As one observes, two inversion temperatures exist for each pressure below a certain critical

pressure p_{\max} . The inversion curve is a parabola in the Tp diagram, which separates the region of cooling from the region of reheating. Also shown in the diagram are the isenthalpics ($H(p, T) = \text{const.}$). The slope of these curves is just the Joule–Thomson coefficient, according to Eq (11.75). The inversion curve connects the maxima of the isenthalpics.

If the relaxation of the gas happens over a wide range of pressures, one has to integrate the Joule–Thomson coefficient δ over the pressure change (here we reverse the substitution $N_A^2 a \rightarrow a$ and $N_A b \rightarrow b$):

$$\begin{aligned} \Delta T &= \int_{p_0}^{p_1} \left. \frac{\partial T}{\partial p} \right|_H dp \\ &= \int_{p_0}^{p_1} \frac{N}{C_p} \left(\frac{2a}{kT} - b - 3 \frac{abp}{(kT)^2} \right) dp \end{aligned} \quad (11.81)$$

Here T and p , of course, are not independent variables. For each infinitesimal pressure change the temperature also changes in a fixed way. The variables T and p are mutually related via $H(p, T) = \text{const.}$, and the relaxation happens along an isenthalpic in Fig 11.7

The irreversible expansion of real gases has great technical importance for achieving very low temperatures, as well as in the liquefaction of technical gases. It is used, for example, in *Linde's liquefaction process* (Fig 11.8). To use the temperature decrease more efficiently one leads the expanded, cooled gas through a heat exchanger, whereby the highly compressed gas is further cooled down.

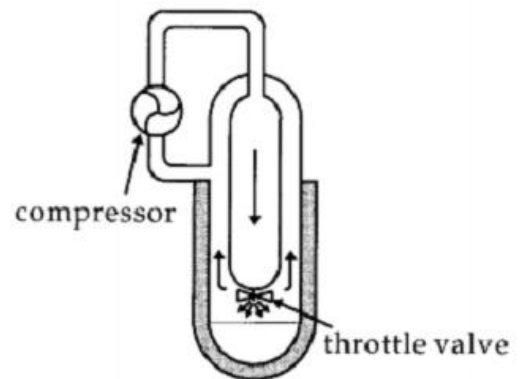
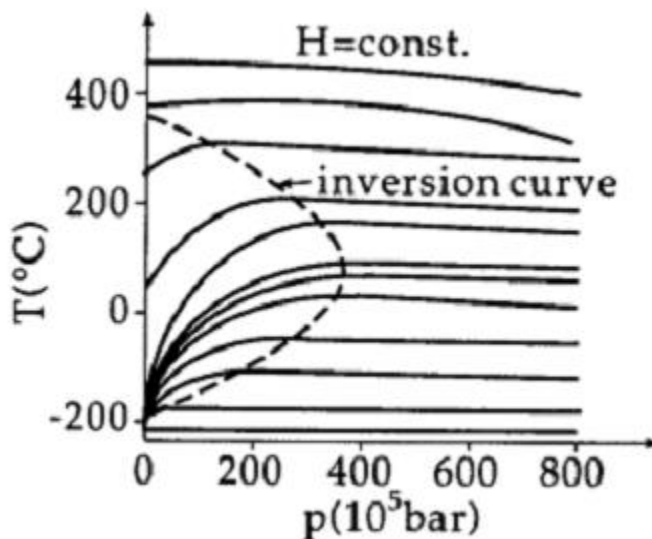


Fig 11.7. Experimental inversion curve and **Fig 11.8.** Linde's liquefaction process isenthalpics ($H = \text{const}$) for nitrogen (schematically)

However, this process works only for gases which have an inversion temperature (at a given compressor pressure) above that of room temperature (e.g., air, CO_2 , N_2 , ...).

For hydrogen precooling is necessary, since the inversion temperature of hydrogen ($\approx -80^\circ\text{C}$) lies below room temperature.

A temperature decrease always happens in the *reversible* expansion of real gases, since the gas has to additionally perform external work. This process, however, is more difficult to realize and is thus of no great technical importance.

While discussing the Joule–Thomson experiment we calculated the Joule–Thomson coefficient

$$\delta = \left. \frac{\partial T}{\partial p} \right|_H \quad (11.82)$$

If δ is to be expressed by the known enthalpy $H(T, p)$, one obtains this with the help of

$$\left. \frac{\partial T}{\partial p} \right|_H = \frac{\partial(T, H)}{\partial(p, H)} = \frac{\partial(T, H)}{\partial(p, T)} \frac{\partial(p, T)}{\partial(p, H)} = \frac{\partial(T, H)}{\partial(p, T)} \bigg/ \frac{\partial(p, H)}{\partial(p, T)} \quad (11.83)$$

or

$$\left. \frac{\partial T}{\partial p} \right|_H = - \frac{\partial(H, T)}{\partial(p, T)} \bigg/ \frac{\partial(p, H)}{\partial(p, T)} = - \left. \frac{\partial H}{\partial p} \right|_T \bigg/ \left. \frac{\partial H}{\partial T} \right|_p \quad (11.84)$$

which, of course, agrees with the result above.

11.8. Phase transition

The surface of the equation of state of a typical substance is shown in Fig. 11.9. where the shaded areas are cylindrical surfaces, representing regions of phase transition. The P - V and P - T diagrams are shown in Fig. 11.10. We study here the implications of the second law for these phase transitions.

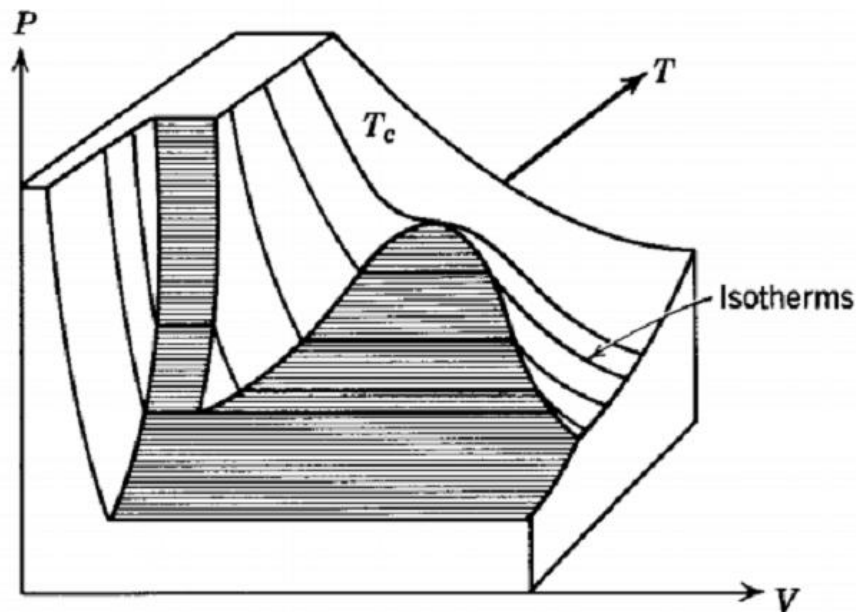


Fig. 11.9. Surface of equation of state of a typical substance (not to scale)

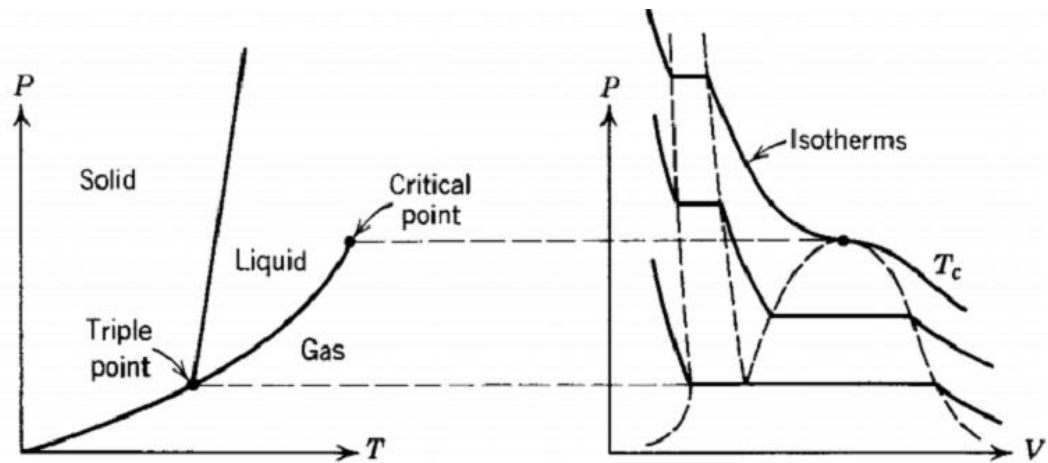


Fig. 11.10. P - V and P - T diagrams of a typical substance (not to scale)

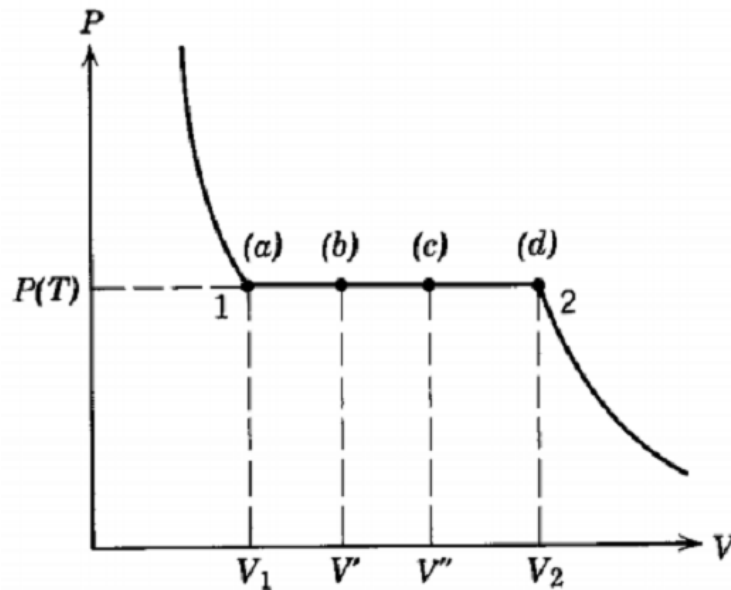


Fig. 11.11. An isotherm exhibiting a phase transition

Let us consider the transition between the gas phase and the liquid phase. The transition takes place at a constant temperature and pressure, as shown in Fig. 11.11. This pressure $P(T)$ is called the vapor pressure at the temperature T . Let the system be initially in state 1, where it is all liquid. When heat is added to the system, some of the liquid will be converted into gas, and so on until we reach state 2, where the system is all gas, as schematically shown in Fig. 11.12. The important facts are that

- (a) during the phase transition both P and T remain constant;
- (b) in the gas-liquid mixture the liquid exists in the same state as at 1 and the gas exists in the same state as at 2.

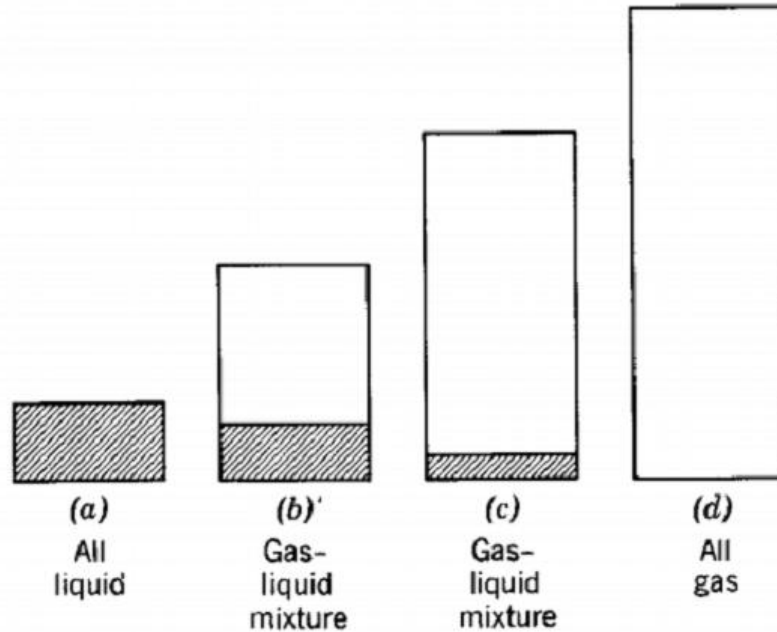


Fig. 11.12. Schematic illustration of a first-order phase transition. The temperature and the pressure of the system remain constant throughout the transition. The total volume of the system changes as the relative amount of the substance in the two phases changes, because the two phases have different densities.

As a result, knowing the properties of the states 1 and 2 suffices for a complete description of the phase transition. The isotherm in the P - V diagram is horizontal during the phase transition, because the gas phase has a smaller density than the liquid phase. Consequently, when a certain mass of liquid is converted into gas, the total volume of the system expands, although P and T remain unchanged. Such a transition is known as a “first-order transition.”

The dependence of the vapor pressure $P(T)$ on the temperature may be found by applying the second law. Consider a gas-liquid mixture in equilibrium at temperature T and vapor pressure $P(T)$. Let the mass of the liquid be m_1 and the mass of the gas be m_2 . If the system is in equilibrium with the given T and

$P(T)$, the Gibbs potential of this state must be at a minimum. That is, if any parameters other than T and P are varied slightly, we must have $\delta G = 0$. Let us vary the composition of the mixture by converting an amount δm of liquid to gas, so that

$$-\delta m_1 = \delta m_2 = \delta m \quad (11.85)$$

The total Gibbs potential of the gas-liquid mixture may be represented, with neglect of surface effects, as

$$G = m_1 g_1 + m_2 g_2 \quad (11.86)$$

where g_1 is the Gibbs potential per unit mass of the liquid in state 1 and g_2 is that for the gas in state 2. They are also called *chemical potentials*. They are independent of the total mass of the phases but may depend on the density of the phases (which, however, are not altered when we transfer mass from one phase to the other). Thus

$$\delta G = 0 = -(g_1 - g_2) \delta m \quad (11.87)$$

The condition for equilibrium is then

$$g_1 = g_2 \quad (11.88)$$

This condition determines the vapor pressure, as we shall see.

The chemical potentials $g_1(P, T)$ and $g_2(P, T)$ are two state functions of the liquid and gas respectively. Recall that in each phase we have

$$\left(\frac{\partial g}{\partial T} \right)_P = -s \quad (\text{entropy per unit mass}) \quad (11.89)$$

$$\left(\frac{\partial g}{\partial P} \right)_T = v \quad (\text{volume per unit mass}) \quad (11.90)$$

We see that the first derivative of g_1 is different from that of g_2 at the transition temperature and pressure:

$$\left[\frac{\partial (g_2 - g_1)}{\partial T} \right]_P = -(s_2 - s_1) < 0 \quad (11.91)$$

$$\left[\frac{\partial (g_2 - g_1)}{\partial P} \right]_T = v_2 - v_1 > 0 \quad (11.92)$$

This is why the transition is called “first-order.” The behavior of $g_1(P, T)$ and $g_2(P, T)$ are qualitatively sketched in Fig. 11.13

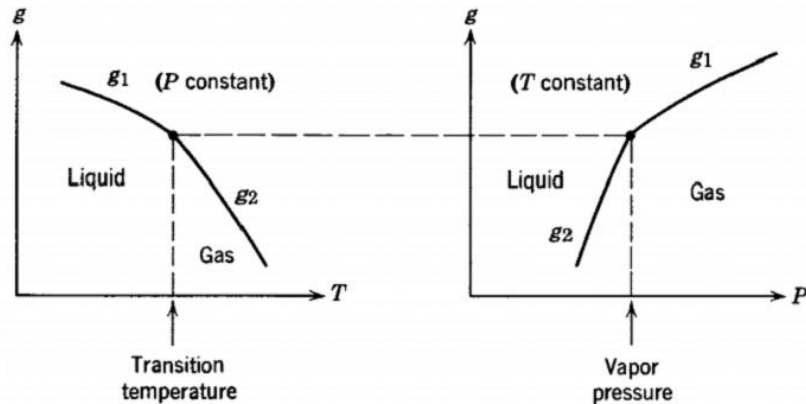


Fig. 11.13. Chemical potentials g_1, g_2 for the two phases in a first-order phase transition

To determine the vapor pressure we proceed as follows. Let

$$\begin{aligned}\Delta g &= g_2 - g_1 \\ \Delta s &= s_2 - s_1 \\ \Delta v &= v_2 - v_1\end{aligned}\tag{11.93}$$

where all quantities are evaluated at the transition temperature T and vapor pressure P . The condition for equilibrium is that T and P be such as to make $\Delta g = 0$. Dividing (11.91) by (11.92), we have

$$\frac{(\partial \Delta g / \partial T)_P}{(\partial \Delta g / \partial P)_T} = -\frac{\Delta s}{\Delta v}\tag{11.94}$$

By the chain relation,

$$\left(\frac{\partial \Delta g}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_{\Delta g} \left(\frac{\partial P}{\partial \Delta g}\right)_T = -1\tag{11.95}$$

or

$$\frac{(\partial \Delta g / \partial T)_P}{(\partial \Delta g / \partial P)_T} = -\left(\frac{\partial P}{\partial T}\right)_{\Delta g}\tag{11.96}$$

The reason the chain relation is valid here is that Δg is a function of T and P , and hence there must exist a relation of the form $f(T, P, \Delta g) = 0$. The derivative

$$\frac{dP(T)}{dT} = \left(\frac{\partial P}{\partial T}\right)_{\Delta g=0}\tag{11.97}$$

is precisely the derivative of the vapor pressure with respect to temperature under equilibrium conditions, for Δg is held fixed at the value zero. Combining (11.97), (11.96) and (11.95), we obtain

$$\frac{dP(T)}{dT} = \frac{\Delta s}{\Delta v}\tag{11.98}$$

The quantity

$$l = T\Delta s\tag{11.99}$$

is called the *latent heat of transition*. Thus

$$\frac{dP(T)}{dT} = \frac{l}{T\Delta v}\tag{11.100}$$

This is known as the *Clapeyron equation*. It governs the vapor pressure in any first-order transition.

It may happen in a phase transition that $s_2 - s_1 = 0$ and $v_2 - v_1 = 0$. When this is so the first derivatives of the chemical potentials are continuous across the transition point. Such a transition is not of the first order and would not be governed by the Clapeyron equation, and its isotherm would not have a horizontal part in the P - V diagram. Ehrenfest defines a phase transition to be an n th-order transition if, at the transition point,

$$\frac{\partial^n g_1}{\partial T^n} \neq \frac{\partial^n g_2}{\partial T^n} \quad \text{and} \quad \frac{\partial^n g_1}{\partial P^n} \neq \frac{\partial^n g_2}{\partial P^n} \quad (11.101)$$

whereas all lower derivatives are equal. A well-known example is the second-order transition in superconductivity. On the other hand many examples of phase transitions cannot be described by this scheme. Notable among these are the Curie point transition in ferromagnets, the order-disorder transition in binary alloys, and the λ transition in liquid helium. In these cases the specific heat diverges logarithmically at the transition point. Since the specific heat is related to the second derivative of g these examples cannot be characterized by the behaviors of the higher derivatives of g , because they do not exist. Modern usage distinguishes only between first-order and higher-order transitions, and the latter are usually indiscriminately called “second-order” transitions.

A miscellany of applications.

The Second Law tell us to increase entropy.
And move towards lower chemical potential
It doesn't say how.

Ammonia Fountain

https://www.youtube.com/watch?v=gMqRxbv_IW8

$$dg = dh - s.dT + v.dP + mg.dz$$

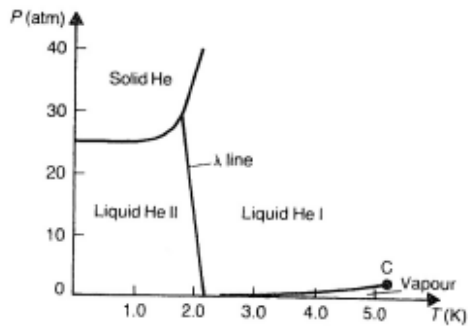
If $\Delta h < mg\Delta z$ (P, T constant) things move up.

Ammonia dissolves in water with large, negative Δh .

Helium II Fountain effect

<https://www.youtube.com/watch?v=kCJ24176enM>

<https://www.youtube.com/watch?v=2Z6UJbwxBZI>

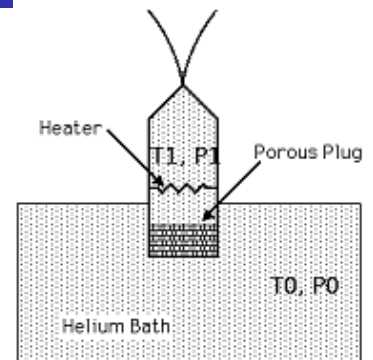


- He II is a “mixture” of superfluid and “normal” He.
- Superfluid component: “all particles in ground state”
- So can add a particle to superfluid without changing S .
- “normal” He component has finite entropy.

Helium II Fountain effect

Two vessels of cold He (“system” + “bath”)
only superfluid can flow through plug.

Equilibrium: $\mu = \mu_0$.



If “system” is heated ($T_1 > T_0$), equilibrium requires:

$$-s dT + v dp = 0 \Rightarrow dp/dT = s/v > 0$$

Thus heated “system” is at higher pressure than “bath”.

$$\Delta P = (s/v)\Delta T$$

This pressure difference is sufficient to generate a continuous fountain.

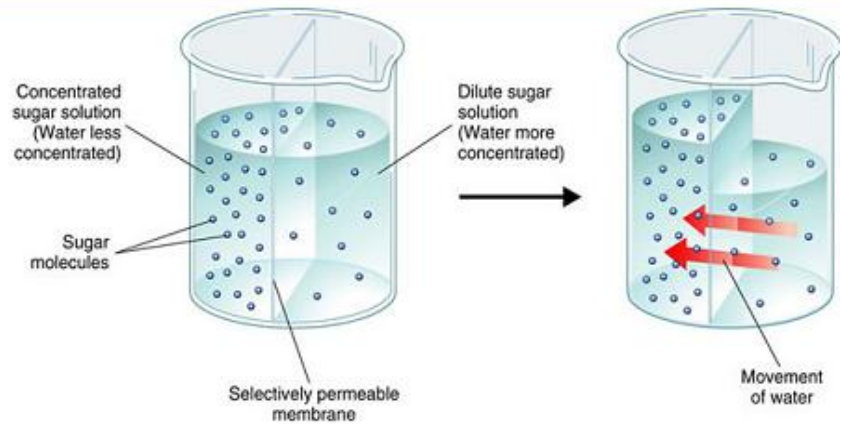
Osmosis: Chemical potential and ergodicity

semipermeable membrane

some particles flow e.g.
water not sugar.

Water flows freely,

$$\mu_A^W = \mu_B^W ; \mu_A^S \neq \mu_B^S ;$$



Simple case - noninteracting molecules $\mu^W \propto p^W$, so $p_A^W = p_B^W$

Total pressure: sum of partial pressure $P = \sum_i p_i$

If A also contains sugar: its *total* pressure is higher by p_B^S .

If water and sugar interact then Raoult's Law fails μ^W depends on sugar concentration and biology happens.

Too much solvent outside a cell reverses flow of water



Take a slug, add salt...

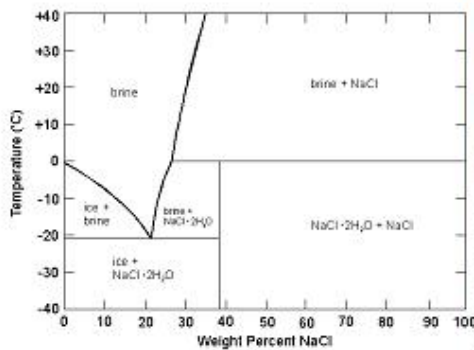
Brinicles

<https://www.youtube.com/watch?v=IAupJzH31tc>

BBC Frozen planet "Finger of Death"

Mix hot salt water and ice at (0°C), atmospheric pressure.

What final temperature will one get?



Salty water and ice → Equilibrium

Coexistence of water in ice, and in liquid brine, $\mu_L = \mu_I$,

Mole fraction of salt: $X = 2N_{\text{Na}^+} / (2N_{\text{Na}^+} + N_L)$.

Taylor expand $\mu_L(P, T, X)$ about $X = 0, T = 0$

$$d\mu_L = \left(\frac{\partial\mu_L}{\partial T}\right)_{P,X} dT + \left(\frac{\partial\mu_L}{\partial X}\right)_{P,T} dX = -s_L dT + \left(\frac{\partial\mu_L}{\partial X}\right)_{P,T} dX$$

For ice (no salt, $X=dX=0$);

$$d\mu_I = \left(\frac{\partial\mu_I}{\partial T}\right)_P dT = -s_I dT$$

On co-existence line $\mu_L = \mu_I$ thus $d\mu_L = d\mu_I$, \Rightarrow

$$\left(\frac{dT}{dX}\right)_{\text{saltwater-ice}} = \left(\frac{\partial\mu_L}{\partial X}\right)_T \left(\frac{1}{s_L - s_I}\right) = \frac{T}{L} \left(\frac{\partial\mu_L}{\partial X}\right)_T$$

where $L = T\Delta S$ is the latent heat of melting.

Hot water and ice, continued

$$\left(\frac{dT}{dX}\right)_{\text{saltwater-ice}} = \left(\frac{\partial\mu_L}{\partial X}\right)_T \left(\frac{1}{s_L - s_I}\right) = \frac{T}{L} \left(\frac{\partial\mu_L}{\partial X}\right)_T$$

Assume ideal solution of salt:

$$\mu_L(X, T) = \mu_L(X = 0, T) + RT \ln\left(\frac{N_L}{N_L + 2N_{\text{Na}^+}}\right)$$

Thus

$$\begin{aligned} \mu_L(X, T) &= \mu_L(X = 0, T) + RT \ln(1 - X) \\ \Rightarrow \left(\frac{\partial\mu_L}{\partial X}\right)_T &= \frac{-RT}{1 - X} = -RT \quad (\text{evaluating at } X=0) \end{aligned}$$

So finally,

$$\boxed{\left(\frac{dT}{dX}\right)_{\text{saltwater-ice}, X=0} = -\frac{RT^2}{L}}$$

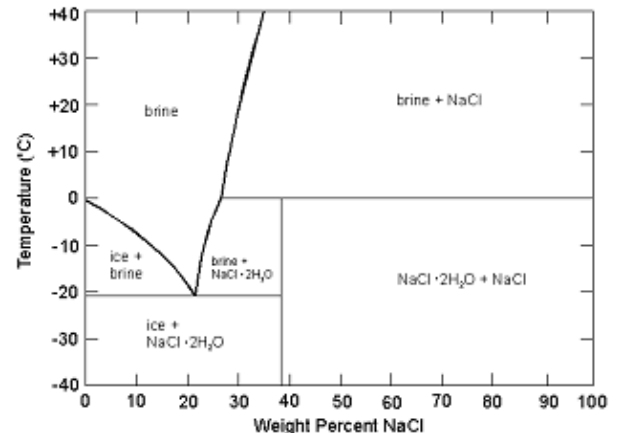
Temperature drops as we add salt water to ice.

Chemical Cooling

$$\boxed{\left(\frac{dT}{dX}\right)_{\text{saltwater-ice}, X=0} = -\frac{RT^2}{L}}$$

assumptions: Ideal solution, constant L, coexistence possible

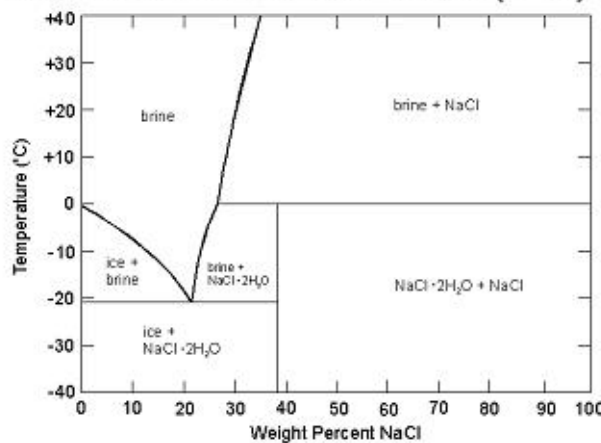
- Independent of which salt.
- Plug in numbers:
 $\Delta T = -16.5\text{K}$.
- Actual limit: -21.1°C for NaCl
- Below -21.1°C
pure ice + hydrated salt.



Brinicles

BBC Frozen planet "Finger of Death"

Mix hot salt water and ice at (0°C), atmospheric pressure.



Self assembling structure - ice around descending colume of brine.

Planck's insight

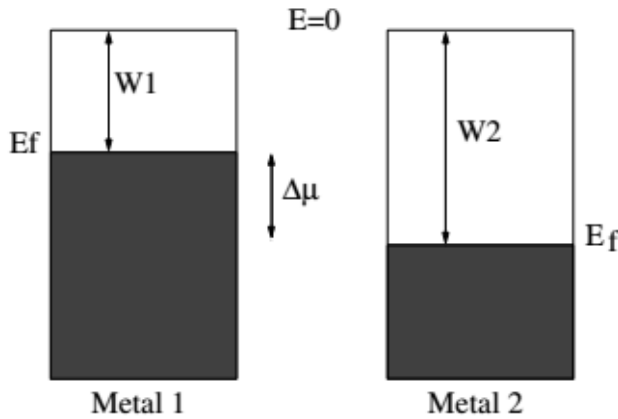
- Photons can spontaneously be created or absorbed.
- spontaneous process cannot increase G.
- $dG_{creation} \leq 0$ and $dG_{annihilation} \leq 0$;
 $\implies dG_{creation} = dG_{annihilation}$
- Chemical potential of a photon must be zero!

$$g = G/V = 0 = U/V + P - TS/V = u + \frac{u}{3} - Ts = 0$$

Entropy of a photon gas is $s = \frac{4u}{3T}$.

Electrons and Fermi Energy

In a metal, electrons occupy energy states up to the "Fermi Level".



Adding an electron: $\mu = E_F$.
 Placing two metals together means E_F must be the same.
 $E=0 \implies$ Electron at infinity.
 But ...
 Work functions, ϵ_W are different.
 Electrons must flow to equalise E_F

$$V = (W_1 - W_2)/e$$

a "pile" forms a battery.

On earth, as it is in heaven



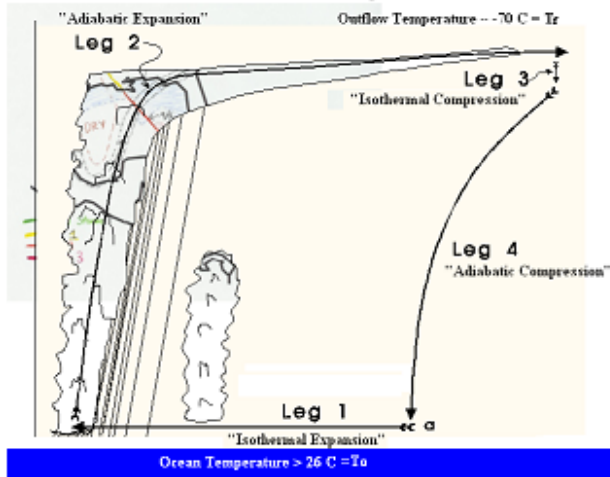
Hurricanes

A hurricane is a self assembling heat engine.

The hot reservoir is the ocean surface ($T_h \approx 300K$),

The cold reservoir is the top of the atmosphere, ($T_c \approx 200K$)

Work is done creating winds.



Isothermal expansion - air spirals towards the eye. (+ absorb water)
Adiabatic expansion Hot air rises to (low P).

Isothermal compression Water vapour condenses and falls as rain, releasing latent heat.

Adiabatic compression In theory, air drops back to sea level.

It's my law, I'll break it if I want to: Self-gravitating disks



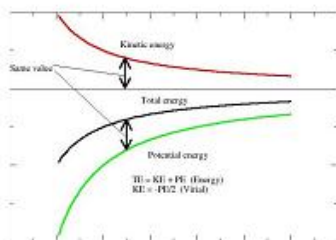
The virial theorem...

For a self-interacting system the average kinetic energy is equal to half the average potential energy



Clausius again!

$$\frac{\Delta(TE)}{\Delta(KE)} = -1 \propto \frac{\Delta U}{\Delta T}$$



- Self-gravitating star clusters
- black holes floating in a vacuum ($P=0$)
- They *expand* when energy is added,

Inhomogeneous Systems: violate definition of equilibrium.

Add "heat" - Reduce KE *Negative heat capacity!?*

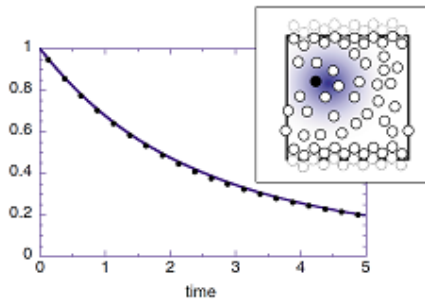
Intensive entropy ("heat") may decrease, the total entropy does not.

paper by Mr and Mrs Lynden-Bell MNRAS, 181, 405 (1977)



Breaking the Law

Small system, small time, *possible* to violate the Kelvin statement,



- Drag a micron sized particle.
- Measure piconewton forces.
- Work = force \times distance.
- *Sometimes* moving particle gets hit from behind more than in front.
- Extract work without supplying heat.
- Second Law violations *not predictable*

G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles & D. J. Evans (2002). "Experimental demonstration of violations of the Second Law of Thermodynamics for small systems and short time scales". *Physical Review Letters* 89 (5): 050601

Stating the obvious

Non-interacting objects in the same system can be treated as *independent* ideal gases, thanks to ...

Dalton's Law

Total pressure is the sum of partial pressures

$$P = \sum_i p_i$$

Raoult's Law

Partial pressure is proportional to concentration

$$p_i V = N_i RT$$



e.g. dilute chemicals in solution, photons in a cavity etc.



Thermodynamics in Chemistry

Molecules react to form other molecules.

A chemical potential can be defined for each.

$$dU = TdS - PdV + \sum_i \mu_i dN_i$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

Total Gibbs, G is also the sum of the chemical potentials

$$G = \sum_i \mu_i N_i \implies dG = \sum_i N_i d\mu_i + \mu_i dN_i$$

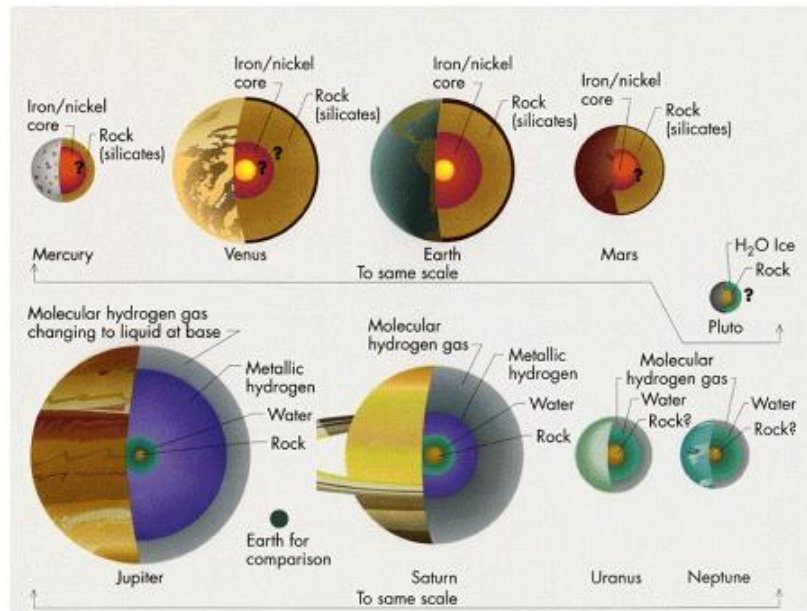


Equating these expressions for dG yields the **Gibbs-Duhem relation**:

$$\sum_i N_i d\mu_i = -S dT + V dp$$

This gives balance of concentration of components i

Phase separation in Planets



Chemical potential includes gravity: $\mu = u - Ts + Pv + mg_r h$.
 Heavy atoms fall to the bottom: can be drawn up if soluble (u)

Gibbs phase rule

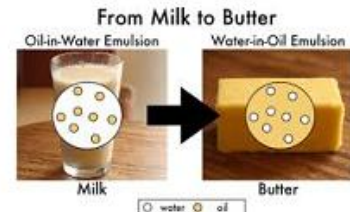
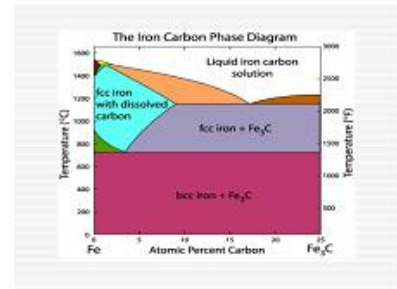
How much information is needed to specify system?

...equivalently...

How many degrees of freedom does a system have?

$$F = C + 2 - P$$

- C: Chemical species - reactions
- P: Number of phases present



What must be given to define the state: Gibbs phase rule

$$F = C + 2 - P$$

- **Single phase water:** $F = 1 + 2 - 1 = 2$. P and T must be specified.
- **Ice/water mix** $F = 1 + 2 - 2 = 1$. Specifying P defines T.
- **Triple point** $F = 1 + 2 - 3$. no freedom, unique P, T.
- **Critical point** No freedom, unique P, T $\implies P = 3$. (!)
- **Gaseous O_2 , H_2 and H_2O :** $F = 3 + 2 - 1$.
Leaves four d.o.f, e.g. T, P, N_{O_2} , N_{H_2}
- **...+reaction** $\frac{1}{2}O_2 + H_2 \rightleftharpoons H_2O$ $F = 2 + 2 - 1$,
Leaves three d.o.f.
(Assuming known reaction constant K, q.v.).

Order of phase transitions

$$g_1 = g_2$$

- First order: discontinuous change of state variables (e.g. s or v)

$$\frac{\partial g_1}{\partial T} \neq \frac{\partial g_2}{\partial T}$$

- Second order: continuous change of state variables, but discontinuous derivatives (e.g. c_v , K , β)

$$\frac{\partial g_1}{\partial T} = \frac{\partial g_2}{\partial T}$$

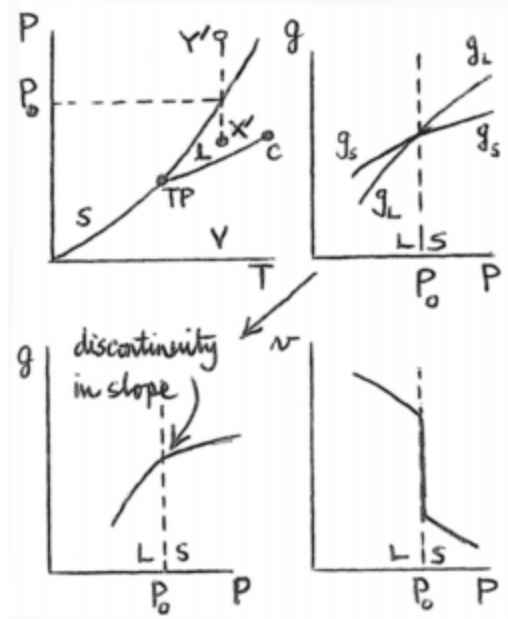
$$\frac{\partial^2 g_1}{\partial T^2} \neq \frac{\partial^2 g_2}{\partial T^2}$$

- Third order: continuous change of state variables and derivatives.

Discontinuous \equiv 1st order transitions

Isothermal process traverse

X'Y'



At the phase boundary.

$$g_1 = g_2 \text{ always } \dots$$

For first order, derivatives change...

$$-\left(\frac{\partial g_1}{\partial T}\right)_P \neq -\left(\frac{\partial g_2}{\partial T}\right)_P$$

$$\left(\frac{\partial g_1}{\partial P}\right)_T \neq \left(\frac{\partial g_2}{\partial P}\right)_T$$

$$s_1 \neq s_2 \text{ and } v_1 \neq v_2$$

Discontinuous transition \equiv 1st order

Second derivatives?

$$\text{Isobaric Heat Capacity } T \left(\frac{\partial s}{\partial T} \right)_P = T \left(\frac{\partial^2 g}{\partial T^2} \right)_P$$

$$\text{Thermal Expansivity } \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial^2 g}{\partial T \partial P} \right)_P$$

$$\text{Isothermal Compressibility } \frac{-1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{-1}{V} \left(\frac{\partial^2 g}{\partial P^2} \right)_T$$

The 'discontinuities' at continuous phase changes

In a second order transition

$$-\left(\frac{\partial g_1}{\partial T} \right)_P = -\left(\frac{\partial g_2}{\partial T} \right)_P \quad \text{and} \quad \left(\frac{\partial g_1}{\partial P} \right)_T = \left(\frac{\partial g_2}{\partial P} \right)_T$$

$\Delta S = 0$ means no latent heat. $\Delta V = 0$ means no volume change.

S and V are anyway related by $\left(\frac{\partial s}{\partial P} \right)_T \stackrel{\text{Maxwell}}{=} - \left(\frac{\partial v}{\partial T} \right)_P$

No latent heat or volume change: same internal energy $dU = TdS - PdV$

Clausius Clapeyron = 0/0.

Two types of transition look like "second order"

"Critical fluctuation" is where regions of the system fluctuate into the other phase in and uncorrelated way.

e.g. ferromagnet.

"Coexistence" is where one phase the system is effectively two-component.

e.g. Bose condensate.

Paul Ehrenfest (1880-1933)



Einstein, my upset stomach hates your theory [of General Relativity]—it almost hates you yourself! How am I to provide for my students? What am I to answer to the philosophers?!!

— Paul Ehrenfest —

AZ QUOTES

The Ehrenfest equations

Clausius-Clapeyron gives 0/0 for second order boundary.

Consider entropy at points A and B on the phase boundary, at (T, P) and $(T + dT, P + dP)$,

For *second order* transitions there is no change in s or v .

$$\text{at A} \quad s_1(T, P) = s_2(T, P)$$

$$\text{at B} \quad s_1(T + dT, P + dP) = s_2(T + dT, P + dP)$$

use a Taylor expansion on B

$$\left(\frac{\partial s_1}{\partial T}\right)_P dT + \left(\frac{\partial s_1}{\partial P}\right)_T dP = \left(\frac{\partial s_2}{\partial T}\right)_P dT + \left(\frac{\partial s_2}{\partial P}\right)_T dP$$

Multiply through by T and use c_P, β : "first Ehrenfest equation":

$$\left(\frac{dP}{dT}\right)_{\text{phaseboundary}} = \frac{c_{P,1} - c_{P,2}}{Tv(\beta_1 - \beta_2)} = \frac{C_{P,1} - C_{P,2}}{TV(\beta_1 - \beta_2)}$$

Second Ehrenfest equation

“Second Ehrenfest equation”

$$\left(\frac{dP}{dT}\right)_{\text{phaseboundary}} = \frac{\beta_2 - \beta_1}{\kappa_2 - \kappa_1}$$

Similar derivation starting from $v_1 = v_2$

Measuring 3/4 of ΔC_P , $\Delta\beta$, $\Delta\kappa$, ν suffices to measure slope of transition line.

Measuring slope provides information about ΔC_P , $\Delta\beta$, $\Delta\kappa$, ν

Scaling Laws

In critical region close to the transition, $\pm\Delta T_{\text{crit}}$ around T_c
e.g. Heat Capacity

$$C_V \propto (T - T_C)^{-\alpha}$$

e.g. correlations between magnetic spins

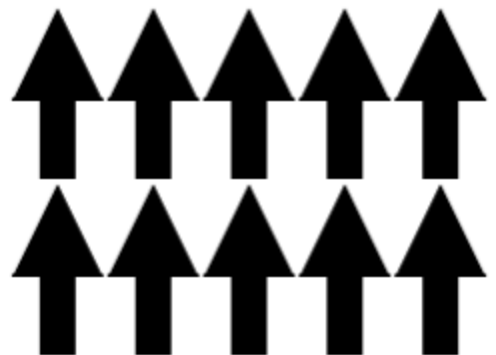
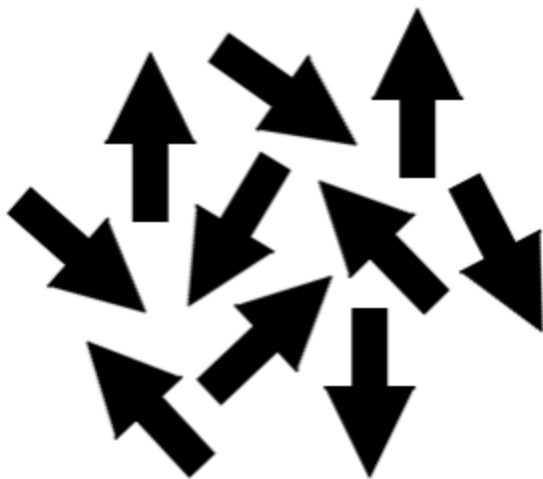
$$\langle S_i \cdot S_j \rangle \propto r^{-\nu}$$

Power Law dependence implies there is no characteristic scale.
Universality: conjecture that α , ν are independent of material.
In Economics and Ecology, forthcoming transitions often characterized by big fluctuations.

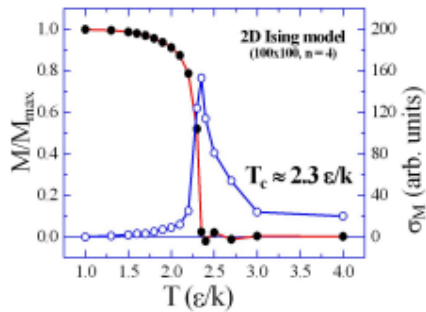
Giraffe



Ferromagnet



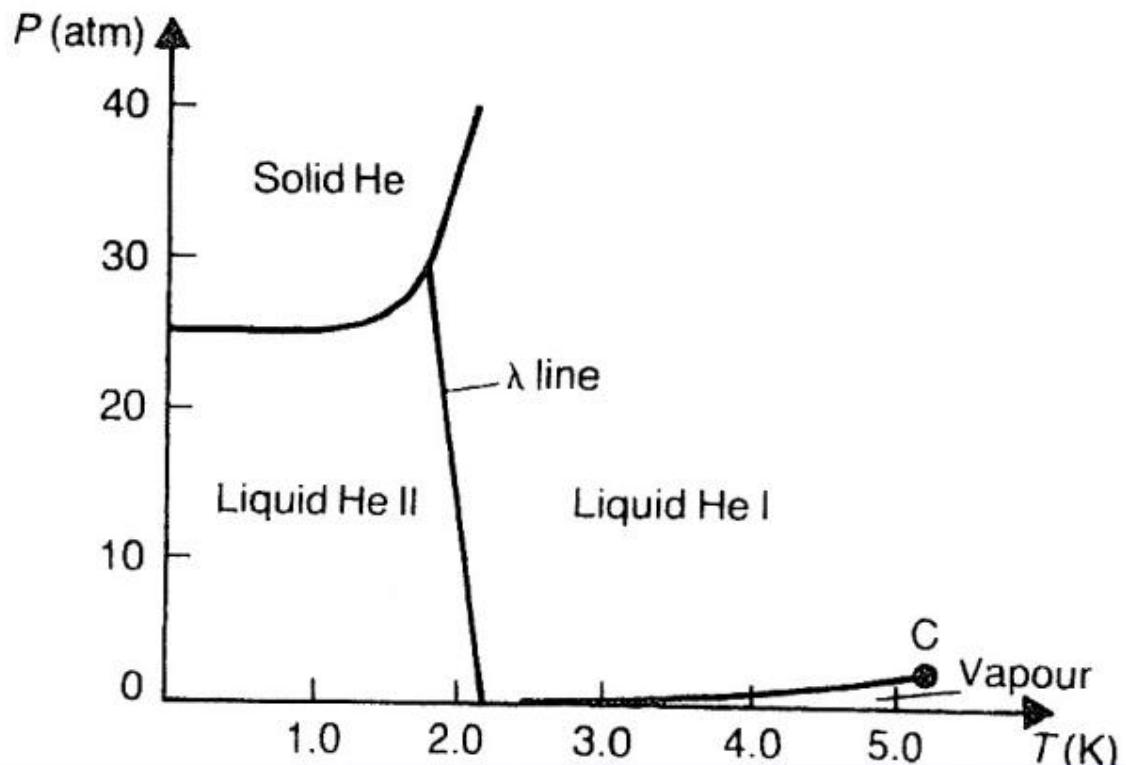
Ising Ferromagnet



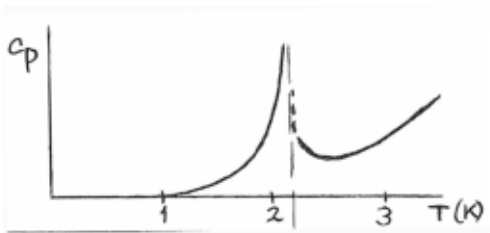
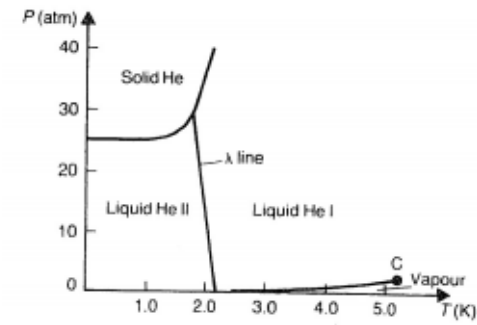
$$U = \epsilon \sum_{i,j} \sigma_i \sigma_j$$

- Equation(s) of state: $M = (T - T_c)^\beta$ and $\chi = \frac{dM}{dH} = \left(\frac{C}{T - T_c}\right)^\gamma$
- MACRO: zero magnetisation to finite magnetisation
- MICRO: transition from aligned spins to randomly oriented spins.
- SUSCEPTIBILITY (UNSOLVED)
- $\frac{dM}{dT}$ massive near transition.
- Materials near phase transitions can be very sensitive.

Liquid Helium

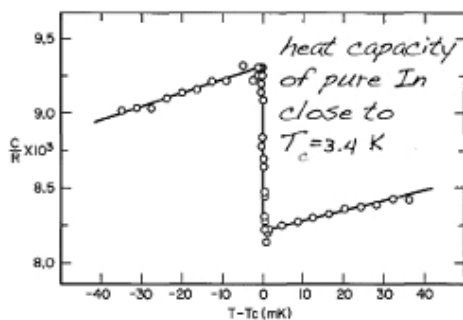


Liquid Helium



- At $T_\lambda = 2.2$ K, on cooling (He I) to “superfluid” (He II)
- Only for ^4He (Bose Condensation)
- Finite fraction of atoms in same (ground) quantum state
- The He II phase shows no viscous effects “superfluid”.
- Marked peak in C_p at transition line.
- Looks like a λ , hence T_λ .
- There is no latent heat: second order
- Heat capacity continuous: third order

Superconductivity



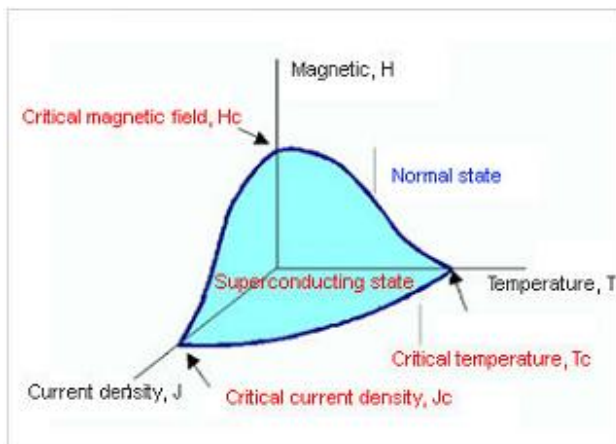
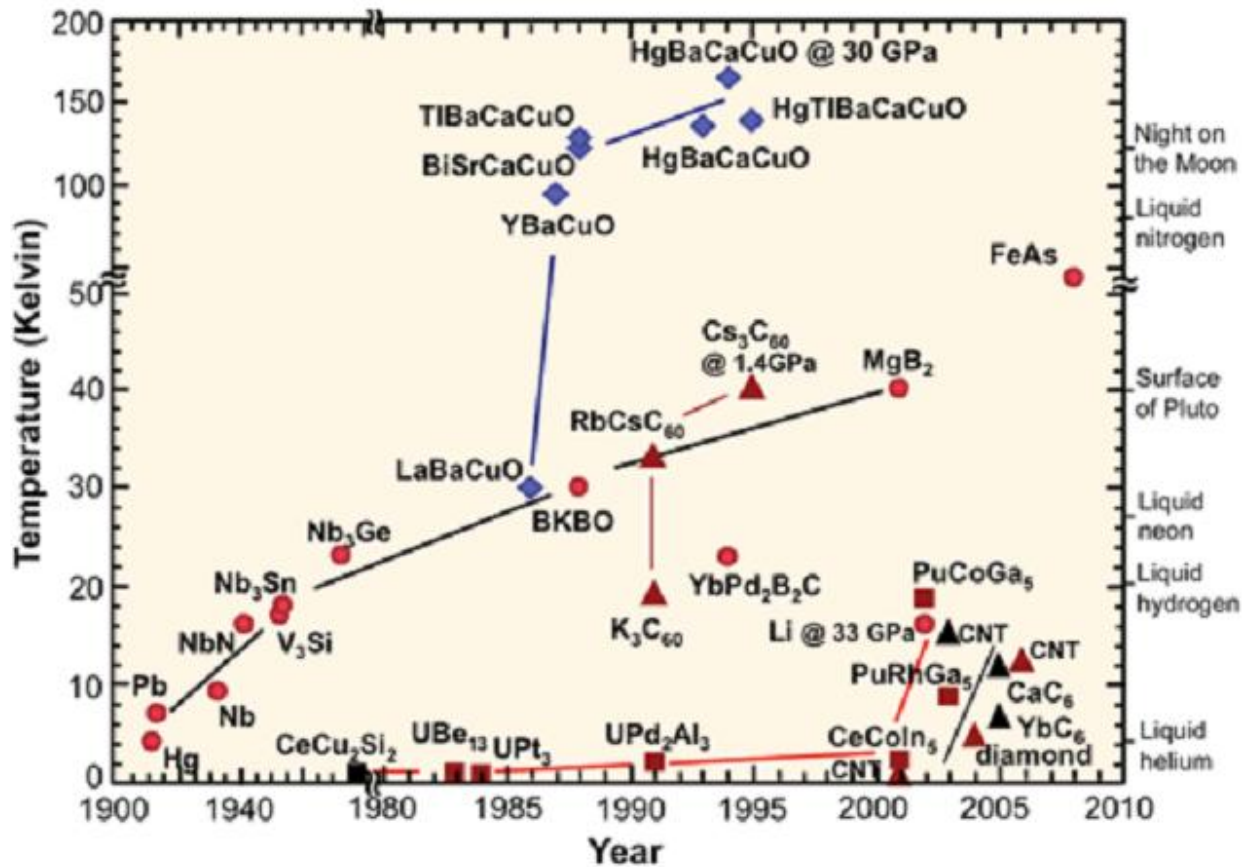
Heat capacity of pure indium in zero field

- Below $T_c = 3.4$ K electrical resistance is zero.
- “Two component model”
- Electrons couple to form “Cooper pairs” (bosons).
- Finite fraction of electrons (N_1) in ground state

Consider resistors in parallel:

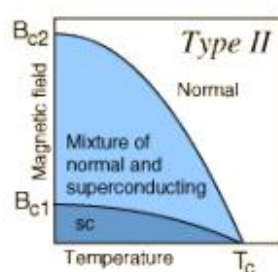
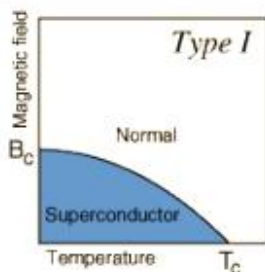
$$\frac{1}{R} = \frac{N_1}{R_1} + \frac{N_2}{R_2}$$

$$R_1 = 0 \implies R = 0$$



Superconductivity suppressed by

- High temperature
- High field
- High current
- Type I excludes all magnetic fields
- Type II allows some magnetic field



The Microscopic origin of Thermodynamics

DEFINITION: A micro-state...

a way the particles could be arranged at one instant in a given phase.

DEFINITION: Ergodicity means...

it is actually possible to move from any microstate to any other.

- If $S = k_B \ln W$, zero entropy means unique arrangement ($W = 1$).
Electrons in insulator: all fermion states below E_F occupied
Bose condensate: All bosons in ground state
- Third Law: at $T=0$, $S=0$ only one microstate, the ground state.
- Negative entropy impossible for quantised system $\implies W < 1$
- $S = k_B \ln W$ implies all W states equally likely
- More generally, Gibbs Entropy $S = -Nk_B p_i \ln p_i$

Counting

There are five laws of Thermodynamics.



5,4,3,2 ... ?

Laws of Thermodynamics

2, 1, 0, 3, and ?

Third Law

What is the entropy at absolute zero?

$$S = \int_0^T \frac{dQ}{T} + S_0$$

Unless $S = 0$ defined, ratios of entropies S_1/S_2 are meaningless.

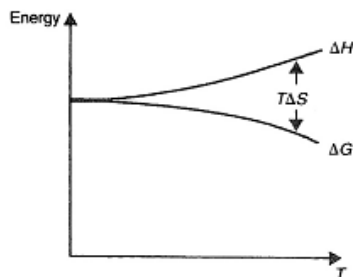
The Nernst Heat Theorem



Consider a system undergoing a process between initial and final equilibrium states as a result of external influences, such as pressure. The system experiences a change in entropy, and the change tends to zero as the temperature characterising the process tends to zero.

Nernst Heat Theorem: based on Experimental observation

Nernst saw that for any exothermic chemical process at temperature T .
 ΔH increases with T ,
 ΔG decreases with T .



As $T \rightarrow 0$, observed that
 $\Delta G \rightarrow \Delta H$ asymptotically

$$\begin{aligned}\Delta G &= G_f - G_i = \Delta H - \Delta(TS) \\ &= H_f - H_i - T(S_f - S_i) \\ &= \Delta H - T\Delta S\end{aligned}$$

So from Nernst's observation

$$\frac{d}{dT}(\Delta H - \Delta G) \rightarrow 0 \implies \Delta S \rightarrow 0$$



Planck statement of the Third Law:

The entropy of all perfect crystals is the same at absolute zero, and may be taken to be zero.

Planck Third Law

- All perfect crystals have the same entropy at $T = 0$.
- Thermodynamics : choose this to be $S_0 = 0$
- Supported by experimental evidence.
- Microscopics : $S = k \ln W$ all atom positions uniquely defined.
- $W = 1$
- Permuting atoms doesn't count.

Last point comes from Ergodicity - atoms can't swap - or from indistinguishability: state is the same if they do swap.

Simon Third Law



Sir Francis Simon (ne Franz Eugen Simon)
Student of Nernst
Also invented U^{235} separation via gaseous diffusion of UF_6

*The contribution to the entropy from each **aspect** of a system which in thermodynamic equilibrium disappears at absolute zero.*

- "configurational entropy": various arrangements of atoms on sites
- "vibrational entropy": various positions of vibrating atoms.
- "magnetic entropy": various arrangements of spins.

Isentropic process conserves TOTAL entropy.



The validity of the Third Law, however stated, stems from

- observation of properties of substances in general
- successful use in describing the low temperature behaviour of a wide range of processes and parameters.

Vanishing Thermal expansion coefficient, β

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T$$

- Isothermal derivative.
- Third Law, as T approaches zero, $\Delta S \rightarrow 0$,
...and so as T approaches zero, $\beta \rightarrow 0$.
- This is true *for any material*

Vanishing Heat capacity

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

Use $\frac{d}{dT} \ln T = \frac{1}{T} \Rightarrow d \ln T = \frac{dT}{T}$ to get

$$C_V = \left(\frac{\partial S}{\partial \ln T} \right)_V$$

As $T \rightarrow 0$, $\ln T \rightarrow -\infty$,

For infinitesimal ΔT , Third law has $\Delta S \rightarrow 0$

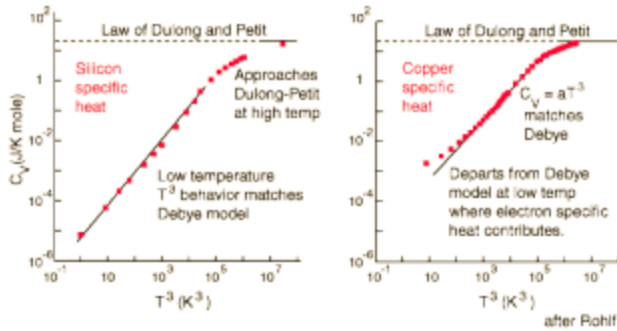
So $\frac{\Delta S}{\Delta \ln T} \rightarrow 0$

The consequence is that $C_V \rightarrow 0$ as $T \rightarrow 0$.

The same conclusion is found for all specific heats for all materials.

n.b. The heat capacity for an Ideal gas is $c_v = 3R/2$...
... means that the ideal gas doesn't properly describe low-T.

Heat Capacity of Metals



For metals at low temperatures
 $c_v \approx c_p = aT + bT^3$

aT associated with the conduction electrons **aspect**,
 bT^3 associated with the lattice vibrations **aspect**.

Using $\frac{c_V}{T} = \left(\frac{dS}{dT}\right)_V = a + bT^2$; and integrating we see that:

$$S(T) = aT + \frac{1}{3}bT^3$$

both contributions to entropy tend to zero as $T \rightarrow 0$

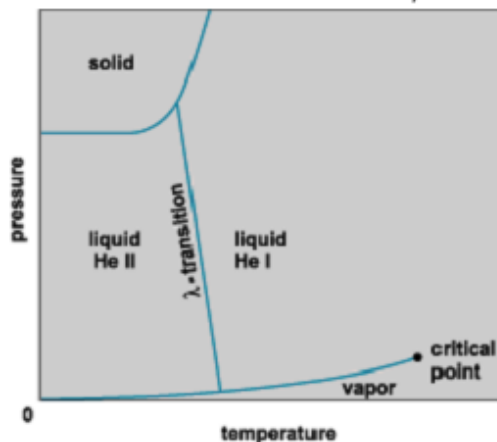
All electron states below E_F are occupied.

All lattice vibrations (quantum harmonic oscillators) in ground state.

Zero slope of the phase boundary for first order transition

From derivation of Clausius-Clapeyron, we know that $\left(\frac{dP}{dT}\right)_{PB} = \frac{\Delta S}{\Delta V}$

But $\Delta S \rightarrow 0$ as $T \rightarrow 0$, so the slope of the phase line must be zero.



e.g. He^4 in the low temperature limit.
 liquid phase II / solid phase transition

Quantum statement of Third Law

$$S = k \ln W$$

A quantised, finite amount of energy is needed to get out of the ground state ($W=1$).

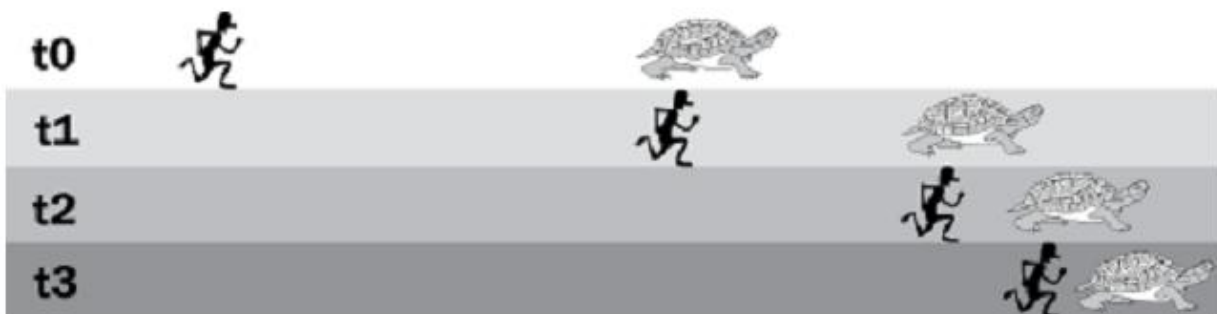
An infinitesimal change in temperature cannot provide this.

Therefore, an infinitesimal process at $T = 0$ cannot change W

Unattainability of absolute zero (Zeno statement)

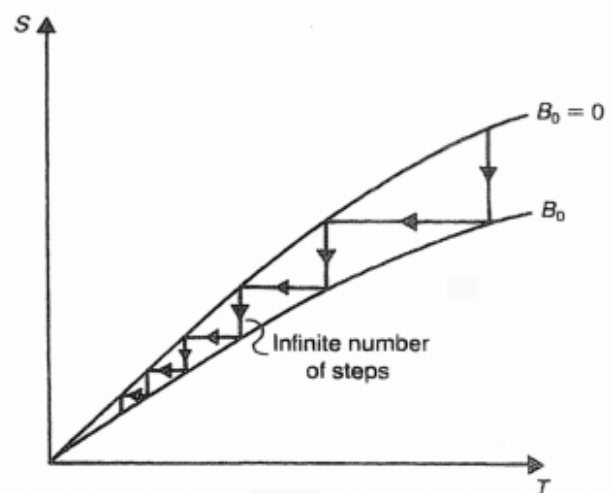
Another statement of the Third Law:

It is impossible to reach absolute zero in a finite number of processes.



Magnetic cooling again

- Cooling by adiabatic demagnetisation (Lecture 12).
- Field on: Reduce entropy by aligning spins
- Field off: Adiabatic equilibration = cooling.
- Repeat this **process**.
 $\Delta T_n \propto \Delta S_n$



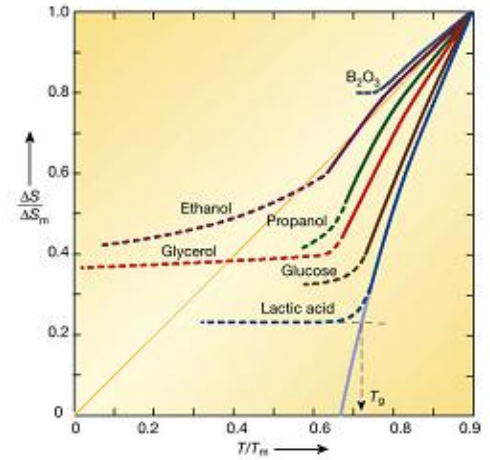
As $T \rightarrow 0$ entropy changes get smaller at each step.

Disobeying the Third Law?

Kauzmann's paradox

see also Nature 410, 259-267(2001)

Temperature dependence of the "heat content" (label $\Delta S/\Delta S_M$) between supercooled liquids and their stable crystals.



- Glasses look as if their entropy doesn't go to zero at 0 K
- Implication is they are *not* at equilibrium.

Counting up to two, three times

Three particles, two partitions A and B. State defined by N_A

- $W(N_A = 0) = 1(BBB)$;
- $W(N_A = 1) = 3(ABB/BAB/BBA)$
- $W(N_A = 2) = 3(AAB/ABA/BAA)$
- $W(N_A = 3) = 1(AAA)$

W for N particles: $\binom{N}{k}$ given by Pascal's triangle.

"Average" state is VASTLY more likely

As $N \rightarrow \infty$, width of the peak goes as $1/\sqrt{N}$



Sierpinski Gasket - Pascal's triangle is 100% Even numbers



Monty Hall Problem as an irreversible process

Entropy collapses when a measurement is made.



3 doors, two goats, one car.

Pick one door (3), Monty opens another (1) to show a goat.

Is the car more likely to be in (2) or (3)?

Initial Entropy: $k \ln 3 = 0.4771 \dots$

$W \ni [GGC, GCG, CGG]$

Final Entropy: $k \ln 2 = 0.3010k \dots$

$W \ni [GGC, GCG] ?$

NO, $-k(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3}) = 0.2764k$

What changed? - TWO bits of extra information...

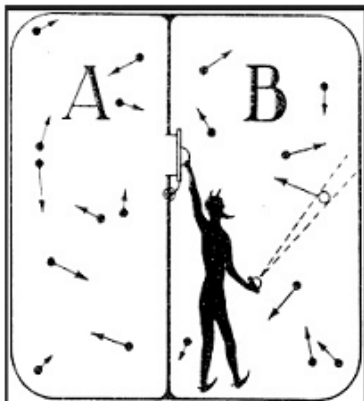
If Monty chose at random (may have revealed a car), no advantage switching

If Monty chose a goat-door, more information, some advantage switching

Breaking the law: Maxwell's Demon

If the Second Law of Thermodynamics is statistical, then...

There's a *chance* of breaking it.



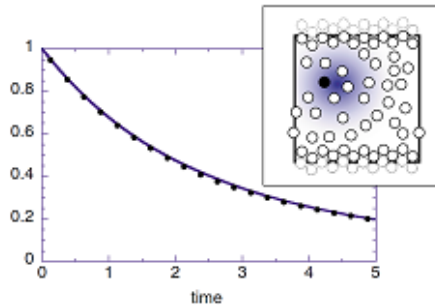
- Demon moves shutter ... only lets fast atoms go $A \rightarrow B$.
- Moves heat to hotter side
- Violates Clausius 2nd Law

Demon needs *information* about atom velocity: Demon itself creates entropy.

Moral. The 2nd law of thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful of water out again. Maxwell, 1874

Breaking the Law

Small system, small time, *possible* to violate the Kelvin statement,



- Drag a micron sized particle.
- Measure piconewton forces.
- Work = force \times distance.
- *Sometimes* moving particle gets hit from behind more than in front.
- Extract work without supplying heat.
- Second Law violations *not predictable*

G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles & D. J. Evans (2002). "Experimental demonstration of violations of the Second Law of Thermodynamics for small systems and short time scales". *Physical Review Letters* 89 (5): 050601

Other definitions of entropy beyond this course

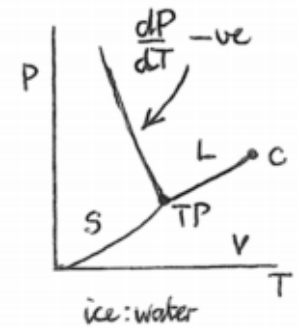
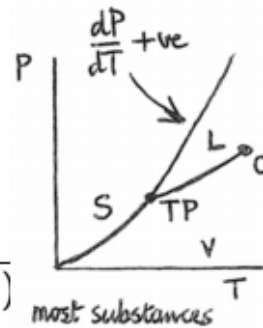
- The probability interpretation the Gibbs Entropy: $S = -k_B \sum_i p_i \ln p_i$
- Quantum probability interpretation: von Neumann entropy
 $S = -\text{tr}(\rho \ln \rho)$, With ρ the density matrix.
- Shannon Entropy $H = -\sum_i p_i \log_b p_i$
Quantifies how much information is contained in a message (and therefore, how much the message can be compressed).

Remarkably, they are all the same, and the missing entropy in Maxwell's Demon is the information in the Demon's brain!

Clausius-Clapeyron equation

Clausius-Clapeyron equation, from combination of latent heat and relation for $(dP/dT)_{pt}$

$$\left(\frac{dP}{dT}\right)_{pt} = \frac{l}{T(v_2 - v_1)} = \frac{L}{T(V_2 - V_1)}$$



- l is always positive going from low T (solid) to high T phase (liquid).
- For $v_L > v_S$ (solid expands on melting), dP/dT is positive.
- For $v_L < v_S$ (solid – like ice – contracts on melting) dP/dT is negative.
- REMEMBER THE SMALL PRINT:
It's $\frac{dP}{dT}$ along the phase boundary line. "Isophaseboundaryic"

How does the boiling point vary with pressure

Specific volumes v_S and v_L , for vapour and liquid.

Assume $v_v \gg v_L$: $v_v - v_L = v_v = RT/P$, giving

$$\frac{dP}{dT} \approx \left(\frac{l}{T}\right) \left(\frac{P}{RT}\right)$$

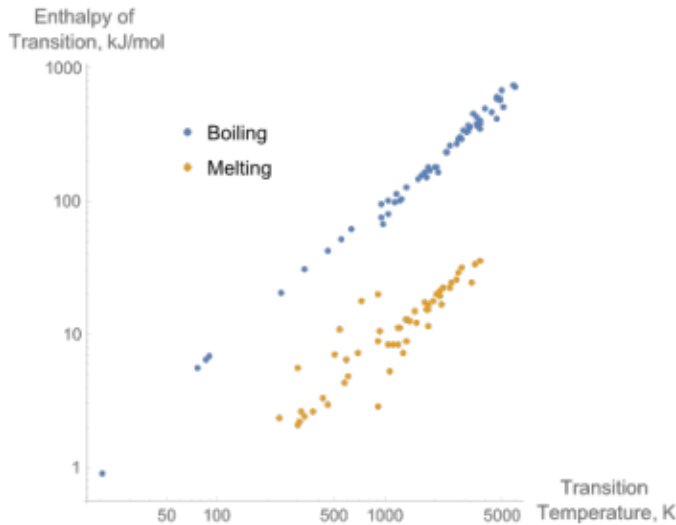
Integrate, assuming that the specific latent heat l is constant to get the equation for the vapourization line on a PT diagram.

$$\ln P = -\frac{l}{RT} + \text{constant}$$

Boiling point changes logarithmically with pressure.

Trouton's Rule (1884)

If the structure of all liquids were the same, the entropy would be similar.
 Entropy of vaporization = $10.5R$. Latent heat = $10.5RT_{vap}$ (not constant!)



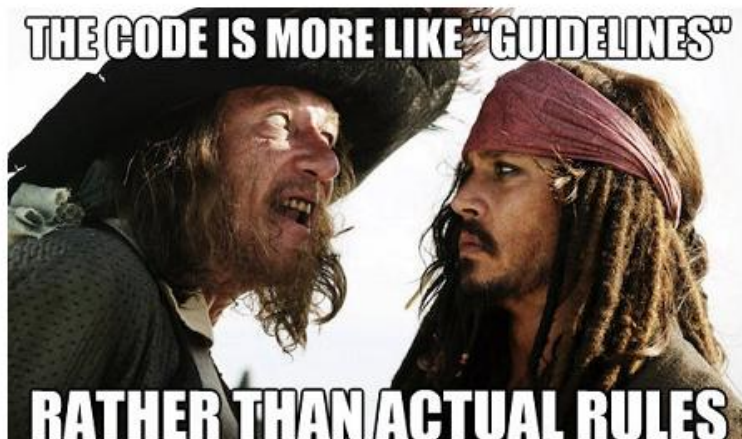
Measure enthalpy, because...
 Gibbs: $g = h - Ts$
 Phases have equal g , $\Delta g = 0$
 $\Delta h_{vap} = T_{vap}\Delta s_{vap}$

$$\frac{dP}{dT} \approx \left(\frac{1}{T}\right) \left(\frac{P}{RT}\right) \approx \left(\frac{10.5P}{T}\right) \implies P/P_0 \approx (T/T_0)^{10.5}$$

Trouton's Rule, with pirates

If the structure of all liquids were the same, the entropy would be similar.
 Entropy of vaporization = $10.5R$. Latent heat = $10.5RT_{vap}$

$$\frac{dP}{dT} \approx \left(\frac{10.5P}{T}\right) \implies P/P_0 \approx (T/T_0)^{10.5}$$



Defining Magnetic Central Equation

But defining work is trickier.

Magnetic Energy = $-BM$;

Define increasing magnetisation as "Work": $\delta W = \mathbf{B} \cdot d\mathbf{M}$

Magnetic Central Equation:

$$du = Tds + BdM$$

with associated Maxwell Relations such as $\left(\frac{dB}{dS}\right)_M = \left(\frac{dT}{dM}\right)_S$
 We could define magnetic equivalent of *enthalpy* $e_{tot} = -BM + u$.

$$de_{tot} = Tds - MdB$$

Similarly, equivalents of Gibbs and Helmholtz free energy; four magnetic Maxwell relations, etc.

Magnetic Cooling Cycle

a) Isothermal magnetisation process
 loses heat:

$$\left(\frac{dQ}{dB}\right)_T = T \left(\frac{dS}{dB}\right)_T = T \left(\frac{dM}{dT}\right)_B$$

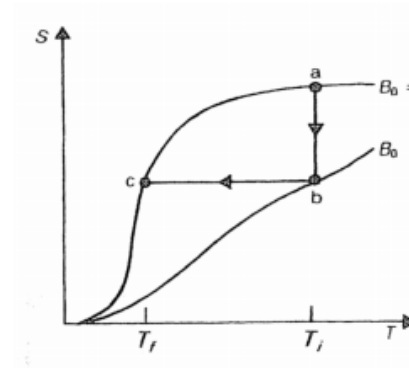
where we use a magnetic Maxwell relation.

b) Adiabatic/isenthalpic
 demagnetisation reduces temperature

$$\left(\frac{dT}{dB}\right)_S = - \left(\frac{dT}{dS}\right)_B \left(\frac{dS}{dB}\right)_T = - \frac{T}{c_B} \left(\frac{dM}{dT}\right)_B = - \frac{TB}{c_B} \left(\frac{d\chi}{dT}\right)_B$$

Using Maxwell and product rules,
 susceptibility, heat capacity at
 constant field

$$\chi = M/B; c_B = T(\partial S/\partial T)_B$$



Navigation icons: back, forward, search, etc.

Magnetic equation of state: Curie Weiss Law

Defined by

$$M = aB/(T - T_c).$$

$$c_B = c_B(B = 0) + aTB^2/(T - T_c)^3. \quad \leftarrow \text{Note } c_B \text{ is infinite at } T = T_c$$

Above T_c , this gives $(\frac{dT}{dB})_S = (T - T_c)/B$.

Magnetic cycle starting at T_1 , raising to B_1 then dropping to B_2 gives

$$\frac{T_1 - T_c}{T_2 - T_c} = \frac{B_1}{B_2}$$

A cycle with complete demagnetisation would cool to T_c

Work through details in handin, and note approximations like neglecting $c_B(B = 0)$ and assuming $B = \mu_0 H$ mean that in practice the performance will be less good.

Equipartition in society



US Declaration of Independence (1776)

We hold these truths to be self-evident, that all men are created equal, *But when a long train of abuses and usurpations, pursuing invariably the same Object evinces a design to reduce them under absolute Despotism, it is their right, it is their duty, to throw off such Government,* (The King of England is an asshole because...)

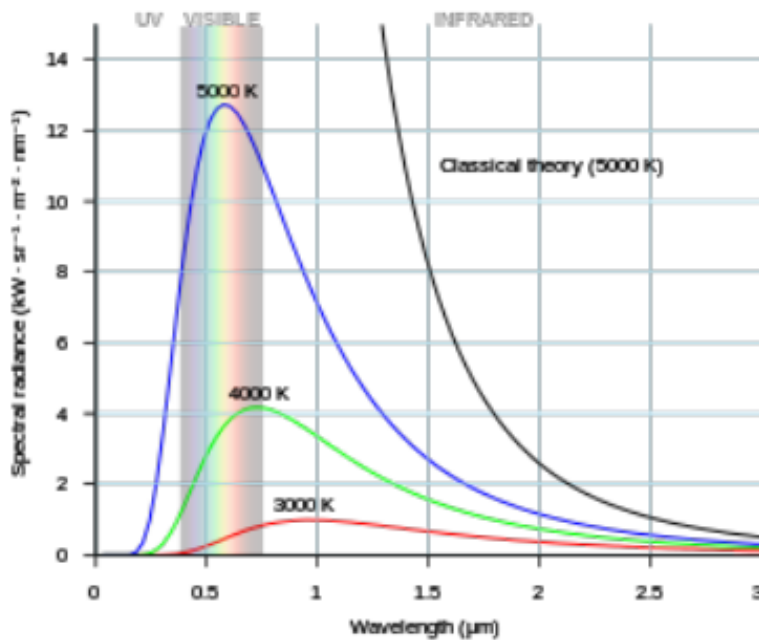


Declaration of Arbroath (1320)

It is in truth not for glory, nor riches, nor honours, that we are fighting, but for freedom.

But if he should give us or our kingdom to the English or the king of the English, we would immediately take steps to drive him out as the enemy and the subverter of his own rights and ours

(The King of England is a auld scunner because...)



Ultraviolet Catastrophe

Allowing equipartition of energy in all wavelengths requires infinite energy.

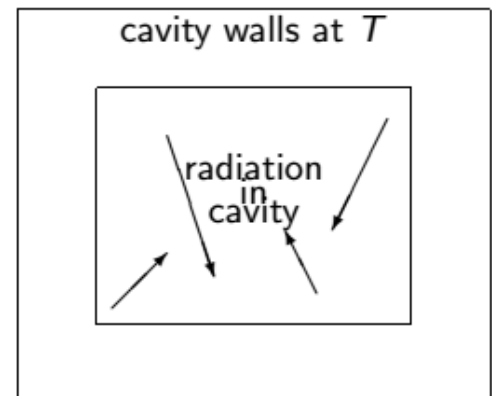
Thermal radiation as a thermodynamic system

System: radiation inside a cavity,
Surroundings :
 Cavity walls = heat bath temperature T .

State Variables for radiation
 Fixed T, V . System energy, $U(T, V)$

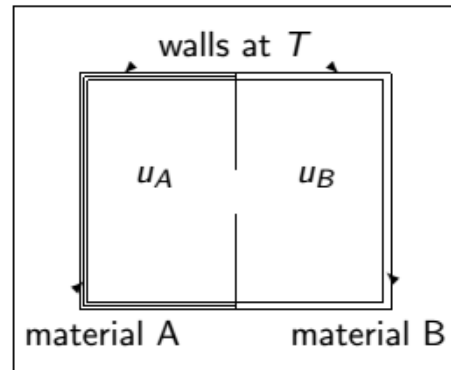
Equation of state from Electromagnetism:
 Radiation **pressure** $\langle S \rangle / c$ (Poynting vector $\mathbf{S} = \mathbf{E} \times \mathbf{H}$)

$$P = \frac{1}{3}u$$



Equipartition in radiation

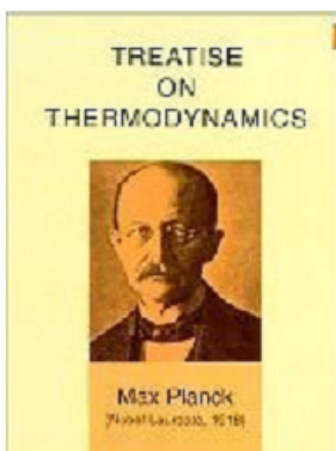
- Consider an partitioned oven.
- A and B: different materials, same T .
- Same value of energy density at equilibrium.
- Crossflow of radiation would make heat pass from A to B. if $u_A > u_B$:
- Clausius violation unless higher $u \implies$ higher T , regardless of volumes.
- $u(T, v) = u(T)$



Consider systems comprising radiation of a given wavelength.

- Same argument: $u_\lambda = u_\lambda(\lambda, T)$. (n.b. λ not a state variable)
- Heat flow between different λ until all T_λ are the same.

How Planck discovered Quantum Theory



*I had no alternative but to tackle the problem again ... from the side of thermodynamics. In fact, my previous studies of the Second Law of Thermodynamics came to stand me in good stead now, for at the very outset I hit upon the idea of correlating not the temperature of the oscillator but its entropy with the energy... While a host of outstanding physicists worked on the problem of the spectral energy distribution ... every one of them directed his efforts solely towards exhibiting the dependence of the intensity of radiation on the temperature. On the other hand, **I suspected that the fundamental connection lies in the dependence of entropy with the energy ...** Nobody paid any attention to the method which I adopted and I could work out by calculations completely at my leisure, with absolute thoroughness, without fear of interference or competition.*

The energy spectrum of cavity radiation

What is the energy density of blackbody radiation in a cavity?

$$u = \int_0^{\infty} u_{\lambda}(\lambda, T) d\lambda$$

(“area under the curve”) is very strongly **temperature**-dependent, but cannot blow up for high or low λ .



Anne Elk's Theory on Brontosaurus
All brontosaurus are thin at one end; much, much thicker in the middle and then thin again at the far end.

The energy spectrum of cavity radiation

What is the total energy of blackbody radiation?

$$u = \int_0^{\infty} u_{\lambda}(\lambda, T) d\lambda$$

(“area under the curve”) is very strongly **temperature**-dependent, but cannot blow up for high or low λ

First consider the explicit dependence of u on T . From the central equation of thermodynamics, and one of the Maxwell's relations

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

Stefan's Law is Thermodynamics

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

Using $P = \frac{1}{3}u$, $U = uV$ and $u = u(T)$ we get

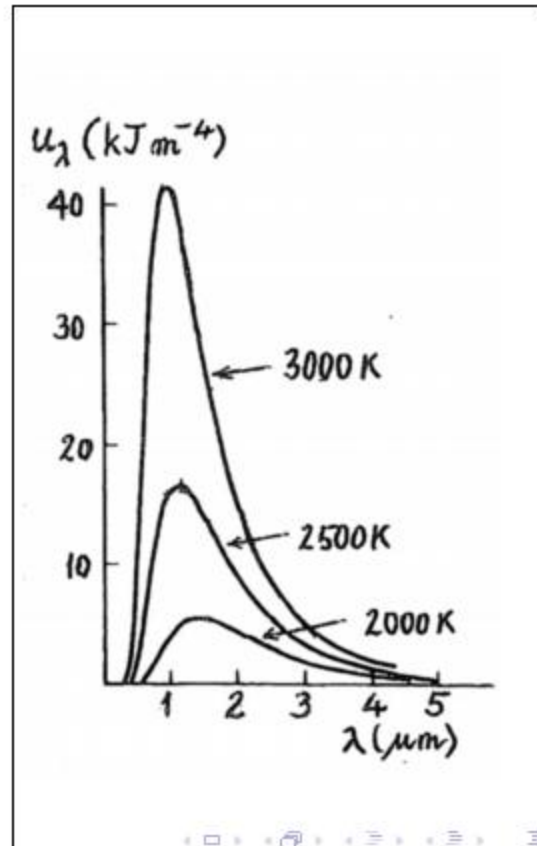
$$u = \frac{1}{3}T \frac{du}{dT} - \frac{1}{3}u \implies 4 \frac{dT}{T} = \frac{du}{u}$$

$$u = \left(\frac{4\sigma}{c}\right) T^4$$

energy density scales as T^4 .

The integration constant σ is "Stefan's constant".

Black body radiation $\propto u(T)$.



Closing in on the Planck distribution

Integrating the Black Body equation of state gives Stefan Law's

$$u(T) = \int_0^\infty u_\lambda(\lambda, T) d\lambda = \left(\frac{4\sigma}{c}\right) T^4$$

and requires for $u_\lambda(\lambda, T)$

- A 5th power in λ (3rd power in ν) for long wavelengths.
- A function which doesn't blow up at high ν (short wavelength)
- Gives the same $T = (\partial H_\lambda / \partial S_\lambda)_P$ for all λ .
- Maximises the entropy for fixed energy.

... but how to calculate the entropy?

Inventing Quantum Mechanics

- Using Maxwell Relations, get expression for entropy $S_\lambda(T)$
- Use $S_\lambda = k \ln \Omega_\lambda$: count discrete states
- Discrete amount of U_λ : photon!
- Can only calculate $\Delta S = k \Delta \ln \Omega$.
- To count Ω , need to know the energy of one photon: Planck's constant.

Meanwhile, Boltzmann was still struggling to get the Germans to accept atoms.

And the ultraviolet catastrophe still lurks in zero-point energy.

Other thermodynamic quantities

Specific heat capacity.

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = 4\sigma_o VT^3$$

with $\sigma_o = 4\sigma/c$, remembering that we've been using energy density, so $U = uV$.

Entropy

$$S = \int \frac{c_v dT}{T} = \frac{4}{3}\sigma_o VT^3$$

Enthalpy

$$H = U + PV = \frac{4}{3}\sigma_o VT^4 = TS$$

which we already knew from $T = \left(\frac{\partial H}{\partial S} \right)_P$.

Gibbs Free Energy,

$$G = uV - TS + PV = \sigma_o VT^4 - \frac{4}{3}\sigma_o VT^4 + \frac{1}{3}\sigma_o VT^4 = 0$$

