Advanced Thermodynamics

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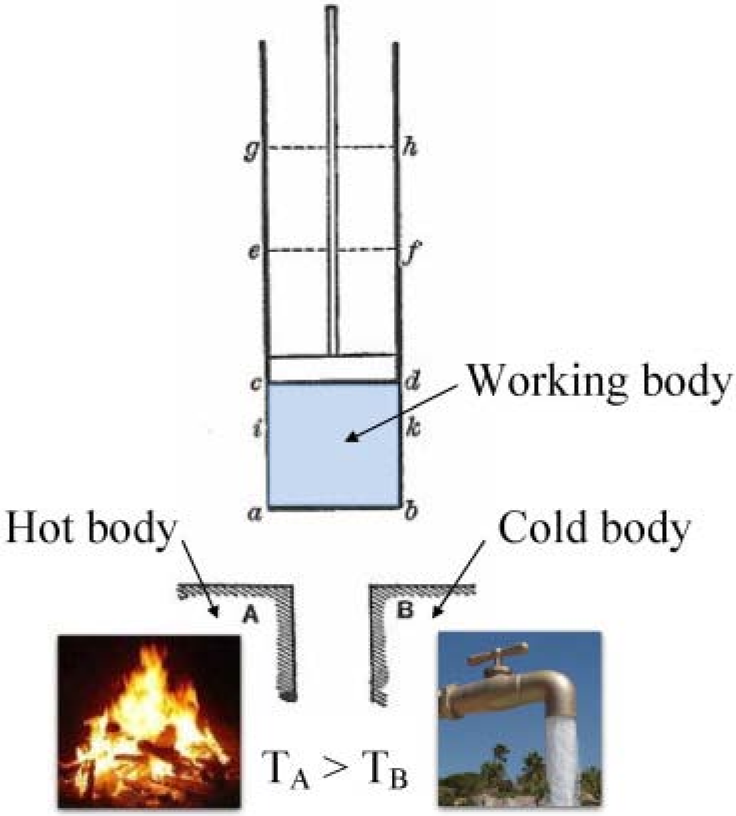
Table of Contents

Chapter- 1

Thermodynamics



Annotated color version of the original 1824 Carnot heat engine showing the hot body (boiler), working body (system, steam), and cold body (water), the letters labeled according to the stopping points in Carnot cycle.

In science, **thermodynamics** (from the Greek θέρμη *therme,* meaning "heat" and δύναμις, *dynamis,* meaning force) is the study of energy conversion between heat and mechanical work, and subsequently the macroscopic variables such as temperature, volume and pressure.

Historically, thermodynamics developed out of a need to increase the efficiency of early steam engines, particularly through the work of French physicist Nicolas Léonard Sadi

Carnot (1824) who believed that engine efficiency was the key that could help France win the Napoleonic Wars. The first to give a concise definition of the subject was Scottish physicist William Thomson who in 1854 stated that:

Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency.

Two fields of thermodynamics emerged in the following decades. Statistical thermodynamics, or statistical mechanics, (1860) concerned itself with statistical predictions of the collective motion of particles from their microscopic behavior, while chemical thermodynamics (1873) studies the nature of the role of entropy in the process of chemical reaction.

Introduction

The starting point for most thermodynamic considerations are the laws of thermodynamics, which postulate that energy can be exchanged between physical systems as heat or work. They also postulate the existence of a quantity named entropy, which can be defined for any isolated system that is in thermodynamic equilibrium.

In thermodynamics, interactions between large ensembles of objects are studied and categorized. Central to this are the concepts of *system* and *surroundings*. A system is composed of particles, whose average motions define its properties, which in turn are related to one another through equations of state. Properties can be combined to express internal energy and thermodynamic potentials, which are useful for determining conditions for equilibrium and spontaneous processes.

With these tools, thermodynamics can be used to describe how systems respond to changes in their environment. This can be applied to a wide variety of topics in science and engineering, such as engines, phase transitions, chemical reactions, transport phenomena, and even black holes. The results of thermodynamics are essential for other fields of physics and for chemistry, chemical engineering, aerospace engineering, mechanical engineering, cell biology, biomedical engineering, materials science, and economics, to name a few.

The present article is focused mainly on classical thermodynamics, which is concerned with systems in thermodynamic equilibrium. It is wise to distinguish classical thermodynamics from non-equilibrium thermodynamics, which is concerned with systems that are not in thermodynamic equilibrium.

École Polytechnique	Glasgow school	Berlin school	Edinburgh school
Sadi Carnot (1796-1832)	William Thomson (1824-1907)	Rudolf Clausius (1822-1888)	James Maxwell (1831-1879)
Vienna school	Gibbsian school	Dresden school	Dutch school
Ludwig Boltzmann (1844-1906)	Willard Gibbs (1839-1903)	Gustav Zeuner (1828-1907)	Johannes der Waals (1837-1923)

Table of the thermodynamicists representative of the original eight founding schools of thermodynamics. The schools having the most-lasting effect in founding the modern versions of thermodynamics, being the **Berlin school**, particularly as established in Rudolf Clausius's 1865 textbook *The Mechanical Theory of Heat*, which is the prototype of all modern textbooks on thermodynamics, the **Vienna school**, with the statistical mechanics of Ludwig Boltzmann, and the **Gibbsian school** at Yale University, American engineer Willard Gibbs' 1876 *On the Equilibrium of Heterogeneous Substances* launching chemical thermodynamics.

History

The history of thermodynamics as a scientific discipline generally begins with Otto von Guericke who, in 1650, built and designed the world's first vacuum pump and demonstrated a vacuum using his Magdeburg hemispheres. Guericke was driven to make a vacuum in order to disprove Aristotle's long-held supposition that 'nature abhors a vacuum'. Shortly after Guericke, the English physicist and chemist Robert Boyle had learned of Guericke's designs and, in 1656, in coordination with English scientist Robert Hooke, built an air pump. Using this pump, Boyle and Hooke noticed a correlation between pressure, temperature, and volume. In time, Boyle's Law was formulated, which states that pressure and volume are inversely proportional. Then, in 1679, based on these concepts, an associate of Boyle's named Denis Papin built a steam digester, which was a closed vessel with a tightly fitting lid that confined steam until a high pressure was generated.

Later designs implemented a steam release valve that kept the machine from exploding. By watching the valve rhythmically move up and down, Papin conceived of the idea of a piston and a cylinder engine. He did not, however, follow through with his design. Nevertheless, in 1697, based on Papin's designs, engineer Thomas Savery built the first engine, followed by Thomas Newcomen in 1712. Although these early engines were crude and inefficient, they attracted the attention of the leading scientists of the time. Their work led 127 years later to Sadi Carnot, the "father of thermodynamics", who, in 1824, published *Reflections on the Motive Power of Fire*, a discourse on heat, power, and engine efficiency. The paper outlined the basic energetic relations between the Carnot engine, the Carnot cycle, and motive power. It marked the start of thermodynamics as a modern science.

The term *thermodynamics* was coined by James Joule in 1849 to designate the science of relations between heat and power. By 1858, "thermo-dynamics", as a functional term, was used in William Thomson's paper *An Account of Carnot's Theory of the Motive Power of Heat.* The first thermodynamic textbook was written in 1859 by William Rankine, originally trained as a physicist and a civil and mechanical engineering professor at the University of Glasgow. The first and second laws of thermodynamics emerged simultaneously in the 1850s, primarily out of the works of William Rankine, Rudolf Clausius, and William Thomson (Lord Kelvin).

The foundations of statistical thermodynamics were set out by physicists such as James Clerk Maxwell, Ludwig Boltzmann, Max Planck, Rudolf Clausius and J. Willard Gibbs.

During the years 1873-76 the American mathematical physicist Josiah Willard Gibbs published a series of three papers, the most famous being *On the Equilibrium of Heterogeneous Substances*, in which he showed how thermodynamic processes could be graphically analyzed, by studying the energy, entropy, volume, temperature and pressure of the thermodynamic system in such a manner, one can determine if a process would occur spontaneously. During the early 20th century, chemists such as Gilbert N. Lewis, Merle Randall, and E. A. Guggenheim began to apply the mathematical methods of Gibbs to the analysis of chemical processes.

Interpretations

Thermodynamics has developed into several related branches of science, each with a different focus.

Classical thermodynamics

Classical thermodynamics is concerned with macroscopic thermodynamic states and properties of large, near-equilibrium systems. It is used to model exchanges of energy, work and heat based on the laws of thermodynamics. The term "classical" reflects the fact that it represents the level of knowledge in the early 19th century. An atomic interpretation of these principles was provided later by the development of statistical mechanics. Nonetheless, classical thermodynamics is still a practical and widely-used science.

Statistical mechanics

Statistical mechanics (or statistical thermodynamics) emerged only with the development of atomic and molecular theories in the late 19th century and early 20th century, giving thermodynamics a molecular interpretation. This field relates the microscopic properties of individual atoms and molecules to the macroscopic or bulk properties of materials that can be observed in everyday life, thereby explaining thermodynamics as a natural result of statistics and mechanics (classical and quantum) at the microscopic level. This statistical approach is in contrast to classical thermodynamics, which is a more phenomenological approach.

Chemical thermodynamics

Chemical thermodynamics is the study of the interrelation of energy with chemical reactions or with a physical change of state within the confines of the laws of thermodynamics.

Treatment of equilibrium

Equilibrium thermodynamics is the systematic study of transformations of matter and energy in systems as they approach equilibrium. The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potentials, or driving forces, within the system. A central aim in equilibrium thermodynamics is: given a system in a well-defined initial state, subject to accurately specified constraints, to calculate what the state of the system will be once it has reached equilibrium.

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with systems that are not in thermodynamic equilibrium. Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems. The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods.

Laws of thermodynamics

Thermodynamics defines four laws which do not depend on the details of the systems under study or how they interact. Hence these laws are generally valid, can be applied to systems about which one knows nothing other than the balance of energy and matter transfer. Examples of such systems include Einstein's prediction of spontaneous emission, and ongoing research into the thermodynamics of black holes.

These four laws are:

- Zeroth law of thermodynamics: *If two systems are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.*

Systems are said to be in equilibrium if the small, random exchanges (due to Brownian motion, for example) between them do not lead to a net change in the total energy summed over all systems. This law is tacitly assumed in every measurement of temperature. Thus, if we want to know if two bodies are at the same temperature, it is not necessary to bring them into contact and to watch whether their observable properties change with time.

This law was considered so obvious it was added as a virtual afterthought, hence the designation Zeroth, rather than Fourth. In short, if the temperature of material A is equal to the temperature of material B, and B is equal to the temperature of material C, then A and C must also be equal. This implies that thermal equilibrium is an equivalence relation on the set of thermodynamic systems.

- First law of thermodynamics: *The internal energy of an isolated system is constant.*

The first law of thermodynamics, an expression of the principle of conservation of energy, states that energy can be transformed (changed from one form to another), but cannot be created or destroyed.

It is usually formulated by saying that the change in the internal energy of a closed thermodynamic system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings. Work and heat are due to processes which add or subtract energy, while internal energy is a particular form of energy associated with the system. Internal energy is a property of the system whereas work done and heat supplied are not. A significant result of this distinction is that a given internal energy change can be achieved by many combinations of heat and work.

- Second law of thermodynamics: *Heat can flow spontaneously from a higher temperature body to a lower temperature body, but never from a lower temperature body to a higher temperature body.*

The second law of thermodynamics is an expression of the universal principle of decay observable in nature. The second law is an observation of the fact that over time, differences in temperature, pressure, and chemical potential tend to even out in a physical system that is isolated from the outside world. Entropy is a measure of how much this evening-out process has progressed. Entropy may be considered the *quality* of heat. An object at a higher temperature has the potential to do more work than an object containing an equal amount of heat at a lower temperature (we are only considering heat and not chemical, kinetic or potential energy).

The entropy of an isolated system which is not in equilibrium will tend to increase over time, approaching a maximum value at equilibrium.

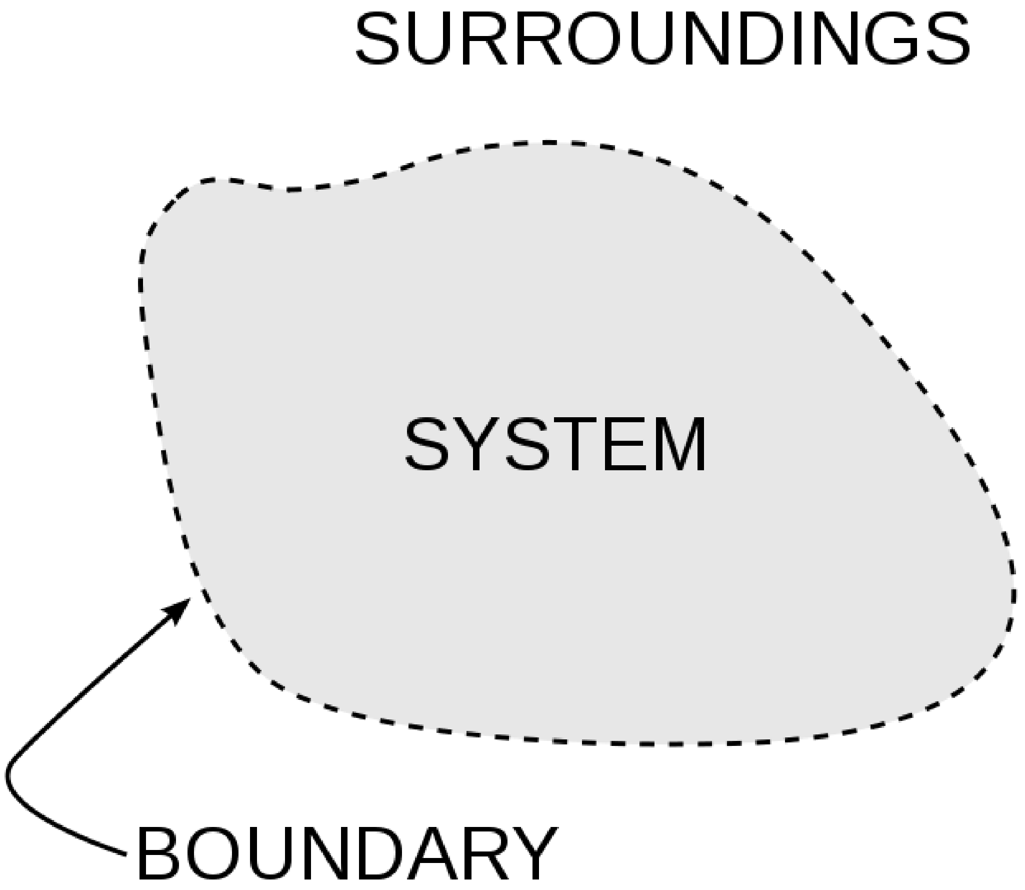
In classical thermodynamics, the second law is a basic postulate applicable to any system involving heat energy transfer; in statistical thermodynamics, the second law is a consequence of the assumed randomness of molecular chaos. There are many versions of the second law, but they all have the same effect, which is to explain the phenomenon of irreversibility in nature.

- Third law of thermodynamics: *As a system approaches absolute zero, all processes cease and the entropy of the system approaches a minimum value.*

The third law of thermodynamics is a statistical law of nature regarding entropy and the impossibility of reaching absolute zero of temperature. This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy. Alternate definitions are, "the entropy of all systems and of all states of a system is smallest at absolute zero," or equivalently "it is impossible to reach the absolute zero of temperature by any finite number of processes".

Absolute zero, at which all activity would stop if it were possible to happen, is −273.15 °C (degrees Celsius), or −459.67 °F (degrees Fahrenheit) or 0 K (kelvin).

System models



A diagram of a generic thermodynamic system

An important concept in thermodynamics is the thermodynamic system, a precisely defined region of the universe under study. Everything in the universe except the system is known as the *surroundings*. A system is separated from the remainder of the universe by a *boundary* which may be notional or not, but which by convention delimits a finite volume. Exchanges of work, heat, or matter between the system and the surroundings take place across this boundary.

In practice, the boundary is simply an imaginary dotted line drawn around a volume when there is going to be a change in the internal energy of that volume. Anything that passes across the boundary that effects a change in the internal energy needs to be accounted for in the energy balance equation. The volume can be the region surrounding a single atom resonating energy, such as Max Planck defined in 1900; it can be a body of steam or air in a steam engine, such as Sadi Carnot defined in 1824; it can be the body of a tropical cyclone, such as Kerry Emanuel theorized in 1986 in the field of atmospheric thermodynamics; it could also be just one nuclide (i.e. a system of quarks) as hypothesized in quantum thermodynamics.

Boundaries are of four types: fixed, moveable, real, and imaginary. For example, in an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. For closed systems, boundaries are real while for open system boundaries are often imaginary.

Generally, thermodynamics distinguishes five classes of systems, defined in terms of what is allowed to cross their boundaries:

Interactions of thermodynamic systems

Type of system	Mass flow	Work	Heat
Open	✓	✓	✓
Closed	✗	✓	✓
Isolated	✗	✗	✗

As time passes in an isolated system, internal differences in the system tend to even out and pressures and temperatures tend to equalize, as do density differences. A system in which all equalizing processes have gone to completion is considered to be in a state of thermodynamic equilibrium.

In thermodynamic equilibrium, a system's properties are, by definition, unchanging in time. Systems in equilibrium are much simpler and easier to understand than systems which are not in equilibrium. Often, when analysing a thermodynamic process, it can be assumed that each intermediate state in the process is at equilibrium. This will also considerably simplify the situation. Thermodynamic processes which develop so slowly as to allow each intermediate step to be an equilibrium state are said to be reversible processes.

States and processes

When a system is at equilibrium under a given set of conditions, it is said to be in a definite thermodynamic state. The state of the system can be described by a number of intensive variables and extensive variables. The properties of the system can be described by an equation of state which specifies the relationship between these variables. State may be thought of as the instantaneous quantitative description of a system with a set number of variables held constant.

A thermodynamic process may be defined as the energetic evolution of a thermodynamic system proceeding from an initial state to a final state. Typically, each thermodynamic process is distinguished from other processes in energetic character according to what parameters, such as temperature, pressure, or volume, etc., are held fixed. Furthermore, it is useful to group these processes into pairs, in which each variable held constant is one member of a conjugate pair.

Several common thermodynamic processes are:

- Isobaric process: occurs at constant pressure
- Isochoric process: occurs at constant volume (also called isometric/isovolumetric)
- Isothermal process: occurs at a constant temperature
- Adiabatic process: occurs without loss or gain of energy by heat
- Isentropic process: a reversible adiabatic process, occurs at a constant entropy
- Isenthalpic process: occurs at a constant enthalpy
- Steady state process: occurs without a change in the internal energy

Instrumentation

There are two types of thermodynamic instruments, the **meter** and the **reservoir**. A thermodynamic meter is any device which measures any parameter of a thermodynamic system. In some cases, the thermodynamic parameter is actually defined in terms of an idealized measuring instrument. For example, the zeroth law states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. This principle, as noted by James Maxwell in 1872, asserts that it is possible to measure temperature. An idealized thermometer is a sample of an ideal gas at constant pressure. From the ideal gas law $pV=nRT$, the volume of such a sample can be used as an indicator of temperature; in this manner it defines temperature. Although pressure is defined mechanically, a pressure-measuring device, called a barometer may also be constructed from a sample of an ideal gas held at a constant temperature. A calorimeter is a device which is used to measure and define the internal energy of a system.

A thermodynamic reservoir is a system which is so large that it does not appreciably alter its state parameters when brought into contact with the test system. It is used to impose a particular value of a state parameter upon the system. For example, a pressure reservoir is a system at a particular pressure, which imposes that pressure upon any test system that it is mechanically connected to. The Earth's atmosphere is often used as a pressure reservoir.

Conjugate variables

In thermodynamics, the internal energy of a system is expressed in terms of pairs of **conjugate variables** such as temperature/entropy or pressure/volume. In fact all thermodynamic potentials are expressed in terms of conjugate pairs.

For a mechanical system, a small increment of energy is the product of a force times a small displacement. A similar situation exists in thermodynamics. An increment in the energy of a thermodynamic system can be expressed as the sum of the products of certain generalized "forces" which, when imbalanced, cause certain generalized "displacements", and the product of the two is the energy transferred as a result. These forces and their associated displacements are called conjugate variables. The thermodynamic force is always an intensive variable and the displacement is always an extensive variable, yielding an extensive energy transfer. The intensive (force) variable is the derivative of the internal energy with respect to the extensive (displacement) variable, while all other extensive variables are held constant.

The thermodynamic square can be used as a tool to recall and derive some of the thermodynamic potentials based on conjugate variables.

Overview

Just as a small increment of energy in a mechanical system is the product of a force times a small displacement, so an increment in the energy of a thermodynamic system can be expressed as the sum of the products of certain generalized "forces" which, when unbalanced, cause certain generalized "displacements" to occur, with their product being the energy transferred as a result. These forces and their associated displacements are called **conjugate variables**. For example, consider the pV conjugate pair. The pressure P acts as a generalized force: Pressure differences force a change in volume dV, and their product is the energy lost by the system due to work. Here pressure is the driving force, volume is the associated displacement, and the two form a pair of conjugate variables. In a similar way, temperature differences drive changes in entropy, and their product is the energy transferred by heat transfer. The thermodynamic force is always an intensive variable and the displacement is always an extensive variable, yielding an extensive energy. The intensive (force) variable is the derivative of the (extensive) internal energy with respect to the extensive (displacement) variable, with all other extensive variables held constant.

The theory of thermodynamic potentials is not complete until we consider the number of particles in a system as a variable on par with the other extensive quantities such as volume and entropy. The number of particles is, like volume and entropy, the displacement variable in a conjugate pair. The generalized force component of this pair is the chemical potential. The chemical potential may be thought of as a force which, when imbalanced, pushes an exchange of particles, either with the surroundings, or between phases inside the system. In cases where there are a mixture of chemicals and phases, this is a useful concept. For example if a container holds liquid water and water vapor, there will be a chemical potential (which is negative) for the liquid which pushes the water molecules into the vapor (evaporation) and a chemical potential for the vapor, pushing vapor molecules into the liquid (condensation). Only when these "forces" equilibrate, and the chemical potentials of each phase is equal, is equilibrium obtained.

The most commonly considered conjugate thermodynamic variables are (with corresponding SI units):

Thermal parameters:

- Temperature: T (K)
- Entropy: S (J K^{-1})

Mechanical parameters:

- Pressure: P (Pa= J m^{-3})
- Volume: V (m^3 = J Pa^{-1})

or, more generally,

- Stress: σ_{ij}(Pa= J m^{-3})
- V × Strain: $V \times \varepsilon_{ij}$($m^3$ = J Pa^{-1})

Material parameters:

- chemical potential: μ (J)
- particle number: N (particles or mole)

For a system with different types i of particles, a small change in the internal energy is given by:

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i\ ,$$

where U is internal energy, T is temperature, S is entropy, P is pressure, V is volume, μ_i is the chemical potential of the i-th particle type, and N_i is the number of i-type particles in the system.

Here, the temperature, pressure, and chemical potential are the generalized forces, which drive the generalized changes in entropy, volume, and particle number respectively. These parameters all affect the internal energy of a thermodynamic system. A small change dU in the internal energy of the system is given by the sum of the flow of energy across the boundaries of the system due to the corresponding conjugate pair. These concepts will be expanded upon in the following sections.

While dealing with processes in which systems exchange matter or energy, classical thermodynamics is not concerned with the rate at which such processes take place, termed kinetics. For this reason, the term *thermodynamics* is usually used synonymously with *equilibrium thermodynamics*. A central notion for this connection is that of quasistatic processes, namely idealized, "infinitely slow" processes. Time-dependent thermodynamic processes far away from equilibrium are studied by non-equilibrium thermodynamics. This can be done through linear or non-linear analysis of irreversible processes, allowing systems near and far away from equilibrium to be studied, respectively.

The pressure/volume and stress/strain pair

As an example, consider the PV conjugate pair. The pressure acts as a generalized force - pressure differences force a change in volume, and their product is the energy lost by the system due to mechanical work. Pressure is the driving force, volume is the associated displacement, and the two form a pair of conjugate variables.

The above holds true only for non-viscous fluids. In the case of viscous fluids, plastic and elastic solids, the pressure force is generalized to the stress tensor, and changes in volume are generalized to the volume multiplied by the strain tensor (Landau & Lifshitz 1986). These then form a conjugate pair. If σ_{ij} is the *ij* component of the stress tensor, and $\varepsilon_{ij}$is the *ij* component of the strain tensor, then the mechanical work done as the result of a stress-induced infinitesimal strain $d\varepsilon_{ij}$is:

$$\delta w = -V \sum_{ij} \sigma_{ij} d\varepsilon_{ij}$$

or, using Einstein notation for the tensors, in which repeated indices are assumed to be summed:

$$\delta w = -V \sigma_{ij} d\varepsilon_{ij}$$

In the case of pure compression (i.e. no shearing forces), the stress tensor is simply the negative of the pressure times the unit tensor so that

$$\delta w = -V \left(-P\delta_{ij}\right) d\varepsilon_{ij} = PV d\varepsilon_{kk}$$

The trace of the strain tensor (ε_{kk}) is just the fractional change in volume so that the above reduces to $\delta w = PdV$ as it should.

The temperature/entropy pair

In a similar way, temperature differences drive changes in entropy, and their product is the energy transferred by heating. We should note that this is the only **heat** term, the other terms are essentially all various forms of **work**.

The chemical potential/particle number pair

The chemical potential is like a force which pushes an increase in particle number. In cases where there are a mixture of chemicals and phases, this is a useful concept. For example if a container holds water and water vapor, there will be a chemical potential (which is negative) for the liquid pushing water molecules into the vapor (evaporation) and a chemical potential for the vapor, pushing vapor molecules into the liquid (condensation). Only when these "forces" equilibrate is equilibrium obtained.

Thermodynamic Potentials

A **thermodynamic potential** is a scalar function used to represent the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term *fundamental functions*. One main thermodynamic potential which has a physical interpretation is the internal energy, U. It is the energy of configuration of a given system of conservative forces (that is why it is a potential) and only has meaning with respect to a defined set of references (or data). Expressions for all other thermodynamic energy potentials are derivable via Legendre transforms from an expression for U. In thermodynamics, certain forces, such as gravity, are typically disregarded when formulating expressions for potentials. For example, while all the working fluid in a steam engine may have higher energy due to gravity while sitting on top of Mt. Everest than it would at the bottom of the Mariana trench, the gravitational potential energy term in the formula for the internal energy would usually be ignored because *changes* in gravitational potential within the engine during operation would be negligible.

Description and interpretation

Five common thermodynamic potentials are:

Name	Symbol	Formula	Natural variables
Internal energy	U	$\int(TdS - pdV + \sum_i \mu_i dN_i)$	$S,V,\{N_i\}$
Helmholtz free energy	F, A	$U - TS$	$T,V,\{N_i\}$
Enthalpy	H	$U + pV$	$S,p,\{N_i\}$
Gibbs free energy	G	$U + pV - TS$	$T,p,\{N_i\}$
Landau Potential (Grand potential)	Ω, Φ_G	$U - TS - \sum_i \mu_i N_i$	$T,V,\{\mu_i\}$

where T = temperature, S = entropy, p = pressure, V = volume. The Helmholtz free energy is often denoted by the symbol F, but the use of A is preferred by IUPAC . N_i is the number of particles of type i in the system and μ_i is the chemical potential for an i-type particle. For the sake of completeness, the set of all N_i are also included as natural variables, although they are sometimes ignored.

These five common potentials are all energy potentials, but there are also entropy potentials. The thermodynamic square can be used as a tool to recall and derive some of the potentials.

Just as in mechanics, where potential energy is defined as capacity to do work, similarly different potentials have different meanings. Internal energy(U) is the capacity to do work plus the capacity to release heat. Gibbs energy is the capacity to do non-mechanical work. Enthalpy is the capacity to do non-mechanical work plus the capacity to release heat. Helmholtz free energy is the capacity to do work (non-mechanical plus mechanical). From these definitions we can say that ΔU is the energy added to the system, ΔF is the total work done on it, ΔG is the non-mechanical work done on it, and ΔH is the sum of non-mechanical work done on the system and the heat given to it. Thermodynamic potentials are very useful when calculating the equilibrium results of a chemical reaction, or when measuring the properties of materials in a chemical reaction. The chemical reactions usually take place under some simple constraints such as constant pressure and temperature, or constant entropy and volume, and when this is true, there is a corresponding thermodynamic potential which comes into play. Just as in mechanics, the system will tend towards lower values of potential and at equilibrium, under these constraints, the potential will take on an unchanging minimum value. The thermodynamic potentials can also be used to estimate the total amount of energy available from a thermodynamic system under the appropriate constraint.

In particular:

- When the entropy (S) and "external parameters" (e.g. volume) of a closed system are held constant, the internal energy (U) decreases and reaches a minimum value at equilibrium. This follows from the first and second laws of thermodynamics and is called the principle of minimum energy. The following three statements are directly derivable from this principle.
- When the temperature (T) and external parameters of a closed system are held constant, the Helmholtz free energy (F) decreases and reaches a minimum value at equilibrium.
- When the pressure (p) and external parameters of a closed system are held constant, the enthalpy (H) decreases and reaches a minimum value at equilibrium.
- When the temperature (T), pressure (p) and external parameters of a closed system are held constant, the Gibbs free energy (G) decreases and reaches a minimum value at equilibrium.

Natural variables

The variables that are held constant in this process are termed the **natural variables** of that potential. The natural variables are important not only for the above mentioned reason, but also because if a thermodynamic potential can be determined as a function of its natural variables, all of the thermodynamic properties of the system can be found by taking partial derivatives of that potential with respect to its natural variables and this is true for no other combination of variables. Conversely, if a thermodynamic potential is not given as a function of its natural variables, it will not, in general, yield all of the thermodynamic properties of the system.

Notice that the set of natural variables for the above four potentials are formed from every combination of the T-S and P-V variables, excluding any pairs of conjugate variables. There is no reason to ignore the $\mu_i - N_i$ conjugate pairs, and in fact we may define four additional potentials for each species. Using IUPAC notation in which the brackets contain the natural variables (other than the main four), we have:

Formula	**Natural variables**
$U[\mu_j] = U - \mu_j N_j$	$S, V, \{N_{i\neq j}\}, \mu_j$
$F[\mu_j] = U - TS - \mu_j N_j$	$T, V, \{N_{i\neq j}\}, \mu_j$
$H[\mu_j] = U + pV - \mu_j N_j$	$S, p, \{N_{i\neq j}\}, \mu_j$
$G[\mu_j] = U + pV - TS - \mu_j N_j$	$T, p, \{N_{i\neq j}\}, \mu_j$

If there is only one species, then we are done, but if there are, say two species, then there will be additional potentials such as $U[\mu_1,\mu_2] = U - \mu_1 N_1 - \mu_2 N_2$ and so on. If there are D dimensions to the thermodynamic space, then there are 2^D unique thermodynamic potentials. For the most simple case, a single phase ideal gas, there will be three dimensions, yielding eight thermodynamic potentials.

In statistical mechanics, the relationship between the Helmholtz free energy and the partition function is fundamental, and is used to calculate the thermodynamic properties of matters.

The fundamental equations

The definitions of the thermodynamic potentials may be differentiated and, along with the first and second laws of thermodynamics, a set of differential equations known as the *fundamental equations* follow . By the first law of thermodynamics, any differential change in the internal energy U of a system can be written as the sum of heat flowing into the system and work done by the system on the environment, along with any change due to the addition of new particles to the system:

$$\mathrm{d}U = \delta Q - \delta W + \sum_i \mu_i \,\mathrm{d}N_i$$

where δQ is the infinitesimal heat flow into the system, and δW is the infinitesimal work done by the system, μ_i is the chemical potential of particle type i and N_i is the number of type i particles. (Note that neither δQ nor δW are exact differentials. Small changes in these variables are therefore represented with δ rather than d.)

By the second law of thermodynamics, we can express the internal energy change in terms of state functions and their differentials. In case of quasistatic changes we have:

$$\begin{aligned}\delta Q &= T\,\mathrm{d}S \\ \delta W &= p\,\mathrm{d}V\end{aligned}$$

where

T is temperature,
S is entropy,
p is pressure,

and *V* is volume, and the equality holds for reversible processes.

This leads to the standard differential form of the internal energy in case of a quasistatic reversible change:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \,\mathrm{d}N_i$$

Since U, S and V are thermodynamic functions of state, the above relation holds also for arbitrary non-reversible changes. If the system has more external variables than just the volume that can change, the fundamental thermodynamic relation generalizes to:

$$dU = T\,dS - \sum_i X_i\,dx_i + \sum_j \mu_j\,dN_j$$

Here the X_i are the generalized forces corresponding to the external variables x_i.

Applying Legendre transforms repeatedly, the following differential relations hold for the four potentials:

$$\begin{aligned}
\mathrm{d}U &= T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \,\mathrm{d}N_i \\
\mathrm{d}F &= -S\,\mathrm{d}T - p\mathrm{d}V + \sum_i \mu_i \,\mathrm{d}N_i \\
\mathrm{d}H &= T\,\mathrm{d}S + V\mathrm{d}p + \sum_i \mu_i \,\mathrm{d}N_i \\
\mathrm{d}G &= -S\,\mathrm{d}T + V\mathrm{d}p + \sum_i \mu_i \,\mathrm{d}N_i
\end{aligned}$$

Note that the infinitesimals on the right hand side of each of the above equations are of the natural variables of the potential on the left hand side. Similar equations can be developed for all of the other thermodynamic potentials of the system. There will be one fundamental equation for each thermodynamic potential, resulting in a total of 2^D fundamental equations.

The equations of state

We can use the above equations to derive some differential definitions of some thermodynamic parameters. If we define Φ to stand for any of the thermodynamic potentials, then the above equations are of the form:

$$\mathrm{d}\Phi = \sum_i x_i \, \mathrm{d}y_i$$

where x_i and y_i are conjugate pairs, and the y_i are the natural variables of the potential Φ. From the chain rule it follows that:

$$x_j = \left(\frac{\partial \Phi}{\partial y_j}\right)_{\{y_{i \neq j}\}}$$

Where $\{y_{i \neq j}\}$ is the set of all natural variables of Φ except y_j. This yields expressions for various thermodynamic parameters in terms of the derivatives of the potentials with respect to their natural variables. These equations are known as **equations of state** since they specify parameters of the thermodynamic state. If we restrict ourselves to the potentials U,F,H and G, then we have:

$$\begin{aligned}
+T &= \left(\frac{\partial U}{\partial S}\right)_{V,\{N_i\}} = \left(\frac{\partial H}{\partial S}\right)_{p,\{N_i\}} \\
-p &= \left(\frac{\partial U}{\partial V}\right)_{S,\{N_i\}} = \left(\frac{\partial F}{\partial V}\right)_{T,\{N_i\}} \\
+V &= \left(\frac{\partial H}{\partial p}\right)_{S,\{N_i\}} = \left(\frac{\partial G}{\partial p}\right)_{T,\{N_i\}} \\
-S &= \left(\frac{\partial G}{\partial T}\right)_{p,\{N_i\}} = \left(\frac{\partial F}{\partial T}\right)_{V,\{N_i\}} \\
\mu_j &= \left(\frac{\partial \phi}{\partial N_j}\right)_{X,Y,\{N_{i \neq j}\}}
\end{aligned}$$

where, in the last equation, φ is any of the thermodynamic potentials U, F, H, G and $X, Y, \{N_{j \neq i}\}$ are the set of natural variables for that potential, excluding N_i. If we use all potentials, then we will have more equations of state such as

$$-N_j = \left(\frac{\partial U[\mu_j]}{\partial \mu_j}\right)_{S,V,\{N_{i \neq j}\}}$$

and so on. In all, there will be *D* equations for each potential resulting in a total of $D\ 2^D$ equations of state. If the *D* equations of state for a particular potential are known, then the fundamental equation for that potential can be determined. This means that all thermodynamic information about the system will be known, and that the fundamental equations for any other potential can be found, along with the corresponding equations of state.

The Maxwell relations

Again, define x_i and y_i to be conjugate pairs, and the y_i to be the natural variables of some potential Φ. We may take the "cross differentials" of the state equations, which obey the following relationship:

$$\left(\frac{\partial}{\partial y_j}\left(\frac{\partial \Phi}{\partial y_k}\right)_{\{y_{i\neq k}\}}\right)_{\{y_{i\neq j}\}} = \left(\frac{\partial}{\partial y_k}\left(\frac{\partial \Phi}{\partial y_j}\right)_{\{y_{i\neq j}\}}\right)_{\{y_{i\neq k}\}}$$

From these we get the Maxwell relations. There will be *(D-1)/2* of them for each potential giving a total of *D(D-1)/2* equations in all. If we restrict ourselves the U, F, H, G

$$\left(\frac{\partial T}{\partial V}\right)_{S,\{N_i\}} = -\left(\frac{\partial p}{\partial S}\right)_{V,\{N_i\}}$$
$$\left(\frac{\partial T}{\partial p}\right)_{S,\{N_i\}} = +\left(\frac{\partial V}{\partial S}\right)_{p,\{N_i\}}$$
$$\left(\frac{\partial S}{\partial V}\right)_{T,\{N_i\}} = +\left(\frac{\partial p}{\partial T}\right)_{V,\{N_i\}}$$
$$\left(\frac{\partial S}{\partial p}\right)_{T,\{N_i\}} = -\left(\frac{\partial V}{\partial T}\right)_{p,\{N_i\}}$$

Using the equations of state involving the chemical potential we get equations such as:

$$\left(\frac{\partial T}{\partial N_j}\right)_{V,S,\{N_{i\neq j}\}} = \left(\frac{\partial \mu_j}{\partial S}\right)_{V,\{N_i\}}$$

and using the other potentials we can get equations such as:

$$\left(\frac{\partial N_j}{\partial V}\right)_{S,\mu_j,\{N_{i\neq j}\}} = -\left(\frac{\partial p}{\partial \mu_j}\right)_{S,V\{N_{i\neq j}\}}$$

$$\left(\frac{\partial N_j}{\partial N_k}\right)_{S,V,\mu_j,\{N_{i\neq j,k}\}} = -\left(\frac{\partial \mu_k}{\partial \mu_j}\right)_{S,V\{N_{i\neq j}\}}$$

Euler integrals

Again, define x_i and y_i to be conjugate pairs, and the y_i to be the natural variables of the internal energy. Since all of the natural variables of the internal energy U are extensive quantities

$$U(\{\alpha y_i\}) = \alpha U(\{y_i\})$$

it follows from Euler's homogeneous function theorem that the internal energy can be written as:

$$U(\{y_i\}) = \sum_j y_j \left(\frac{\partial U}{\partial y_j}\right)_{\{y_{i\neq j}\}}$$

From the equations of state, we then have:

$$U = TS - pV + \sum_i \mu_i N_i$$

Substituting into the expressions for the other main potentials we have:

$$\begin{aligned} F &= -pV + \sum_i \mu_i N_i \\ H &= TS + \sum_i \mu_i N_i \\ G &= \sum_i \mu_i N_i \end{aligned}$$

As in the above sections, this process can be carried out on all of the other thermodynamic potentials. Note that the Euler integrals are sometimes also referred to as fundamental equations.

The Gibbs–Duhem relation

Deriving the Gibbs–Duhem equation from basic thermodynamic state equations is straightforward. The Gibbs free energy G can be expanded locally at equilibrium in terms of the thermodynamic state as:

$$\mathrm{d}G = \left.\frac{\partial G}{\partial p}\right|_{T,N} \mathrm{d}p + \left.\frac{\partial G}{\partial T}\right|_{p,N} \mathrm{d}T + \sum_{i=1}^{I} \left.\frac{\partial G}{\partial N_i}\right|_{p,N_{j\neq i}} \mathrm{d}N_i$$

With the substitution of two of the Maxwell relations and the definition of chemical potential, this is transformed into:

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum_{i=1}^{I} \mu_i \mathrm{d}N_i$$

The chemical potential is just another name for the partial molar Gibbs free energy, and as such:

$$G = \sum_{i=1}^{I} \mu_i N_i$$

$$\mathrm{d}G = \sum_{i=1}^{I} \mu_i \,\mathrm{d}N_i + \sum_{i=1}^{I} N_i \,\mathrm{d}\mu_i$$

Subtracting yields the Gibbs–Duhem relation:

$$\sum_{i=1}^{I} N_i \,\mathrm{d}\mu_i = -S\,\mathrm{d}T + V\,\mathrm{d}p$$

The Gibbs–Duhem is a relationship among the intensive parameters of the system. It follows that for a simple system with *I* components, there will be *I* + 1 independent parameters, or degrees of freedom. For example, a simple system with a single component will have two degrees of freedom, and may be specified by only two parameters, such as pressure and volume for example. The law is named after Josiah Willard Gibbs and Pierre Duhem.

Chemical reactions

Changes in these quantities are useful for assessing the degree to which a chemical reaction will proceed. The relevant quantity depends on the reaction conditions, as shown in the following table. *Δ* denotes the change in the potential and at equilibrium the change will be zero.

	Constant *V*	**Constant *p***
Constant *S*	ΔU	ΔH
Constant *T*	ΔF	ΔG

Most commonly one considers reactions at constant *p* and *T*, so the Gibbs free energy is the most useful potential in studies of chemical reactions.

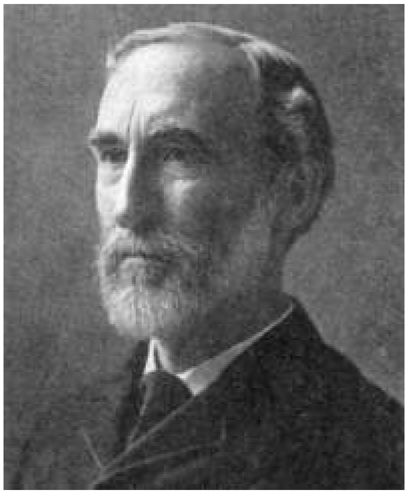
Chapter- 2

Chemical Thermodynamics

Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Chemical thermodynamics involves not only laboratory measurements of various thermodynamic properties, but also the application of mathematical methods to the study of chemical questions and the *spontaneity* of processes.

The structure of chemical thermodynamics is based on the first two laws of thermodynamics. Starting from the first and second laws of thermodynamics, four equations called the "fundamental equations of Gibbs" can be derived. From these four, a multitude of equations, relating the thermodynamic properties of the thermodynamic system can be derived using relatively simple mathematics. This outlines the mathematical framework of chemical thermodynamics.

History



J. Willard Gibbs - founder of *chemical thermodynamics*

In 1865, the German physicist Rudolf Clausius, in his *Mechanical Theory of Heat*, suggested that the principles of thermochemistry, e.g. such as the heat evolved in combustion reactions, could be applied to the principles of thermodynamics. Building on the work of Clausius, between the years 1873-76 the American mathematical physicist

Willard Gibbs published a series of three papers, the most famous one being the paper *On the Equilibrium of Heterogeneous Substances*. In these papers, Gibbs showed how the first two laws of thermodynamics could be measured graphically and mathematically to determine both the thermodynamic equilibrium of chemical reactions as well as their tendencies to occur or proceed. Gibbs' collection of papers provided the first unified body of thermodynamic theorems from the principles developed by others, such as Clausius and Sadi Carnot.

During the early 20th century, two major publications successfully applied the principles developed by Gibbs to chemical processes, and thus established the foundation of the science of chemical thermodynamics. The first was the 1923 textbook *Thermodynamics and the Free Energy of Chemical Substances* by Gilbert N. Lewis and Merle Randall. This book was responsible for supplanting the chemical affinity for the term free energy in the English-speaking world. The second was the 1933 book *Modern Thermodynamics by the methods of Willard Gibbs* written by E. A. Guggenheim. In this manner, Lewis, Randall, and Guggenheim are considered as the founders of modern chemical thermodynamics because of the major contribution of these two books in unifying the application of thermodynamics to chemistry.

Overview

The primary objective of chemical thermodynamics is the establishment of a criterion for the determination of the feasibility or spontaneity of a given transformation. In this manner, chemical thermodynamics is typically used to predict the energy exchanges that occur in the following processes:

1. Chemical reactions
2. Phase changes
3. The formation of solutions

The following state functions are of primary concern in chemical thermodynamics:

- Internal energy (U)
- Enthalpy (H).
- Entropy (S)
- Gibbs free energy (G)

Most identities in chemical thermodynamics arise from application of the first and second laws of thermodynamics, particularly the law of conservation of energy, to these state functions.

Chemical energy

Chemical energy is the potential of a chemical substance to undergo a transformation through a chemical reaction or to transform other chemical substances. Breaking or making of chemical bonds involves energy, which may be either absorbed or evolved from a chemical system.

Energy that can be released (or absorbed) because of a reaction between a set of chemical substances is equal to the difference between the energy content of the products and the reactants. This change in energy is called the change in internal energy of a chemical reaction. Where $\Delta U_{f\,\mathrm{reactants}}^{\circ}$ is the internal energy of formation of the reactant molecules that can be calculated from the bond energies of the various chemical bonds of the molecules under consideration and $\Delta U_{f\,\mathrm{products}}^{\circ}$ is the internal energy of formation of the product molecules. The internal energy change of a process is equal to the heat change if it is measured under conditions of constant volume, as in a closed rigid container such as a bomb calorimeter. However, under conditions of constant pressure, as in reactions in vessels open to the atmosphere, the measured heat change is not always equal to the internal energy change, because pressure-volume work also releases or absorbs energy. (The heat change at constant pressure is called the enthalpy change; in this case the enthalpy of formation).

Another useful term is the heat of combustion, which is the energy released due to a combustion reaction and often applied in the study of fuels. Food is similar to hydrocarbon fuel and carbohydrate fuels, and when it is oxidized, its caloric content is similar (though not assessed in the same way as a hydrocarbon fuel).

In chemical thermodynamics the term used for the chemical potential energy is chemical potential, and for chemical transformation an equation most often used is the Gibbs-Duhem equation.

Chemical reactions

In most cases of interest in chemical thermodynamics there are internal degrees of freedom and processes, such as chemical reactions and phase transitions, which always create entropy unless they are at equilibrium, or are maintained at a "running equilibrium" through "quasi-static" changes by being coupled to constraining devices, such as pistons or electrodes, to deliver and receive external work. Even for homogeneous "bulk" materials, the free energy functions depend on the composition, as do all the extensive thermodynamic potentials, including the internal energy. If the quantities $\{ N_i \}$, the number of chemical species, are omitted from the formulae, it is impossible to describe compositional changes.

Gibbs function

For a "bulk" (unstructured) system they are the last remaining extensive variables. For an unstructured, homogeneous "bulk" system, there are still various *extensive* compositional variables $\{ N_i \}$ that G depends on, which specify the composition, the amounts of each chemical substance, expressed as the numbers of molecules present or (dividing by Avogadro's number), the numbers of moles

$$G = G(T, P, \{N_i\})\ .$$

For the case where only *PV* work is possible

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

in which μ_i is the chemical potential for the *i*-th component in the system

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i},etc.}\ .$$

The expression for d*G* is especially useful at constant *T* and *P*, conditions which are easy to achieve experimentally and which approximates the condition in living creatures

$$(dG)_{T,P} = \sum_i \mu_i dN_i\ .$$

Chemical affinity

In chemical physics and physical chemistry, **chemical affinity** is the electronic property by which dissimilar chemical species are capable of forming chemical compounds. Chemical affinity can also refer to the tendency of an atom or compound to combine by chemical reaction with atoms or compounds of unlike composition.

According to chemistry historian Henry Leicester, the influential 1923 textbook *Thermodynamics and the Free Energy of Chemical Reactions* by Gilbert N. Lewis and Merle Randall led to the replacement of the term "affinity" by the term "free energy" in much of the English-speaking world.

Modern conceptions

In modern terms, we relate affinity to the phenomenon whereby certain atoms or molecules have the tendency to aggregate or bond. For example, in the 1919 book *Chemistry of Human Life* physician George W. Carey states that, "Health depends on a proper amount of iron phosphate $Fe_3(PO_4)_2$ in the blood, for the molecules of this salt have chemical affinity for oxygen and carry it to all parts of the organism." In this antiquated context, chemical affinity is sometimes found synonymous with the term "magnetic attraction". Many writings, up until about 1925, also refer to a "law of chemical affinity".

Thermodynamics

In 1923, the Belgian mathematician and physicist Théophile de Donder derived a relation between affinity *A* and the Gibbs free energy *G* of a chemical reaction. Through a series of derivations, de Donder showed that if we consider a mixture of chemical species with the possibility of chemical reaction, it can be proven that the following relation holds:

$$A = -\Delta_r G$$

With the writings of Théophile de Donder as precedent, Ilya Prigogine and Defay in *Chemical Thermodynamics* (1954) defined chemical affinity (denoted by *A*) as a function of the increments in uncompensated heat of reaction and reaction progress variable (denoted by dQ' and $d\xi$, respectively):

$$A = \frac{dQ'}{d\xi}.$$

This definition is useful for quantifying the factors responsible both for the state of equilibrium systems (where $A = 0$), and for changes of state of non-equilibrium systems (where $A \neq 0$).

The present IUPAC definition is that affinity is the negative partial derivative of Gibbs energy with respect to extent of reaction at constant pressure and temperature. That is,

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{P,T}.$$

It follows that affinity is positive for spontaneous reactions.

History

"Chemical affinity", historically, refers to the "force" that causes chemical reactions. A broad definition, used generally throughout history, is that chemical affinity is that whereby substances enter into or resist decomposition. In current use, it

Ilya Prigogine summarized the concept of affinity, saying, "All chemical reactions drive the system to a state of equilibrium in which the *affinities* of the reactions vanish."

The term *affinity* has been used figuratively since c. 1600 in discussions of structural relationships in chemistry, philology, etc., and reference to "natural attraction" is from 1616.

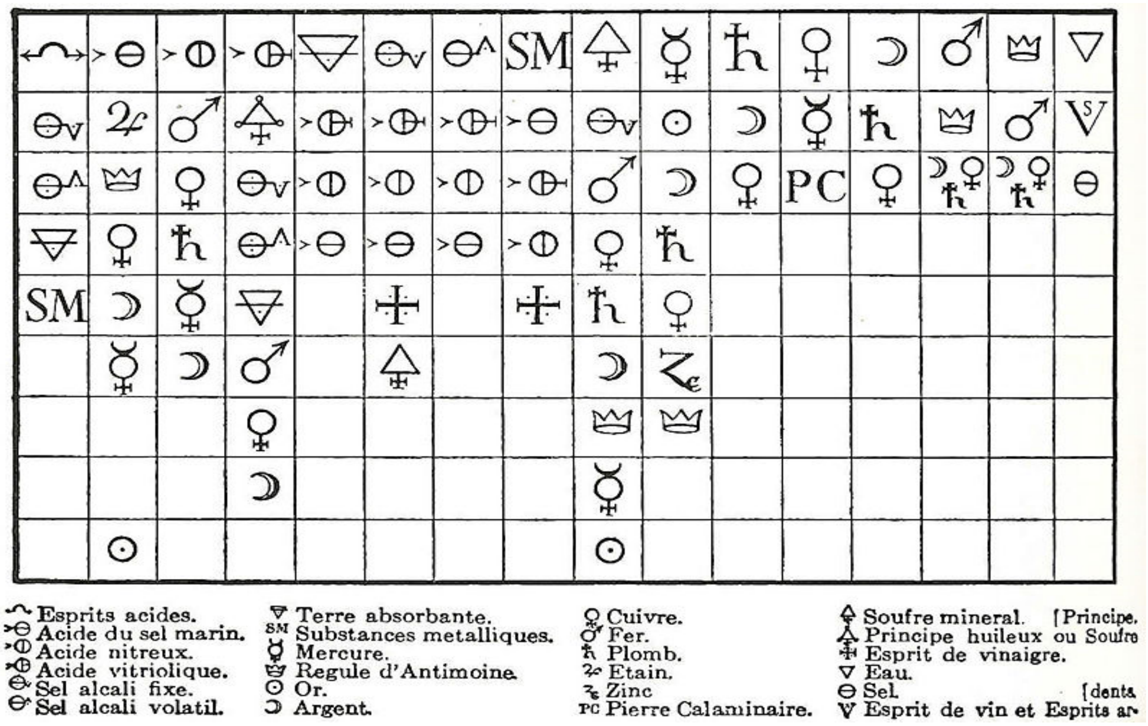
The idea of *affinity* is extremely old. Many attempts have been made at identifying its origins. The majority of such attempts, however, except in a general manner, end in futility since "affinities" lie at the basis of all magic, thereby pre-dating science. Physical chemistry, however, was one of the first branches of science to study and formulate a "theory of affinity". The name *affinitas* was first used in the sense of chemical relation by German philosopher Albertus Magnus near the year 1250. Later, those as Robert Boyle, John Mayow, Johann Glauber, Isaac Newton, and Georg Stahl put forward ideas on elective affinity in attempts to explain how heat is evolved during combustion reactions.

The modern term chemical affinity is a somewhat modified variation of its eighteenth-century precursor "elective affinity" or elective attractions, a coinage of the Swedish chemist Torbern Olof Bergman from his book *De attractionibus electivis* (1775). Antoine Lavoisier, in his famed 1789 *Traité Élémentaire de Chimie (Elements of Chemistry)*, refers to Bergmann's work and discusses the concept of elective affinities or attractions.

Goethe used the concept in his novel Elective Affinities, (1809)

Geoffroy's 1718 affinity table

The first-ever *affinity table*, which was based on displacement reactions, was published in 1718 by the French chemist Étienne François Geoffroy. Geoffroy's name is best known in connection with these tables of "affinities" (*tables des rapports*), which were first presented to the French Academy in 1718 and 1720, as shown below:



Geoffroy's **Affinity Table** (1718): At the head of the column is a substance with which all the substances below can combine, where each column below the header is ranked by degrees of "**affinity**".

These were lists, prepared by collating observations on the actions of substances one upon another, showing the varying degrees of affinity exhibited by analogous bodies for different reagents, and they retained their vogue for the rest of the century, until displaced by the profounder conceptions introduced by Claude Berthollet.

Solutions

In solution chemistry and biochemistry, the Gibbs free energy decrease ($\partial G/\partial\xi$, in molar units, denoted cryptically by ΔG) is commonly used as a surrogate for ($-T$ times) the entropy produced by spontaneous chemical reactions in situations where there is no work being done; or at least no "useful" work; i.e., other than perhaps some $\pm\, P\mathrm{d}V$. The assertion that all *spontaneous reactions have a negative* ΔG is merely a restatement of the fundamental thermodynamic relation, giving it the physical dimensions of energy and somewhat obscuring its significance in terms of entropy. When there is no useful work being done, it would be less misleading to use the Legendre transforms of the entropy appropriate for constant T, or for constant T and P, the Massieu functions $-F/T$ and $-G/T$ respectively.

Non equilibrium

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with systems that are not in thermodynamic equilibrium. Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems. The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics. Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods; the fundamental difficulty for macroscopic thermodynamics is in defining entropy for systems not in thermodynamic equilibrium.

The most widely understood approach to non-equilibrium thermodynamics can (Jou, Casas-Vázquez, Lebon (1993)) be called **classical irreversible thermodynamics**. This approach demands spatial and temporal continuity of locally defined intensive variables such as temperature and internal energy density, which requires what is known as **local thermodynamic equilibrium**. These are very stringent demands. This present article is focused on the restricted subject of classical irreversible thermodynamics.

Other concepts of particular importance for non-equilibrium thermodynamics include time rate of dissipation of energy (Section II of Rayleigh (1873)), and of time rate of entropy production (Onsager 1931), and dissipative structure.

Non-equilibrium thermodynamics is most successful in the study of steady states, where there are nonzero flows and entropy production, but no time variation, and of systems with dissipative structure. Such steady states and dissipative structures can sometimes be understood in terms of extremal principles in non-equilibrium thermodynamics.

There are other approaches to non-equilibrium thermodynamics, for example **extended irreversible thermodynamics**), but they are hardly touched on in the present article

Basic concepts

There are many examples of stationary non-equilibrium systems, some very simple, like a system confined between two thermostats at different temperatures or the ordinary Couette flow, a fluid enclosed between two flat walls moving in opposite directions and defining non-equilibrium conditions at the walls. Laser action is also a non-equilibrium thermodynamic process. Here a strong temperature difference is maintained between two molecular degrees of freedom (with molecular laser, vibrational and rotational molecular motion). Damping of acoustical perturbations or shock waves are non-stationary non-equilibrium processes. Driven complex fluids, turbulent systems and glasses are other examples of non-equilibrium systems.

The mechanics of macroscopic systems depends on a number of extensive quantities. It should be stressed that all systems are permanently interacting with their surroundings, thereby causing unavoidable fluctuations of extensive quantities. Equilibrium conditions of thermodynamic systems are related to the maximum property of the entropy. If the only extensive quantity that is allowed to fluctuate is the internal energy, all the other ones being kept strictly constant, the temperature of the system is measurable and meaningful. The system's properties are then most conveniently described using the thermodynamic potential Helmholtz free energy ($A = U - TS$), a Legendre transformation of the energy. If, next to fluctuations of the energy, the macroscopic dimensions (volume) of the system are left fluctuating, we use the Gibbs free energy ($G = U + PV - TS$), where the system's properties are determined both by the temperature and by the pressure. Non-equilibrium systems are much more complex and they may undergo fluctuations of more extensive quantities. The boundaries conditions impose to them particular intensive variables, like temperature gradients or distorted collective motions (shear motions, vortices, etc), often called thermodynamic forces. If free energies are very useful in equilibrium thermodynamics, it must be stressed that there is no general law defining stationary non-equilibrium properties of the energy as is the second law of thermodynamics for the entropy in equilibrium thermodynamics. That is why in such cases a more generalized Legendre transformation should be considered. This is the extended Massieu potential. By definition, the entropy (S) is a function of the collection of extensive quantities E_i. Each extensive quantity has a conjugate intensive variable I_i (a restricted definition of intensive variable is used here by comparison to the definition given in this link) so that:

$$I_i = \partial S / \partial E_i.$$

We then define the extended Massieu function as follows:

$$k_b M = S - \sum_i (I_i E_i),$$

where k_b is Boltzmann's constant, whence

$$k_b\,dM = \sum_i (E_i\,dI_i).$$

The independent variables are the intensities.

Intensities are global values, valid for the system as a whole. When boundaries impose to the system different local conditions, (e.g. temperature differences), there are intensive variables representing the average value and others representing gradients or higher moments. The latter are the thermodynamic forces driving fluxes of extensive properties through the system.

It may be shown that the Legendre transformation changes the maximum condition of the entropy (valid at equilibrium) in a minimum condition of the extended Massieu function for stationary states, no matter whether at equilibrium or not.

Stationary states, fluctuations, and stability

In thermodynamics one is often interested in a stationary state of a process, allowing that the stationary state include the occurrence of unpredictable and experimentally unreproducible fluctuations in the state of the system. The fluctuations are due to the system's internal sub-processes and to exchange of matter or energy with the system's surrounds that create the constraints that define the process.

If the stationary state of the process is stable, then the unreproducible fluctuations involve local transient decreases of entropy. The reproducible response of the system is then to increase the entropy back to its maximum by irreversible processes: the fluctuation cannot be reproduced with a significant level of probability. Fluctuations about stable stationary states are extremely small except near critical points (Kondepudi and Prigogine 1998, page 323). The stable stationary state has a local maximum of entropy and is locally the most reproducible state of the system. There are theorems about the irreversible dissipation of fluctuations. Here 'local' means local with respect to the abstract space of thermodynamic coordinates of state of the system.

If the stationary state is unstable, then any fluctuation will almost surely trigger the virtually explosive departure of the system from the unstable stationary state. This can be accompanied by increased export of entropy.

Local thermodynamic equilibrium

The scope of classical non-equilibrium thermodynamics does not cover all physical processes.

Classical non-equilibrium thermodynamics of matter in laboratory conditions

According to Wildt, current versions of non-equilibrium thermodynamics ignore radiant heat; they can do so because they refer to matter under laboratory conditions with temperatures well below the those of stars. At laboratory temperatures, in laboratory quantities of matter, thermal radiation is weak and can be practically nearly ignored. For example, atmospheric physics is concerned with large amounts of matter, occupying cubic kilometers, that are not necessarily within the scope of laboratory conditions. Thus current versions of classical non-equilibrium thermodynamics might be called **classical non-equilibrium thermodynamics of matter in laboratory conditions**. The exact boundaries of its scope may not be fully known, but one wants some confidence in what one is doing, and so one says that a sufficient condition for the validity of many studies in classical non-equilibrium thermodynamics of matter is that they deal with what is known as **local thermodynamic equilibrium** . In classical thermodynamics, macroscopic variables such as temperature and entropy are strictly speaking defined only in systems at thermodynamic equilibrium.

Local thermodynamic equilibrium of matter means that conceptually, for study and analysis, the system can be spatially and temporally divided into 'cells' of small (infinitesimal) size, in which classical thermodynamical equilibrium conditions for matter are fulfilled to good approximation. These conditions are unfulfilled, for example, in very rarefied gases, in which molecular collisions are infrequent; and in the boundary layers of a star, where radiation is passing energy to space; and for interacting fermions at very low temperature, where dissipative processes become ineffective. When these 'cells' are defined, one admits that matter and energy may pass freely between contiguous 'cells', slowly enough to leave the 'cells' in local thermodynamic equilibrium.

One can think here of two 'relaxation times' separated by order of magnitude. The longer relaxation time is of the order of magnitude of times taken for the macroscopic dynamical structure of the system to change. The shorter is of the order of magnitude of times taken for a single 'cell' to reach local thermodynamic equilibrium. If these two relaxation times are not well separated, then the classical non-equilibrium thermodynamical concept of local thermodynamic equilibrium loses its meaning. For example, in the atmosphere, the speed of sound is much greater than the wind speed; this favours the idea of local thermodynamic equilibrium of matter for atmospheric heat transfer studies.

Milne's 1928 definition of local thermodynamic equilibrium in terms of radiative equilibrium

Milne (1928), thinking about stars, gave a definition of 'local thermodynamic equilibrium' in terms of the thermal radiation of the matter in the 'cell'. He forgot Planck's (1914) careful insistence on the presence and radiative equilibrium of a black body for the production of the Kirchhoff-Planck so-called "universal" thermal radiative spectrum. Milne (1928) defined 'local thermodynamic equilibrium' by requiring that the 'cell' radiate as if it were a black body in radiative equilibrium in a cavity at the temperature of the matter of the 'cell'. In the absence of a black body in radiative equilibrium with the 'cell' and in the absence of a specification of the walls of the cavity, this definition is devoid of physical meaning. Milne (1928)) wrongly assumed that even in the absence of these requirements the cell would necessarily radiate as if it were a black body in thermodynamic equilibrium.

Flows and forces

The fundamental relation of classical equilibrium thermodynamics

$$dS = \frac{1}{T}dU + \frac{p}{T}dV + \sum_{i=1}^{s} \frac{\mu_i}{T}dN_i$$

expresses the change in entropy dS of a system as a function of the intensive quantities temperature T, pressure p and i^{th} chemical potential μ_i and of the differentials of the extensive quantities energy U, volume V and i^{th} particle number N_i.

Following Onsager (1931,I), let us extend our considerations to thermodynamically non-equilibrium systems. As a basis, we need locally defined versions of the extensive macroscopic quantities U, V and N_i and of the intensive macroscopic quantities T, p and μ_i.

For classical non-equilibrium studies, we will consider some new locally defined intensive macroscopic variables. We can, under suitable conditions, derive these new variables by locally defining the gradients and flux densities of the basic locally defined macroscopic quantities.

Such locally defined gradients of intensive macroscopic variables are called 'thermodynamic forces'. They 'drive' flux densities, perhaps misleadingly often called 'fluxes', which are dual to the forces. These quantities are defined in the article on Onsager reciprocal relations.

Establishing the relation between such forces and flux densities is a problem in statistical mechanics. Flux densities (J_i) may be coupled. The article on Onsager reciprocal relations considers the stable near-steady thermodynamically non-equilibrium regime, which has dynamics linear in the forces and flux densities.

In stationary conditions, such forces and associated flux densities are by definition time invariant, as also are the system's locally defined entropy and rate of entropy production. Notably, according to Ilya Prigogine and others , when an open system is in conditions that allow it to reach a stable stationary thermodynamically non-equilibrium state, it organizes itself so as to minimize total entropy production defined locally. This is considered further below.

One wants to take the analysis to the further stage of describing the behaviour of surface and volume integrals of non-stationary local quantities; these integrals are macroscopic fluxes and production rates. In general the dynamics of these integrals are not adequately described by linear equations, though in special cases they can be so described.

The Onsager relations

Following Section III of Rayleigh (1873), Onsager (1931, I) showed that in the regime where both the flows are small and the thermodynamic forces vary slowly, there will be a linear relation between them, parametrized by a matrix of coefficients conventionally denoted *L*:

$$J_i = \sum_j L_{ij} \nabla I_j$$

The second law of thermodynamics requires that the matrix *L* be positive definite. Statistical mechanics considerations involving microscopic reversibility of dynamics imply that the matrix *L* is symmetric. This fact is called the *Onsager reciprocal relations*.

Thermodynamic Extremum Principles for Energy Dissipation and Entropy Production

Jou, Casas-Vazquez, Lebon (1993) note that classical non-equilibrium thermodynamics "has seen an extraordinary expansion since the second world war", and they refer to the Nobel prizes for work in the field awarded to Lars Onsager and Ilya Prigogine. Martyushev and Seleznev (2006) note the importance of entropy in the evolution of natural dynamical structures: "Great contribution has been done in this respect by two scientists, namely Clausius, ... , and Prigogine." Prigogine in his 1977 Nobel Lecture said: "... non-equilibrium may be a source of order. Irreversible processes may lead to a new type of dynamic states of matter which I have called “dissipative structures”." Glansdorff and Prigogine (1971) wrote on page xx: "Such 'symmetry breaking instabilities' are of special interest as they lead to a spontaneous 'self-organization' of the system both from the point of view of its *space order* and its *function*."

These advances have led to proposals for various extremal principles for the "self-organized" régimes that are possible for systems governed by classical linear and non-linear non-equilibrium thermodynamical laws, with stable stationary régimes being particularly investigated, and it is these that Prigogine called "dissipative structures".

Principles of Maximum Entropy Production and Minimum Energy Dissipation

Onsager (1931, I) wrote: "Thus the vector field *J* of the heat flow is described by the condition that the rate of increase of entropy, less the dissipation function, be a maximum." Careful note needs to be taken of the opposite signs of the rate of entropy production and of the dissipation function, appearing in the left-hand side of Onsager's equation (5.13) on Onsager's page 423.

Although largely unnoticed at the time Ziegler approached the idea early with his work in the mechanics of plastics in 1961, and later in his book on thermomechanics revised in 1983, and in various papers (e.g., Ziegler (1987),). Ziegler never stated his principle as a universal law but he may have intuited this. He demonstrated his principle using vector space geometry based on an “orthogonality condition” which only worked in systems where the velocities were defined as a single vector or tensor, and thus, as he wrote at p. 347, was “impossible to test by means of macroscopic mechanical models”, and was, as he pointed out, invalid in “compound systems where several elementary processes take place simultaneously”.

Chandrasekhar (1961) wrote "Instability occurs at the minimum temperature gradient at which a balance can be maintained between the kinetic energy dissipated by viscosity and the internal energy released by the buoyancy force."

Glansdorff and Prigogine (1971) on page xv wrote "Dissipative structures have a quite different [from equilibrium structures] status: they are formed and maintained through the effect of exchange of energy and matter in non-equilibrium conditions." They were referring to the dissipation function of Rayleigh (1873) that was used also by Onsager (1931, I, 1931, II). On page 79 of their book Glansdorff and Prigogine (1971) concluded that at a stable steady state, the dissipation function was minimum.

Sawada (1981), postulating a principle of largest amount of entropy increment per unit time, cites work in fluid mechanics by Malkus and Veronis (1958) as having "proven a principle of maximum heat current, which in turn is a maximum entropy production for a given boundary condition". According to Tuck (2008), "On the macroscopic level, the way has been pioneered by a meteorologist (Paltridge 1975, 2001). Initially Paltridge (1975) used the terminology "minimum entropy exchange", but after that, for example in Paltridge (1978), and in Paltridge (1979)), he used the now current terminology "maximum entropy production" to describe the same thing. This point is clarified in the review by Ozawa, Ohmura, Lorenz, Pujol (2003). Paltridge (1978) cited Busse's (1967) fluid mechanical work concerning an extremum principle. Nicolis and Nicolis (1980) discuss Paltridge's work, and they comment that the behaviour of the entropy production is far from simple and universal. Again investigating planetary atmospheric dynamics, Shutts (1981) used an approach to the definition of entropy production, different from Paltridge's, to investigate a more abstract way to check the principle of maximum entropy production, and found a good fit.

C. Nicolis (1999) concludes that one model of atmospheric dynamics has an attractor which is not a regime of maximum or minimum dissipation; she says this seems to rule out the existence of a global organizing principle, and comments that this is to some extent disappointing; she also points to the difficulty of finding a thermodynamically consistent form of entropy production; in the present writer's opinion, there are few as expert in the theory of entropy production as Nicolis. Another top expert offers an extensive discussion of the possibilities for principles of extrema of entropy production and of dissipation of energy: Chapter 12 of Grandy (2008) is very cautious, and finds difficulty in defining the 'rate of internal entropy production' in many cases, and finds that sometimes for the prediction of the course of a process, an extremum of the quantity called the rate of dissipation of energy may be more useful than that of the rate of entropy production; this quantity appeared in Onsager's 1931 origination of this subject. Grandy (2008) in section 4.3 on page 55 is careful to distinguish between the idea that entropy is related to order (which he considers to be a "mischaracterization" that needs "debunking"), and the idea of E.T. Jaynes that entropy is related to the experimental reproducibility of process (which Grandy regards as correct).

Beretta (1986), in an attempt to unify quantum mechanics and thermodynamics, proposed a generalization of the time-dependent Schroedinger equation of quantum mechanics, that postulates and implements at the single particle level the principle of maximum entropy production (even though, at that time, he named it "steepest entropy ascent dynamics"). Beretta (2008) has also extended his steepest-entropy-ascent nonlinear dynamical equation to model the time evolution of non-equilibrium probability distributions in discrete, non-quantum contexts.

Using the information theoretical formalism of Jaynes, Dewar (2003, 2005) claimed to have derived a principle of maximum entropy production applying to nonlinear stationary states. With a background of previous literature, a number of authors cited Dewar’s purported proof. Grinstein and Linsker (2007) showed that Dewar’s derivation was invalid due to an unnoticed physical assumption of linearity in the purported proof; they concluded that "the question of the existence of possible extremal principles (and in particular, of MaxEP) that might apply to far-from-equilibrium regimes (having non-linear constitutive relations) has not been settled by [,]". Lucia offers a proof of a theorem for the eventual steady state of a constrained open system: "The principle of maximum irreversible entropy: The irreversible entropy reaches its maximum at the stability." Unfortunately, Lucia's proof is limited to the theory of so-called "rational thermodynamics" in which there is not necessarily an empirically verifiable definition of entropy, let alone entropy production.

Prigogine’s Theorem of Minimum Entropy Production

In 1945 Prigogine) proposed a “Theorem of Minimum Entropy Production” which applies only to the linear regime near a stationary but possibly thermodynamically non-equilibrium state, and which some have perhaps mistakenly taken to be contradictory to various proposed principles of maximum rate of entropy production. It is said that they are not contradictory but answer different questions. Prigogine’s theorem can be visualized by imagining a system with several thermodynamic forces which are all allowed to equilibrate or adjust in a time-dependent way except that at least one is maintained so that the system cannot get to equilibrium. The result is that that the entropy production will start at some rate and because the forces are progressively depleted the rate of the entropy production will steadily (monotonically) go down until the system gets as close to equilibrium as it can and then stay in that state as long as the one force is maintained. So the entropy production starts at one place and goes down to a minimum where it stays. This principle refers to perturbations, of thermodynamic flows or thermodynamic forces, that are too small to disrupt the local thermodynamic equilibrium regime. Martyushev and Seleznev (2006) refer to a "popular opinion" that the principle of maximum entropy production does not apply in the linear regime, claiming in their footnote 7 that it was held by Ozawa, Ohmura, Lorenz and Pujol (2003); the nearest that the present writer can find in that review to support that claim of Martyushev and Seleznev (2006) is the apparently innocent couple of sentences on page 18: "The maximum entropy production principle, then, acts as a guiding principle for choosing the most probable state among all other possible states allowed by the nonlinear system. The principle is therefore fundamental to nonlinear systems and should not be confused with Prigogine's one for linear systems"; this seems perhaps to mean that the maximum entropy production principle referred to is concerned with large perturbations that disrupt the local thermodynamic equilibrium that is required for the applicability of Prigogine's principle of minimum entropy production; in this case, there is the possibility of evolution to other régimes of local dynamics, that is to say, to "other possible states allowed by the nonlinear system".

System constraints

In this regard, it is crucial to understand the role of walls and other *constraints*, and the distinction between *independent* processes and *coupling*. Contrary to the clear implications of many reference sources, the previous analysis is not restricted to homogenous, isotropic bulk systems which can deliver only PdV work to the outside world, but applies even to the most structured systems. There are complex systems with many chemical "reactions" going on at the same time, some of which are really only parts of the same, overall process. An *independent* process is one that *could* proceed even if all others were unaccountably stopped in their tracks. Understanding this is perhaps a “thought experiment” in chemical kinetics, but actual examples exist.

A gas reaction which results in an increase in the number of molecules will lead to an increase in volume at constant external pressure. If it occurs inside a cylinder closed with a piston, the equilibrated reaction can proceed only by doing work against an external force on the piston. The extent variable for the reaction can increase only if the piston moves, and conversely, if the piston is pushed inward, the reaction is driven backwards.

Similarly, a redox reaction might occur in an electrochemical cell with the passage of current in wires connecting the electrodes. The half-cell reactions at the electrodes are constrained if no current is allowed to flow. The current might be dissipated as joule heating, or it might in turn run an electrical device like a motor doing mechanical work. An automobile lead-acid battery can be recharged, driving the chemical reaction backwards. In this case as well, the reaction is not an independent process. Some, perhaps most, of the Gibbs free energy of reaction may be delivered as external work.

The hydrolysis of ATP to ADP and phosphate can drive the force times distance work delivered by living muscles, and synthesis of ATP is in turn driven by a redox chain in mitochondria and chloroplasts, which involves the transport of ions across the membranes of these cellular organelles. The coupling of processes here, and in the previous examples, is often not complete. Gas can leak slowly past a piston, just as it can slowly leak out of a rubber balloon. Some reaction may occur in a battery even if no external current is flowing. There is usually a coupling coefficient, which may depend on relative rates, which determines what percentage of the driving free energy is turned into external work, or captured as "chemical work"; a misnomer for the free energy of another chemical process.

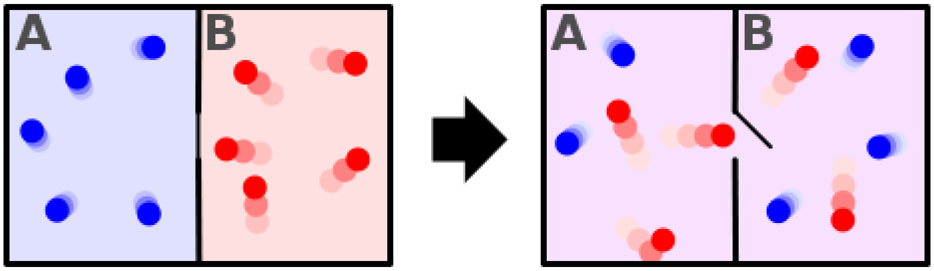
Chapter- 3

Statistical Thermodynamics

Statistical mechanics or **statistical thermodynamics**, is a branch of physics that applies probability theory, which contains mathematical tools for dealing with large populations, to the study of the *thermodynamic* behavior of systems composed of a *large* number of particles. Statistical mechanics provides a framework for relating the microscopic properties of individual atoms and molecules to the macroscopic bulk properties of materials that can be observed in everyday life, therefore explaining thermodynamics as a result of classical and quantum-mechanical description of statistics and mechanics at the microscopic level.

Statistical mechanics provides a molecular-level interpretation of macroscopic thermodynamic quantities such as work, heat, free energy, and entropy. It enables the thermodynamic properties of bulk materials to be related to the spectroscopic data of individual molecules. This ability to make macroscopic predictions based on microscopic properties is the main advantage of statistical mechanics over classical thermodynamics. Both theories are governed by the second law of thermodynamics through the medium of entropy. However, entropy in thermodynamics can only be known empirically, whereas in statistical mechanics, it is a function of the distribution of the system on its micro-states.

Statistical mechanics was initiated in 1870 with the work of Austrian physicist Ludwig Boltzmann, much of which was collectively published in Boltzmann's 1896 *Lectures on Gas Theory*. Boltzmann's original papers on the statistical interpretation of thermodynamics, the H-theorem, transport theory, thermal equilibrium, the equation of state of gases, and similar subjects, occupy about 2,000 pages in the proceedings of the Vienna Academy and other societies. The term "statistical thermodynamics" was proposed for use by the American thermodynamicist and physical chemist J. Willard Gibbs in 1902. According to Gibbs, the term "statistical", in the context of mechanics, i.e. statistical mechanics, was first used by the Scottish physicist James Clerk Maxwell in 1871.



Statistical Mechanics

Overview

The essential problem in statistical thermodynamics is to calculate the distribution of a given amount of energy *E* over *N* identical systems. The goal of statistical thermodynamics is to understand and to interpret the measurable macroscopic properties of materials in terms of the properties of their constituent particles and the interactions between them. This is done by connecting thermodynamic functions to quantum-mechanic equations. Two central quantities in statistical thermodynamics are the Boltzmann factor and the partition function.

Fundamentals

Central topics covered in statistical thermodynamics include:

- Microstates and configurations
- Boltzmann distribution law
- Partition function, Configuration integral or configurational partition function
- Thermodynamic equilibrium - thermal, mechanical, and chemical.
- Internal degrees of freedom - rotation, vibration, electronic excitation, etc.
- Heat capacity – Einstein solids, polyatomic gases, etc.
- Nernst heat theorem
- Fluctuations
- Gibbs paradox
- Degeneracy

Lastly, and most importantly, the formal definition of entropy of a thermodynamic system from a statistical perspective is called statistical entropy, and is defined as:

$$S = k_B \ln \Omega$$

where

k_B is Boltzmann's constant 1.38066×10^{-23} J K^{-1} and
Ω is the number of microstates corresponding to the observed thermodynamic macrostate.

This equation is valid only if each microstate is equally accessible (each microstate has an equal probability of occurring).

Boltzmann distribution

If the system is large the Boltzmann distribution could be used (the Boltzmann distribution is an approximate result)

$$n_i \propto e^{-\frac{U_i}{k_B T}}.$$

This can now be used with $\rho_i = \frac{n_i}{N}$:

$$\rho_i = \frac{n_i}{N} = \frac{e^{-\frac{U_i}{k_B T}}}{\sum_{i=1}^{\text{all levels}} e^{-\frac{U_i}{k_B T}}}.$$

History

In 1738, Swiss physicist and mathematician Daniel Bernoulli published *Hydrodynamica* which laid the basis for the kinetic theory of gases. In this work, Bernoulli posited the argument, still used to this day, that gases consist of great numbers of molecules moving in all directions, that their impact on a surface causes the gas pressure that we feel, and that what we experience as heat is simply the kinetic energy of their motion.

In 1859, after reading a paper on the diffusion of molecules by Rudolf Clausius, Scottish physicist James Clerk Maxwell formulated the Maxwell distribution of molecular velocities, which gave the proportion of molecules having a certain velocity in a specific range. This was the first-ever statistical law in physics. Five years later, in 1864, Ludwig Boltzmann, a young student in Vienna, came across Maxwell’s paper and was so inspired by it that he spent much of his life developing the subject further.

Hence, the foundations of statistical thermodynamics were laid down in the late 1800s by those such as Maxwell, Boltzmann, Max Planck, Clausius, and Josiah Willard Gibbs who began to apply statistical and quantum atomic theory to ideal gas bodies. Predominantly, however, it was Maxwell and Boltzmann, working independently, who reached similar conclusions as to the statistical nature of gaseous bodies. Yet, one must consider Boltzmann to be the "father" of statistical thermodynamics with his 1875 derivation of the relationship between entropy *S* and multiplicity *Ω*, the number of microscopic arrangements (microstates) producing the same macroscopic state (macrostate) for a particular system.

Fundamental postulate

The fundamental postulate in statistical mechanics (also known as the *equal a priori probability postulate*) is the following:

> *Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates.*

This postulate is a fundamental assumption in statistical mechanics - it states that a system in equilibrium does not have any preference for any of its available microstates. Given Ω microstates at a particular energy, the probability of finding the system in a particular microstate is $p = 1/\Omega$.

This postulate is necessary because it allows one to conclude that for a system at equilibrium, the thermodynamic state (macrostate) which could result from the largest number of microstates is also the most probable macrostate of the system.

The postulate is justified in part, for classical systems, by Liouville's theorem (Hamiltonian), which shows that if the distribution of system points through accessible phase space is uniform at some time, it remains so at later times.

Similar justification for a discrete system is provided by the mechanism of detailed balance.

This allows for the definition of the *information function* (in the context of information theory):

$$I = -\sum_i \rho_i \ln \rho_i = \langle \ln \rho \rangle .$$

When all the probabilities (ρ_i) are equal, I is maximal, and we have minimal information about the system. When our information is maximal (i.e., one rho is equal to one and the rest to zero, such that we know what state the system is in), the function is minimal.

This information function is the same as the *reduced entropic function* in thermodynamics.

Statistical ensembles

The modern formulation of statistical mechanics is based on the description of the physical system by an ensemble that represents all possible configurations of the system and the probability of realizing each configuration.

Each ensemble is associated with a partition function that, with mathematical manipulation, can be used to extract values of thermodynamic properties of the system.

According to the relationship of the system to the rest of the universe, one of three general types of ensembles may apply, in order of increasing complexity:

- Microcanonical ensemble: describes a completely isolated system, having constant energy, as it does not exchange energy or mass with the rest of the universe.
- Canonical community: describes a system in thermal equilibrium with its environment. It may only exchange energy in the form of heat with the outside.
- Grand-canonical: used in open systems which exchange energy and mass with the outside.

Summary of enembles in statistical mechanics	**Ensembles:**		
	Microcanonical	Canonical	Grand canonical
Constant variables	E, N, V o B	T, N, V o B	T, μ, V o B
Microscopic features	Number of microstates Ω	Canonical partition function $Z = \sum_k e^{-\beta E_k}$	Grand canonical partition function $\Xi = \sum_i e^{-\beta(E_k - \mu N_k)}$
Macroscopic function	$S = k_B \ln \Omega$	$F = -k_B T \ln Z$	$F - G = -pV = -k_B T \ln \Xi$

Microcanonical ensemble

In statistical physics, the **microcanonical ensemble** is a theoretical tool used to describe the thermodynamic properties of an isolated system. In such a system, the possible states of the system all have the same energy and the probability for the system to be in any given state is the same. It is also called the **NVE ensemble** because it describes a system with a fixed number of particles ("N"), a fixed volume ("V"), and a fixed energy ("E").

Terminology

A macroscopic system, e.g. a gas in a box, consists of many particles. A **microstate** is a complete description of every particle in the system. For a gas, this would be the position and velocity of all molecules. In quantum mechanics, a microstate would be the complete many-particle wavefunction.

It is impossible to exactly determine the microstate of a large system. Therefore, different microstates that lead to the same macroscopic properties such as volume, temperature or energy are bundled in a **macrostate**.

A **statistical ensemble** is a theoretical tool used to analyze a macroscopic system. One imagines multiple copies of the system. Each copy of the system has a different microstate, but all copies share the same macrostate. To fully describe a statistical ensemble it is also necessary to specify the probability for a certain microstate to occur. Thermodynamic properties of the system are then obtained by taking the average value of all copies in the ensemble. The fundamental assumption of thermodynamics is that each microstate occurs with the same probability.

The Microcanonical Ensemble

In the microcanonical ensemble, all copies of the system have the same number of particles (N), the same volume (V) and the same energy (E). This is precisely what distinguishes an isolated system. If Ω is the number of accessible microstates, the probability that a system chosen at random from the ensemble would be in a given microstate is simply 1 / Ω. It is possible to approximately calculate Ω for a number of systems such as the ideal gas or the 2-state paramagnet.

The benefit of the ensemble is that it allows for calculation of average values for thermodynamic properties. For example, while the pressure of a container of gas fluctuates continuously, we measure the time average of the pressure. The ensemble contains all microstates which the system might inhabit during the period of measurement, so we can replace the time average with an average over the ensemble. Systems for which this is possible are called ergodic.

Relation to the Canonical Ensemble

A canonical ensemble is a distribution over microcanonical ensembles; while in the microcanonical ensemble, the total energy is fixed, the canonical ensemble has only its *average* energy fixed -- it may exchange energy with a larger reservoir.

Entropy

From the number of accessible microstates, Ω, we can obtain the Entropy of the system via

$$S = \ k_B \ln \Omega$$

where k_B is the Boltzmann constant. Or, equivalently,

$$\Omega(U, V, N) = e^{S/k_B}.$$

Some textbooks present this formula as the definition of entropy. If the entropy is defined phenomenologically via the second law of thermodynamics one has to show that the formula above indeed satisfies the law $dU = TdS + dA$.

Notice that, for the microcanonical ensemble, Ω plays the role of the partition function in the canonical and grand canonical ensembles. For this reason, it is also sometimes referred to as the "microcanonical partition function". We should note here that the notion of multiplicity e^{S/k_B} is valid for any thermodynamical system. The same can be said for partition functions and any ensemble. It is only for the microcanonical ensemble that they happen to be the same.

Ω is also called the characteristic state function of the microcanonical ensemble.

An application: residual entropy

The expression for entropy above can be used to calculate the residual entropy.

The third law of thermodynamics says that the entropy of a pure crystalline substance at 0 K is zero. However, in some solids, at temperatures close to 0 K, there may be many molecular orientations. For example, water molecules in ice crystal may arrange themselves in several different ways. In principle, there must be one molecular orientation with the lowest energy. But due the near randomness with which configurations occur, it is often impractical to attempt realization of the lowest energy configuration. This leads to the notion of residual entropy. Furthermore, there is often very little difference between the total energy of the system and different molecular configurations. Therefore, as an approximation, the system can be viewed having fixed energy and the possible configurations as microstates: a microcanonical ensemble. So it is sensible to estimate the residual entropy via the same expression for the microcanonical ensemble entropy:

$$S = \ k_B \ln \Omega$$

where Ω is the number of possible molecular arrangements of the crystal, at some suitable temperature range close to 0 K.

Classical mechanical systems

As with any ensemble of classical systems, we would like to find a corresponding probability measure on the phase space "M". This constant energy assumption means that every system in the ensemble is confined to a submanifold of phase space of constant energy "E". Call this submanifold M_E. From the physical considerations given above, it is already clear what the probability measure on the constant energy surface ("not the full phase space") should be: namely, the trivial one that is constant everywhere. However, while only the submanifold M_E is of interest for the microcanonical ensemble, in other, more general ensembles, it is necessary to consider the full phase space. We now construct a measure on the full phase space that is suitable for the microcanonical ensemble.

The Liouville measure *dqdp* on the full phase space induces a measure *dA* on M_E in the following manner:

The measure of an open subset R of M_E is given by

$$\lim_{\Delta E \to 0} \frac{\mathrm{vol}(Q(E, E + \Delta E)}{\Delta E}$$

Where Q is any open subset of M such that $Q \cap M = R$, $Q(E, E + \Delta E)$ is part of Q with $E < H < E + \Delta E$, and "*vol*" is the usual Liouville volume. Thus any sufficiently good (measurable) subset of M_E can be characterized by its hyperarea(measure) with respect to *dA*.

The density function on the full phase space ρ(*q*,*p*) is the generalized function $\frac{\delta(H(q,p) - E)}{\Omega}$, where *H* is the Hamiltonian and Ω is the hyperarea of M_E. If Δ is a region of the phase space, the probability of a system being in a state within Δ is simply

$$\int_{\Delta} \rho(q,p) dqdp = \frac{1}{\Omega} \int_{\Delta_E} dA.$$

where Δ_E is the intersection of M_E and Δ.

Notice how one can either consider the whole phase space and use the measure whose density is a generalized function, or restrict to the constant energy surface in question and use the measure whose density is a constant function. For instance, consider a 1-dimensional harmonic oscillator. The phase space is $\mathbb{R}^2$(the position-momentum plane) and the constant energy hypersurface is the ellipse

$$\frac{kq^2}{2} + \frac{p^2}{2m} = E$$

The latter can be parametrized as

$$q = \sqrt{\frac{2E}{k}} \cos(\phi)$$
$$p = \sqrt{2mE} \sin(\phi)$$

where φ varies between 0 and 2π. The measure *dA* would then equal *d*φ up to a constant. On the other hand, if one considers the ellipse embedded in the plane, then it would have measure zero, which is why a generalized function is used as the density.

Connection with Liouville's theorem

We have

$$\{H, \rho\} = 0$$

(the curly bracket is Poisson bracket) since ρ is a function of H. Therefore, according to Liouville's theorem (Hamiltonian) we get

$$\frac{d\rho}{dt} = 0.$$

In particular, *dA* is time-invariant, that is, the ensemble is a *stationary* one.

Alternatively, one can say that since the Liouville measure is invariant under the Hamiltonian flow, so is the measure *dA*.

Physically speaking, this means the local density of a region of representative points in phase space is invariant, as viewed by an observer moving along with the systems.

Ergodic hypothesis

A microcanonical ensemble of classical systems provides a natural setting to consider the ergodic hypothesis, that is, the long time average coincides with the ensemble average. More precisely put, an observable is a real valued function *f* on the phase space Γ that is integrable with respect to the microcanonical ensemble measure μ. Let $x(0)$ denote a representative point in the phase space, and $x(t)$ be its image under the Hamiltonian flow at time *t*. The time average of *f* is defined to be

$$\bar{f} = \lim_{T \to \infty} \frac{1}{T} \int_0^T f(x(t))dt,$$

provided that this limit exists μ-almost everywhere. The ensemble average is

$$\langle f \rangle = \int_\Gamma f(x) d\mu(x).$$

The system is said to be *ergodic* if they are equal.

Using the fact that μ is preserved by the Hamiltonian flow, we can show that indeed the time average exists for all observables. Whether classical mechanical flows on constant energy surfaces is in general ergodic is unknown at this time.

Remark

The relationship between the microcanonical ensemble, Liouville's theorem, and ergodic hypothesis can be summarized as follows: The key assumption of a microcanonical ensemble is that all accessible microstates are equally probable. Therefore the density function on the relevant region of phase space is constant, say it is 1 everywhere, i.e. the phase space measure μ is just the Lebesgue measure. But, according to Liouville's theorem, this measure is invariant under the Hamiltonian time evolution. From this follows that the notion of time average makes sense for all observables. The ensemble average is defined using μ. The question of ergodicity is whether they coincide. It should perhaps be emphasized that while the microcanonical ensemble and Liouville's theorem are directly related, they should not be confused as being equivalent to the ergodic hypothesis.

Quantum mechanical systems

Semi-classical treatment

So far, we have assumed the system in question is classical. Slight modification is required for quantum mechanical systems, although the results are essentially the same. For an ensemble consisting of quantum mechanical systems, it no longer makes sense to speak of all members of the ensemble having the same definite energy E. So, instead of a level set $H(q,p) = E$ in the phase space, one considers a small range of energies $E < H < E + dE$ that a system in the ensemble may have and the corresponding region of the phase space. When classical states are replaced by quantum states, the degeneracy needs to be taken into account. Also, in the quantum mechanical case, due to the uncertainty principle, the states can no longer be viewed as continuously distributed in the phase space. Rather, one must find a "fundamental volume" ω_0, which depends on the particulars of a given system. As we would expect, ω_0 is usually related to $\hbar$ in some way. Consequently, the multiplicity is not the total available volume of the phase space Ω but is replaced by $\frac{\Omega}{\omega_0}$, and entropy becomes

$$S = k_B \ln \frac{\Omega}{\omega_0}.$$

Density operators

The microcanonical ensemble can also be described by a density operator. Namely, if Ω is the total number of accessible microstates of the system, and $|\psi_n\rangle$ are all states of the system (accessible and otherwise), then a microcanonical ensemble is the mixed state

$$\rho = \sum p_n |\psi_n\rangle \langle\psi_n|,$$

where $p_n = \frac{1}{\Omega}$ if $|\psi_n\rangle$ is an accessible state and 0 otherwise.

We note here that, in this context, Ω is computed quantum-mechanically, taking into account indistinguishability of particles. The entropy is

$$S = k_B \ln \Omega = -k_B \mathrm{Tr}(\rho \ln \rho).$$

When Ω = 1, the ensemble is said to be a *pure ensemble*. The fact that the entropy vanishes for pure states is essentially the third law of thermodynamics.

Canonical ensemble

A **canonical ensemble** in statistical mechanics is a statistical ensemble representing a probability distribution of microscopic states of the system. The probability distribution is characterised by the proportion p_i of members of the ensemble which exhibit a measurable macroscopic state i, where the proportion of microscopic states for each macroscopic state i is given by the Boltzmann distribution,

$$p_i = \tfrac{1}{Z} e^{-E_i/(kT)} = e^{-(E_i - A)/(kT)}$$

where E_i is the energy of state i. It can be shown that this is the distribution which is most likely, if each system in the ensemble can exchange energy with a heat bath, or alternatively with a large number of similar systems. Equivalently, it is the distribution which has maximum entropy for a given average energy $<E_i>$.

It is also referred to as an NVT ensemble: the number of particles (N), the volume (V), of each system in the ensemble are the same, and the ensemble has a well defined temperature (T), given by the temperature of the heat bath with which it would be in equilibrium.

The quantity k is Boltzmann's constant, which relates the units of temperature to units of energy. It may be suppressed by expressing the absolute temperature using thermodynamic beta, β = 1 / (kT).

The quantities A and Z are constants for a particular ensemble, which ensure that Σp_i is normalised to 1. Z is therefore given by

$$Z = \sum e^{-E_i/(kT)} = \sum e^{-\beta E_i}.$$

This is called the partition function of the canonical ensemble. Specifying this dependence of Z on the energies E_i conveys the same mathematical information as specifying the form of p_i above.

The canonical ensemble (and its partition function) is widely used as a tool to calculate thermodynamic quantities of a system under a fixed temperature. Other related thermodynamic formulas are given in the partition function article. When viewed in a more general setting, the canonical ensemble is known as the Gibbs measure, where, because it has the Markov property of statistical independence, it occurs in many settings outside of the field of physics.

Deriving the Boltzmann factor from ensemble theory

Let E_i be the energy of the microstate i and suppose there are n_i members of the ensemble residing in this state. Further we assume the total number of systems in the ensemble, $\mathcal{N}$, and the total energy of all systems of the ensemble, $\mathcal{E}$, are fixed, i.e.,

$$\mathcal{N} = \sum_i n_i,$$
$$\mathcal{E} = \sum_i n_i E_i\ .$$

Since systems in the ensemble are distinguishable, for each set $\{n_i\}$, the number of ways of shuffling systems is equal to

$$W(\{n_i\}) = \mathcal{N}!/\prod_i n_i!\ .$$

So for a given $\{n_i\}$, there are $W(\{n_i\})$ rearrangements that specify the same state of the ensemble.

The most probable distribution is the one that maximizes $W(\{n_i\})$. The probability for any other distribution to occur is extremely small in the limit $\mathcal{N} \rightarrow \infty$. To determine this distribution, one should maximize $W(\{n_i\})$ with respect to the n_i's, under two constraints specified above. This can be done by using two Lagrange multipliers α and β. (The assumption that $\mathcal{N} \rightarrow \infty$ would be invoked in such calculation, which allows one to apply Stirling's approximation.) The result is

$$n_i = e^{-\alpha-\beta E_i}.$$

This distribution is called the canonical distribution. To determine α and β, it is useful to introduce the partition function as a sum over microscopic states

$$Z(\beta) = \sum_j e^{-\beta E_j}.$$

Comparing with thermodynamic formulae, it can be shown that β, is related to the absolute temperature T as, $\beta = 1/k_B T$. Moreover the expression

$$F = -\ln Z(\beta)/\beta$$

is identified as the Helmholtz free energy *F*. A derivation is given here. Consequently, from the partition function we can obtain the average thermodynamic quantities for the ensemble. For example, the average energy among members of the ensemble is

$$\langle E \rangle = \frac{\mathcal{E}}{\mathcal{N}} = -\frac{\partial}{\partial \beta} \ln Z(\beta).$$

This relation can be used to determine β. α is determined from

$$e^{\alpha} = Z(\beta)/\mathcal{N}.$$

A derivation from heat-bath viewpoint

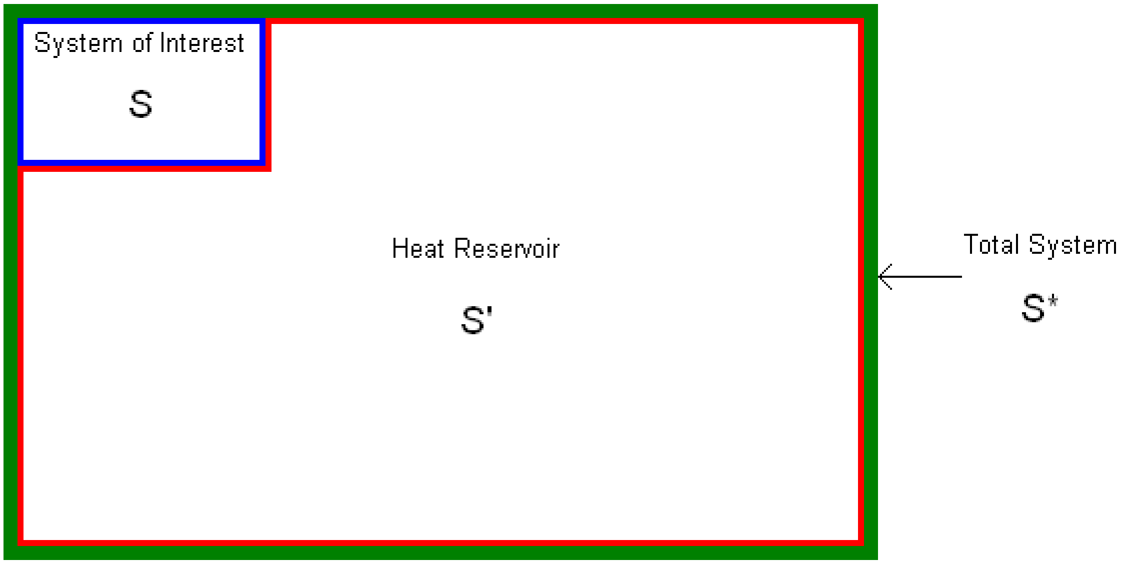


Illustration of a system of interest suspended in a heat bath. The system of interest is taken to be small compared to the heat bath.

Define the following:

- S - the system of interest
- S′ - the heat reservoir in which S resides; S is small compared to S′
- S* - the system consisting of S and S′ combined together
- *m* - an indexing variable which labels all the available energy states of the system S
- E_{m} - the energy of the state corresponding to the index m for the system S
- E' - the energy associated with the heat bath
- E^* - the energy associated with S*
- $\Omega'(E)$ - denotes the number of microstates available at a particular energy E for the heat reservoir.

It is assumed that the system S and the reservoir S′ are in thermal equilibrium. The objective is to calculate the set of probabilities p_m that S is in a particular energy state E_m.

Suppose S is in a microstate indexed by *m*. From the above definitions, the total energy of the system S* is given by

$$E^* = E' + E_m$$

Notice E^* is constant, since the combined system S* is taken to be isolated.

Now, arguably the key step in the derivation is that *the probability of* S *being in the m-th state,* p_m*, is proportional to the corresponding number of microstates available to the reservoir when* S *is in the m-th state*. Therefore,

$$p_m = C'\Omega'(E')$$

for some constant C'. Taking the logarithm gives

$$\ln p_m = \ln C' + \ln \Omega'(E') = \ln C' + \ln \Omega'(E^* - E_m)$$

Since E_m is small compared to E^*, a Taylor series expansion can be performed on the latter logarithm around the energy E^*. A good approximation can be obtained by keeping the first two terms of the Taylor series expansion:

$$\ln \Omega'(E') = \sum_{k=0}^{\infty} \frac{(E' - E^*)^k}{k!} \frac{d^k \ln \Omega'(E^*)}{dE'^k} \approx \ln \Omega'(E^*) - \frac{d}{dE'} \ln \Omega'(E^*) E_m$$

The following quantity is a constant which is traditionally denoted by β, known as the **thermodynamic beta**.

$$\beta = \frac{d}{dE'} \ln \Omega'(E^*) = \left. \frac{d}{dE'} \ln \Omega'(E') \right|_{E'=E^*}$$

Finally,

$$\ln p_m = \ln C' + \ln \Omega'(E^*) - \beta E_m$$

Exponentiating this expression gives

$$p_m = C'\Omega'(E^*)e^{-\beta E_m}$$

The factor in front of the exponential can be treated as a normalization constant *C*, where

$$C = C'\Omega'(E^*)$$

From this

$$p_m = Ce^{-\beta E_m}$$

Normalization to recover the partition function

Since probabilities must sum to 1, it must be the case that

$$\sum_m p_m = 1 = \sum_m Ce^{-\beta E_m} = C\sum_m e^{-\beta E_m} \iff C = \frac{1}{\sum_m e^{-\beta E_m}} \equiv \frac{1}{Z(\beta)}$$

where *Z* is known as the Partition function for the canonical ensemble.

Note on derivation

As mentioned above, the derivation hinges on recognizing that the probability of the system being in a particular state is proportional to the corresponding multiplicities of the reservoir (the same can be said for the grand canonical ensemble). As long as one makes that observation, it is flexible as how one might proceed. In the derivation given, the logarithm is taken, then a linear approximation based on physical arguments is used. Alternatively, one can apply the thermodynamic identity for differential entropy:

$$dS = \frac{1}{T}(dU + PdV - \mu dN)$$

and obtain the same result.

The canonical ensemble is also called the **Gibbs ensemble**, in honor of J.W. Gibbs, widely regarded with Boltzmann as being one of the two fathers of statistical mechanics. In his definitive 1901 book "Elementary Principles in Statistical Mechanics", Gibbs viewed an ensemble as a list of the allowed states of the system (each state appearing once and only once in the list) and the associated statistical weights. The states do not interact with each other, or with a reservoir, until Gibbs treats what happens when two complete ensembles at two different temperatures are allowed to interact weakly (Gibbs, pp 160). Gibbs writes that "...the distribution in phase..." (the phase space density in modern language) "...[is] called canonical...[if] the index of probability" (the logarithm of the statistical weight of the phase space density) "...is a linear function of the energy..." (Gibbs, Ch. 4). In Gibbs' formulation, this requirement (his equation 91), in modern notation

$$P = e^{\frac{E-A}{kT}}$$

is taken to *define* the canonical ensemble and to *be* the fundamental postulate. Gibbs does show that a large collection of interacting microcanonical systems approaches the canonical ensemble, but this is part of his demonstration (Gibbs, pp 169-183) that the principle of equal a priori probabilities, therefore the microcanonical ensemble, are inferior to the canonical ensemble as an axiomatization of statistical mechanics, at every point where the two treatments differ.

Gibbs original formulation is still standard in modern mathematically rigorous treatments of statistical mechanics, where the canonical ensemble is defined as the probability measure

$$e^{\frac{E-A}{kT}} dp\, dq$$

with *p* and *q* being the canonical coordinates.

Characteristic state function

The characteristic state function of the canonical ensemble is the Helmholtz free energy function, as the following relationship holds:

$$Z(T,V,N) = e^{-\beta A}$$

Quantum mechanical systems

By applying the canonical partition function, one can easily obtain the corresponding results for a canonical ensemble of quantum mechanical systems. A quantum mechanical ensemble in general is described by a density matrix. Suppose the Hamiltonian *H* of interest is a self adjoint operator with only discrete spectrum. The energy levels $\{E_n\}$ are then the eigenvalues of *H*, corresponding to eigenvector $|\psi_n\rangle$. From the same considerations as in the classical case, the probability that a system from the ensemble will be in state $|\psi_n\rangle$ is $p_n = Ce^{-\beta E_n}$, for some constant *C*. So the ensemble is described by the density matrix

$$\rho = \sum p_n |\psi_n\rangle\langle\psi_n| = \sum Ce^{-\beta E_n} |\psi_n\rangle\langle\psi_n|$$

(Technical note: a density matrix must be trace-class, therefore we have also assumed that the sequence of energy eigenvalues diverges sufficiently fast.) A density operator is assumed to have trace 1, so

$$\mathrm{Tr}(\rho) = C \underbrace{\sum e^{-\beta E_n}}_{Q} = 1,$$

which means

$$C = \frac{1}{\sum e^{-\beta E_n}} = \frac{1}{Q}.$$

Q is the quantum-mechanical version of the canonical partition function. Putting *C* back into the equation for ρ gives

$$\rho = \frac{1}{\sum e^{-\beta E_n}} \sum e^{-\beta E_n} |\psi_n\rangle \langle \psi_n| = \frac{1}{\mathrm{Tr}(e^{-\beta H})} e^{-\beta H}.$$

By the assumption that the energy eigenvalues diverge, the Hamiltonian *H* is an unbounded operator, therefore we have invoked the Borel functional calculus to exponentiate the Hamiltonian *H*. Alternatively, in non-rigorous fashion, one can consider that to be the exponential power series.

Notice the quantity

$$\mathrm{Tr}(e^{-\beta H})$$

is the quantum mechanical counterpart of the canonical partition function, being the normalization factor for the mixed state of interest.

The density operator ρ obtained above therefore describes the (mixed) state of a canonical ensemble of quantum mechanical systems. As with any density operator, if *A* is a physical observable, then its expected value is

$$\langle A \rangle = \mathrm{Tr}(\rho A).$$

Relations with other ensembles

A generalization of this is the grand canonical ensemble, in which the systems may share particles as well as energy. By contrast, in the microcanonical ensemble, the energy of each individual system is fixed.

Thermodynamic connection

The partition function can be used to find the expected (average) value of any microscopic property of the system, which can then be related to macroscopic variables. For instance, the expected value of the microscopic energy E is *interpreted* as the microscopic definition of the thermodynamic variable internal energy U, and can be obtained by taking the derivative of the partition function with respect to the temperature. Indeed,

$$\langle E\rangle = \frac{\sum_i E_i e^{-\beta E_i}}{Z} = -\frac{1}{Z}\frac{dZ}{d\beta}$$

implies, together with the interpretation of $\langle E\rangle$ as U, the following microscopic definition of internal energy:

$$U \colon = -\frac{d\ln Z}{d\beta}.$$

The entropy can be calculated by

$$\frac{S}{k} = -\sum_i p_i \ln p_i = \sum_i \frac{e^{-\beta E_i}}{Z}(\beta E_i + \ln Z) = \ln Z + \beta U$$

which implies that

$$-\frac{\ln(Z)}{\beta} = U - TS = F$$

is the free energy of the system or in other words,

$$Z = e^{-\beta F}.$$

Having microscopic expressions for the basic thermodynamic potentials U (internal energy), S (entropy) and F (free energy) is sufficient to derive expressions for other thermodynamic quantities. The basic strategy is as follows. There may be an intensive or extensive quantity that enters explicitly in the expression for the microscopic energy E_i, for instance magnetic field (intensive) or volume (extensive). Then, the conjugate thermodynamic variables are derivatives of the internal energy. The macroscopic magnetization (extensive) is the derivative of U with respect to the (intensive) magnetic field, and the pressure (intensive) is the derivative of U with respect to volume (extensive).

The treatment in this section assumes no exchange of matter (i.e. fixed mass and fixed particle numbers). However, the volume of the system is variable which means the density is also variable.

This probability can be used to find the average value, which corresponds to the macroscopic value, of any property, *J*, that depends on the energetic state of the system by using the formula:

$$\langle J \rangle = \sum_i p_i J_i = \sum_i J_i \frac{e^{-\beta E_i}}{Z}$$

where $\langle J \rangle$ is the average value of property *J*. This equation can be applied to the internal energy, *U*:

$$U = \sum_i E_i \frac{e^{-\beta E_i}}{Z}.$$

Subsequently, these equations can be combined with known thermodynamic relationships between *U* and *V* to arrive at an expression for pressure in terms of only temperature, volume and the partition function. Similar relationships in terms of the partition function can be derived for other thermodynamic properties as shown in the following table.

Helmholtz free energy: $F = -\frac{\ln Z}{\beta}$

Internal energy: $U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V}$

Pressure: $P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_{N,T}$

Entropy: $S = k(\ln Z + \beta U)$

Gibbs free energy: $G = F + PV = -\frac{\ln Z}{\beta} + \frac{V}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_{N,T}$

Enthalpy: $H = U + PV$

Constant volume heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$

Constant pressure heat capacity: $C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P}$

Chemical potential: $$\mu_i = -\frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial N_i}\right)_{T,V,N}$$

To clarify, this is not a grand canonical ensemble.

It is often useful to consider the energy of a given molecule to be distributed among a number of modes. For example, translational energy refers to that portion of energy associated with the motion of the center of mass of the molecule. Configurational energy refers to that portion of energy associated with the various attractive and repulsive forces between molecules in a system. The other modes are all considered to be internal to each molecule. They include rotational, vibrational, electronic and nuclear modes. If we assume that each mode is independent (a questionable assumption) the total energy can be expressed as the sum of each of the components:

$$E = E_t + E_c + E_n + E_e + E_r + E_v,$$

where the subscripts *t*, *c*, *n*, *e*, *r*, and *v* correspond to translational, configurational, nuclear, electronic, rotational and vibrational modes, respectively. The relationship in this equation can be substituted into the very first equation to give:

$$\begin{aligned} Z &= \sum_i e^{-\beta(E_{ti}+E_{ci}+E_{ni}+E_{ei}+E_{ri}+E_{vi})} \\ &= \sum_i e^{-\beta E_{ti}} e^{-\beta E_{ci}} e^{-\beta E_{ni}} e^{-\beta E_{ei}} e^{-\beta E_{ri}} e^{-\beta E_{vi}}. \end{aligned}$$

If we can assume all these modes are completely uncoupled and uncorrelated, so all these factors are in a probability sense completely independent, then

$$Z = Z_t Z_c Z_n Z_e Z_r Z_v.$$

Thus a partition function can be defined for each mode. Simple expressions have been derived relating each of the various modes to various measurable molecular properties, such as the characteristic rotational or vibrational frequencies.

Expressions for the various molecular partition functions are shown in the following table.

Nuclear $$Z_n = 1 \qquad (T < 10^8 K)$$

Electronic $$Z_e = W_0 e^{kTD_e} + W_1 e^{-\theta_{e1}/T} + \cdots$$

Vibrational $$Z_v = \prod_j \frac{e^{-\theta_{vj}/2T}}{e^{\theta_{vj}/T} - 1}$$

Rotational (linear) $Z_r = \frac{T}{\sigma\theta_r}$

Rotational (non-linear) $Z_r = \frac{1}{\sigma}\sqrt{\frac{\pi T^3}{\theta_A\theta_B\theta_C}}$

Translational $Z_t = \frac{(2\pi mkT)^{3/2}}{h^3}$

Configurational (ideal gas) $Z_c = V$

These equations can be combined with those in the first table to determine the contribution of a particular energy mode to a thermodynamic property. For example the "rotational pressure" could be determined in this manner. The total pressure could be found by summing the pressure contributions from all of the individual modes, i.e.:

$$P = P_t + P_c + P_n + P_e + P_r + P_v.$$

Grand canonical ensemble

In grand canonical ensemble *V*, *T* and chemical potential are fixed. If the system under study is an open system, (matter can be exchanged), *but* particle number is not conserved, we would have to introduce chemical potentials, μ_j, $j = 1,...,n$ and replace the canonical partition function with the grand canonical partition function:

$$\Xi(V,T,\mu) = \sum_i \exp\left(\beta\left[\sum_{j=1}^{n}\mu_j N_{ij} - E_i\right]\right)$$

where N_{ij} is the number of j^{th} species particles in the i^{th} configuration. Sometimes, we also have other variables to add to the partition function, one corresponding to each conserved quantity. Most of them, however, can be safely interpreted as chemical potentials. In most condensed matter systems, things are nonrelativistic and mass is conserved. However, most condensed matter systems of interest also conserve particle number approximately (metastably) and the mass (nonrelativistically) is none other than the sum of the number of each type of particle times its mass. Mass is inversely related to density, which is the conjugate variable to pressure.

Let's rework everything using a grand canonical ensemble this time. The volume is left fixed and does not figure in at all in this treatment. As before, *j* is the index for those particles of species *j* and *i* is the index for microstate *i*:

$$U = \sum_i E_i \frac{\exp(-\beta(E_i - \sum_j \mu_j N_{ij}))}{\Xi}$$

$$N_j = \sum_i N_{ij} \frac{\exp(-\beta(E_i - \sum_j \mu_j N_{ij}))}{\Xi}.$$

Grand potential: $$\Phi_G = -\frac{\ln \Xi}{\beta}$$

Internal energy: $$U = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_\mu + \sum_i \frac{\mu_i}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu_i}\right)_\beta$$

Particle number: $$N_i = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu_i}\right)_\beta$$

Entropy: $$S = k(\ln \Xi + \beta U - \beta \sum_i \mu_i N_i)$$

Helmholtz free energy: $$F = \Phi_G + \sum_i \mu_i N_i = -\frac{\ln \Xi}{\beta} + \sum_i \frac{\mu_i}{\beta} \left(\frac{\partial \ln \Xi}{\partial \mu_i}\right)_\beta$$

Equivalence between descriptions at the thermodynamic limit

All of the above descriptions differ in the way they allow the given system to fluctuate between its configurations.

In the micro-canonical ensemble, the system exchanges no energy with the outside world, and is therefore not subject to energy fluctuations; in the canonical ensemble, the system is free to exchange energy with the outside in the form of heat.

In the thermodynamic limit, which is the limit of large systems, fluctuations become negligible, so that all these descriptions converge to the same description. In other words, the macroscopic behavior of a system does not depend on the particular ensemble used for its description.

Given these considerations, the best ensemble to choose for the calculation of the properties of a macroscopic system is that ensemble which allows the result to be derived most easily.

Random walks

The study of long chain polymers has been a source of problems within the realms of statistical mechanics since about the 1950s. One of the reasons however that scientists were interested in their study is that the equations governing the behavior of a polymer chain were independent of the chain chemistry. What is more, the governing equation turns out to be a random walk, or diffusive walk, in space. Indeed, the Schrödinger equation is itself a diffusion equation in imaginary time, $t' = it$.

Random walks in time

The first example of a random walk is one in space, whereby a particle undergoes a random motion due to external forces in its surrounding medium. A typical example would be a pollen grain in a beaker of water. If one could somehow "dye" the path the pollen grain has taken, the path observed is defined as a random walk.

Consider a toy problem, of a train moving along a 1D track in the x-direction. Suppose that the train moves either a distance of + or - a fixed distance *b*, depending on whether a coin lands heads or tails when flipped. Lets start by considering the statistics of the steps the toy train takes (where S_i is the ith step taken):

$\langle S_i \rangle = 0$; due to *a priori* equal probabilities

$\langle S_i S_j \rangle = b^2 \delta_{ij}.$

The second quantity is known as the correlation function. The delta is the kronecker delta which tells us that if the indices *i* and *j* are different, then the result is 0, but if *i* = *j* then the kronecker delta is 1, so the correlation function returns a value of b^2. This makes sense, because if *i* = *j* then we are considering the same step. Rather trivially then it can be shown that the average displacement of the train on the x-axis is 0;

$$x = \sum_{i=1}^{N} S_i$$

$$\langle x \rangle = \langle \sum_{i=1}^{N} S_i \rangle$$

$$\langle x \rangle = \sum_{i=1}^{N} \langle S_i \rangle.$$

As stated $\langle S_i \rangle$ is 0, so the sum of 0 is still 0. It can also be shown, using the same method demonstrated above, to calculate the root mean square value of problem. The result of this calculation is given below

$$x_{rms} = \sqrt{\langle x^2 \rangle} = b\sqrt{N}.$$

From the diffusion equation it can be shown that the distance a diffusing particle moves in a media is proportional to the root of the time the system has been diffusing for, where the proportionality constant is the root of the diffusion constant. The above relation, although cosmetically different reveals similar physics, where *N* is simply the number of steps moved (is loosely connected with time) and *b* is the characteristic step length. As a consequence we can consider diffusion as a random walk process.

Random walks in space

Random walks in space can be thought of as snapshots of the path taken by a random walker in time. One such example is the spatial configuration of long chain polymers.

There are two types of random walk in space: *self-avoiding random walks*, where the links of the polymer chain interact and do not overlap in space, and *pure random* walks, where the links of the polymer chain are non-interacting and links are free to lie on top of one another. The former type is most applicable to physical systems, but their solutions are harder to get at from first principles.

By considering a freely jointed, non-interacting polymer chain, the end-to-end vector is $\mathbf{R} = \sum_{i=1}^{N} \mathbf{r}_i$ where $\mathbf{r}_i$is the vector position of the *i*-th link in the chain. As a result of the central limit theorem, if N >> 1 then we expect a Gaussian distribution for the end-to-end vector. We can also make statements of the statistics of the links themselves;

$\langle \mathbf{r}_i \rangle = 0$; by the isotropy of space

$\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = 3b^2 \delta_{ij}$; all the links in the chain are uncorrelated with one another

Using the statistics of the individual links, it is easily shown that $\langle \mathbf{R} \rangle = 0$and $\langle \mathbf{R} \cdot \mathbf{R} \rangle = 3Nb^2$. Notice this last result is the same as that found for random walks in time.

Assuming, as stated, that that distribution of end-to-end vectors for a very large number of identical polymer chains is gaussian, the probability distribution has the following form

$$P = \frac{1}{\left(\frac{2\pi N b^2}{3}\right)^{3/2}} \exp \frac{-3\mathbf{R} \cdot \mathbf{R}}{2Nb^2}$$

What use is this to us? Recall that according to the principle of equally likely *a priori* probabilities, the number of microstates, Ω, at some physical value is directly proportional to the probability distribution at that physical value, *viz*;

$$\Omega\left(\mathbf{R}\right) = cP\left(\mathbf{R}\right)$$

where c is an arbitrary proportionality constant. Given our distribution function, there is a maxima corresponding to $\mathbf{R} = 0$. Physically this amounts to there being more microstates which have an end-to-end vector of 0 than any other microstate. Now by considering

$$S\left(\mathbf{R}\right) = k_B \ln \Omega(\mathbf{R})$$
$$\Delta S\left(\mathbf{R}\right) = S\left(\mathbf{R}\right) - S\left(0\right)$$

$$\Delta F = -T \Delta S (\mathbf{R})$$

where F is the Helmholtz free energy it is trivial to show that

$$\Delta F = k_B T \frac{3R^2}{2Nb^2} = \frac{1}{2} K R^2 \quad ; K = \frac{3k_B T}{Nb^2}$$

A Hookian spring!
This result is known as the *entropic spring result* and amounts to saying that upon stretching a polymer chain you are doing work on the system to drag it away from its (preferred) equilibrium state. An example of this is a common elastic band, composed of long chain (rubber) polymers. By stretching the elastic band you are doing work on the system and the band behaves like a conventional spring. What is particularly astonishing about this result however, is that the work done in stretching the polymer chain can be related entirely to the change in entropy of the system as a result of the stretching.

Classical thermodynamics vs. statistical thermodynamics

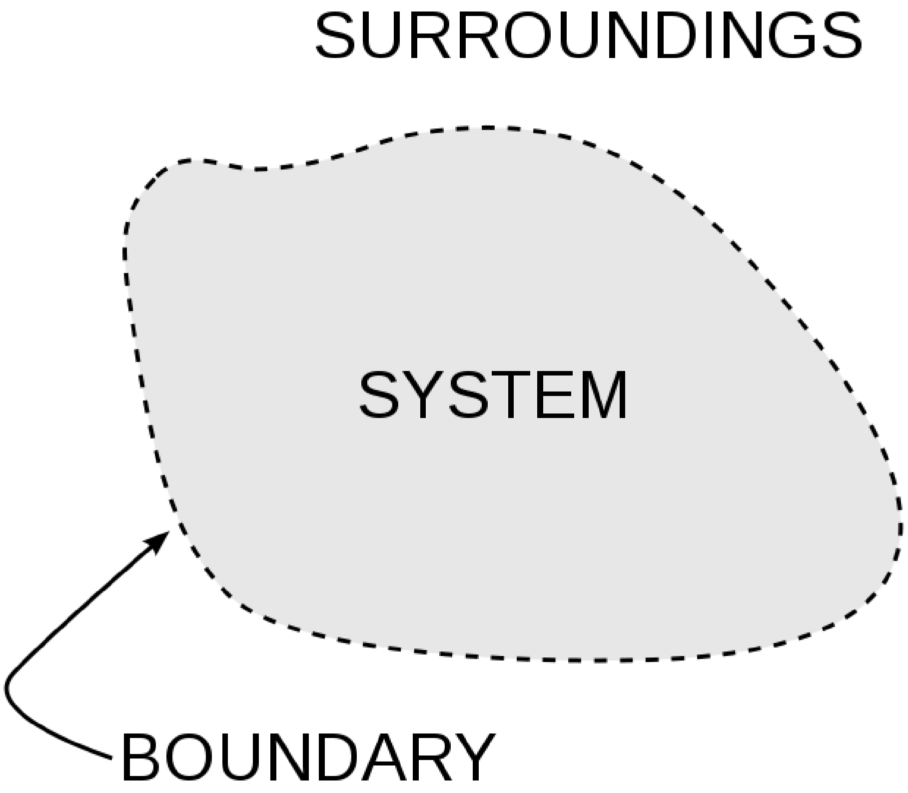
As an example, from a classical thermodynamics point of view one might ask what is it about a thermodynamic system of gas molecules, such as ammonia NH_3, that determines the free energy characteristic of that compound? Classical thermodynamics does not provide the answer. If, for example, we were given spectroscopic data, of this body of gas molecules, such as bond length, bond angle, bond rotation, and flexibility of the bonds in NH_3 we should see that the free energy could not be other than it is. To prove this true, we need to bridge the gap between the microscopic realm of atoms and molecules and the macroscopic realm of classical thermodynamics. From physics, statistical mechanics provides such a bridge by teaching us how to conceive of a thermodynamic *system* as an assembly of *units*. More specifically, it demonstrates how the thermodynamic parameters of a system, such as temperature and pressure, are interpretable in terms of the parameters descriptive of such constituent atoms and molecules.

In a bounded system, the crucial characteristic of these microscopic units is that their energies are quantized. That is, where the energies accessible to a macroscopic system form a virtual continuum of possibilities, the energies open to any of its submicroscopic components are limited to a discontinuous set of alternatives associated with integral values of some quantum number.

Chapter- 4

Thermodynamic System and Equilibrium

Thermodynamic System



A **thermodynamic system** is a precisely defined macroscopic region of the universe, often called a physical system, that is studied using the principles of thermodynamics.

All space in the universe outside the thermodynamic system is known as the *surroundings*, the *environment*, or a *reservoir*. A system is separated from its surroundings by a *boundary* which may be notional or real, but which by convention delimits a finite volume. Exchanges of work, heat, or matter between the system and the surroundings may take place across this boundary. Thermodynamic systems are often classified by specifying the nature of the exchanges that are allowed to occur across its boundary.

A thermodynamic system is characterized and defined by a set of thermodynamic parameters associated with the system. The parameters are experimentally measurable macroscopic properties, such as volume, pressure, temperature, electric field, and others.

The set of thermodynamic parameters necessary to uniquely define a system is called the thermodynamic state of a system. The state of a system is expressed as a functional relationship, the equation of state, between its parameters. A system is in thermodynamic equilibrium when the state of the system does not change with time.

Originally, in 1824, Sadi Carnot described a thermodynamic system as the **working substance** under study.

Overview

Thermodynamics describes the physics of matter using the concept of the *thermodynamic system*, a region of the universe that is under study. All quantities, such as pressure or mechanical work, in an equation refer to the system unless labeled otherwise. As thermodynamics is fundamentally concerned with the flow and balance of energy and matter, systems are distinguished depending on the kinds of interaction they undergo and the types of energy they exchange with the surrounding environment.

Interactions of thermodynamic systems

Type of system	Mass flow	Work	Heat
Open	✓	✓	✓
Closed	✗	✓	✓
Isolated	✗	✗	✗

Isolated systems are completely isolated from their environment. They do not exchange heat, work or matter with their environment. An example of an isolated system is a completely insulated rigid container, such as a completely insulated gas cylinder. *Closed systems* are able to exchange energy (heat and work) but not matter with their environment. A greenhouse is an example of a closed system exchanging heat but not work with its environment. Whether a system exchanges heat, work or both is usually thought of as a property of its boundary. *Open systems* may exchange any form of energy as well as matter with their environment. A boundary allowing matter exchange is called permeable. The ocean would be an example of an open system.

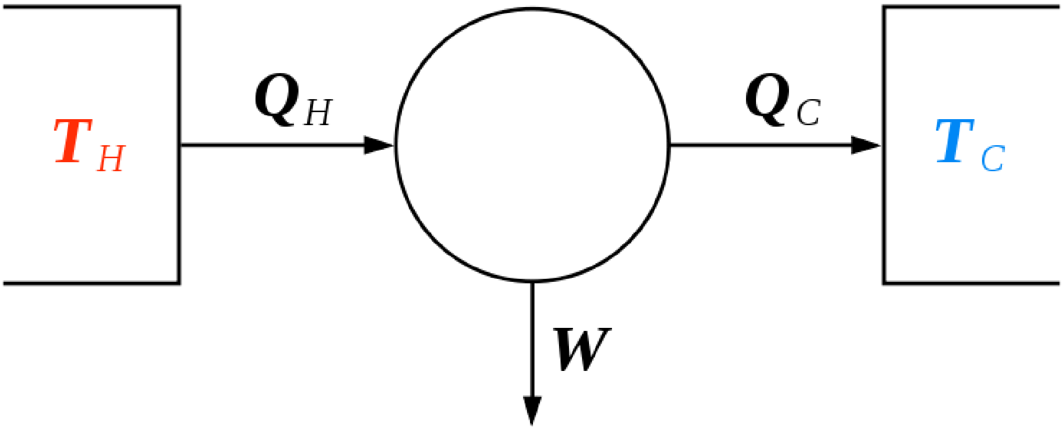
In practice, a system can never be absolutely isolated from its environment, because there is always at least some slight coupling, such as gravitational attraction. In analyzing a system in steady-state, the energy into the system is equal to the energy leaving the system .

An example system is the system of hot liquid water and solid table salt in a sealed, insulated test tube held in a vacuum (the surroundings). The test tube constantly loses heat in the form of black-body radiation, but the heat loss progresses very slowly. If there is another process going on in the test tube, for example the dissolution of the salt crystals, it will probably occur so quickly that any heat lost to the test tube during that time can be neglected. Thermodynamics in general does not measure time, but it does sometimes accept limitations on the time frame of a process.

History

The first to develop the concept of a thermodynamic system was the French physicist Sadi Carnot whose 1824 *Reflections on the Motive Power of Fire* studied what he called the *working substance*, e.g., typically a body of water vapor, in steam engines, in regards to the system's ability to do work when heat is applied to it. The working substance could be put in contact with either a heat reservoir (a boiler), a cold reservoir (a stream of cold water), or a piston (to which the working body could do work by pushing on it). In 1850, the German physicist Rudolf Clausius generalized this picture to include the concept of the surroundings, and began referring to the system as a "working body." In his 1850 manuscript *On the Motive Power of Fire*, Clausius wrote:

> "With every change of volume (to the working body) a certain amount work must be done by the gas or upon it, since by its expansion it overcomes an external pressure, and since its compression can be brought about only by an exertion of external pressure. To this excess of work done by the gas or upon it there must correspond, by our principle, a proportional excess of heat consumed or produced, and the gas cannot give up to the "surrounding medium" the same amount of heat as it receives."



Carnot engine diagram (modern) - where heat flows from a high temperature T_H furnace through the fluid of the "working body" (working substance) and into the cold sink T_C, thus forcing the working substance to do mechanical work W on the surroundings, via cycles of contractions and expansions.

In the diagram shown, the "working body" (system), a term introduced by Clausius in 1850, can be any fluid or vapor body through which heat Q can be introduced or transmitted through to produce work. In 1824, Sadi Carnot, in his famous paper *Reflections on the Motive Power of Fire*, had postulated that the fluid body could be any substance capable of expansion, such as vapor of water, vapor of alcohol, vapor of mercury, a permanent gas, or air, etc. Although, in these early years, engines came in a number of configurations, typically Q_H was supplied by a boiler, wherein water was boiled over a furnace; Q_C was typically a stream of cold flowing water in the form of a condenser located on a separate part of the engine. The output work W here is the movement of the piston as it is used to turn a crank-arm, which was then typically used to turn a pulley so to lift water out of flooded salt mines. Carnot defined work as "weight lifted through a height."

Boundary

A system boundary is a real or imaginary volumetric demarcation region drawn around a thermodynamic system across which quantities such as heat, mass, or work can flow. In short, a thermodynamic boundary is a division between a system and its surroundings.

Boundaries can also be fixed (e.g. a constant volume reactor) or moveable (e.g. a piston). For example, in an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. Boundaries may be real or imaginary. For closed systems, boundaries are real while for open system boundaries are often imaginary. A boundary may be adiabatic, isothermal, diathermal, insulating, permeable, or semipermeable.

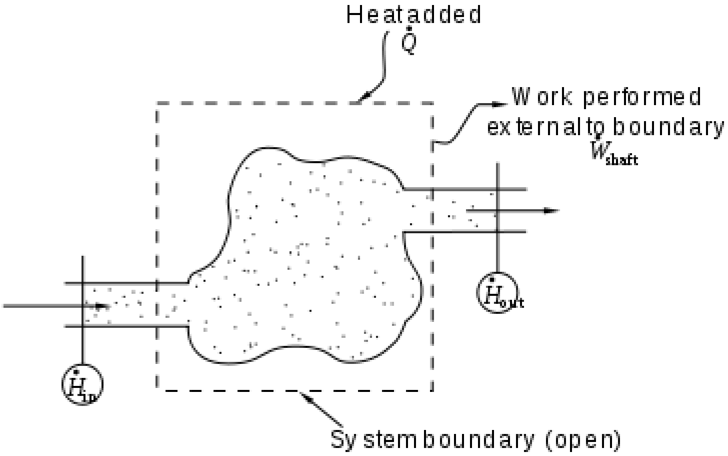
In practice, the boundary is simply an imaginary dotted line drawn around a volume when there is going to be a change in the internal energy of that volume. Anything that passes across the boundary that effects a change in the internal energy needs to be accounted for in the energy balance equation. The volume can be the region surrounding a single atom resonating energy, such as Max Planck defined in 1900; it can be a body of steam or air in a steam engine, such as Sadi Carnot defined in 1824; it can be the body of a tropical cyclone, such as Kerry Emanuel theorized in 1986 in the field of atmospheric thermodynamics; it could also be just one nuclide (i.e. a system of quarks) as hypothesized in quantum thermodynamics.

For an engine, a fixed boundary means the piston is locked at its position; as such, a constant volume process occurs. In that same engine, a moveable boundary allows the piston to move in and out. For closed systems, boundaries are real while for open system boundaries are often imaginary.

Surroundings

The system is the part of the universe being studied, while the *surroundings* is the remainder of the universe that lies outside the boundaries of the system. It is also known as the *environment*, and the *reservoir*. Depending on the type of system, it may interact with the system by exchanging mass, energy (including heat and work), momentum, electric charge, or other conserved properties. The environment is ignored in analysis of the system, except in regards to these interactions.

Open system



During steady, continuous operation, an energy balance applied to an open system equates shaft work performed by the system to heat added plus net enthalpy added.

In open systems, matter may flow in and out of the system boundaries. The first law of thermodynamics for open systems states: *the increase in the internal energy of a system is equal to the amount of energy added to the system by matter flowing in and by heating, minus the amount lost by matter flowing out and in the form of work done by the system.* The first law for open systems is given by:

$$\mathrm{d}U = \mathrm{d}U_{in} + \delta Q - \mathrm{d}U_{out} - \delta W$$

where U_{in} is the average internal energy entering the system and U_{out} is the average internal energy leaving the system

The region of space enclosed by open system boundaries is usually called a control volume, and it may or may not correspond to physical walls. If we choose the shape of the control volume such that all flow in or out occurs perpendicular to its surface, then the flow of matter into the system performs work as if it were a piston of fluid pushing mass into the system, and the system performs work on the flow of matter out as if it were driving a piston of fluid. There are then two types of work performed: *flow work* described above which is performed on the fluid (this is also often called *PV work*) and *shaft work* which may be performed on some mechanical device. These two types of work are expressed in the equation:

$$\delta W = \mathrm{d}(P_{out}V_{out}) - \mathrm{d}(P_{in}V_{in}) + \delta W_{shaft}$$

Substitution into the equation above for the control volume *cv* yields:

$$\mathrm{d}U_{cv} = \mathrm{d}U_{in} + \mathrm{d}(P_{in}V_{in}) - \mathrm{d}U_{out} - \mathrm{d}(P_{out}V_{out}) + \delta Q - \delta W_{shaft}$$

The definition of enthalpy, *H*, permits us to use this thermodynamic potential to account for both internal energy and PV work in fluids for open systems:

$$\mathrm{d}U_{cv} = \mathrm{d}H_{in} - \mathrm{d}H_{out} + \delta Q - \delta W_{shaft}$$

During steady-state operation of a device, any system property within the control volume is independent of time. Therefore, the internal energy of the system enclosed by the control volume remains constant, which implies that $\mathrm{d}U_{cv}$ in the expression above may be set equal to zero. This yields a useful expression for the power generation or requirement for these devices in the absence of chemical reactions:

$$\frac{\delta W_{shaft}}{\mathrm{d}t} = \frac{\mathrm{d}H_{in}}{\mathrm{d}t} - \frac{\mathrm{d}H_{out}}{\mathrm{d}t} + \frac{\delta Q}{\mathrm{d}t}$$

This expression is described by the diagram above.

Closed system

In a closed system, no mass may be transferred in or out of the system boundaries. The system will always contain the same amount of matter, but heat and work can be exchanged across the boundary of the system. Whether a system can exchange heat, work, or both is dependent on the property of its boundary.

- Adiabatic boundary – not allowing any heat exchange
- Rigid boundary – not allowing exchange of work

One example is fluid being compressed by a piston in a cylinder. Another example of a closed system is a bomb calorimeter, a type of constant-volume calorimeter used in measuring the heat of combustion of a particular reaction. Electrical energy travels across the boundary to produce a spark between the electrodes and initiates combustion. Heat transfer occurs across the boundary after combustion but no mass transfer takes place either way.

Beginning with the first law of thermodynamics for an open system, this is expressed as:

$$\mathrm{d}U = Q - W + m_i(h + \frac{1}{2}v^2 + gz)_i - m_e(h + \frac{1}{2}v^2 + gz)_e$$

where U is internal energy, Q is heat transfer, W is work, and since no mass is transferred in or out of the system, both expressions involving mass flow, , zeroes, and the first law of thermodynamics for a closed system is derived. The first law of thermodynamics for a closed system states that the amount of internal energy within the system equals the difference between the amount of heat added to or extracted from the system and the work done by or to the system. The first law for closed systems is stated by:

$$\mathrm{d}U = \delta Q - \delta W$$

where U is the average internal energy within the system, Q is the heat added to or extracted from the system and W is the work done by or to the system.

Substituting the amount of work needed to accomplish a reversible process, which is stated by:

$$\delta W = P\mathrm{d}V$$

where P is the measured pressure and V is the volume, and the heat required to accomplish a reversible process stated by the second law of thermodynamics, the universal principle of entropy, stated by:

$$\delta Q = T\mathrm{d}S$$

where T is the absolute temperature and S is the entropy of the system, derives the fundamental thermodynamic relationship used to compute changes in internal energy, which is expressed as:

$$\delta U = T\mathrm{d}S - P\mathrm{d}V$$

The second law of thermodynamics is only true for closed systems. It states that the entropy of an isolated system not in equilibrium will tend to increase over time, approaching maximum value at equilibrium. Overall, in a closed system, the available energy can never increase, and it complement, entropy, can never decrease.

For a simple system, with only one type of particle (atom or molecule), a closed system amounts to a constant number of particles. However, for systems which are undergoing a chemical reaction, there may be all sorts of molecules being generated and destroyed by the reaction process. In this case, the fact that the system is closed is expressed by stating that the total number of each elemental atom is conserved, no matter what kind of molecule it may be a part of. Mathematically:

$$\sum_{j=1}^{m} a_{ij} N_j = b_i^0$$

where N_j is the number of j-type molecules, a_{ij} is the number of atoms of element *i* in molecule *j* and b_i^0 is the total number of atoms of element *i* in the system, which remains constant, since the system is closed. There will be one such equation for each different element in the system.

Isolated system

An isolated system is more restrictive than a closed system as it does not interact with its surroundings in any way. Mass and energy remains constant within the system, and no energy or mass transfer takes place across the boundary. As time passes in an isolated system, internal differences in the system tend to even out and pressures and temperatures tend to equalize, as do density differences. A system in which all equalizing processes have gone practically to completion is considered to be in a state of thermodynamic equilibrium.

Truly isolated physical systems do not exist in reality (except perhaps for the universe as a whole), because, for example, there is always gravity between a system with mass and masses elsewhere. However, real systems may behave nearly as an isolated system for finite (possibly very long) times. The concept of an isolated system can serve as a useful model approximating many real-world situations. It is an acceptable idealization used in constructing mathematical models of certain natural phenomena.

In the attempt to justify the postulate of entropy increase in the second law of thermodynamics, Boltzmann’s H-theorem used equations which assumed a system (for example, a gas) was isolated. That is all the mechanical degrees of freedom could be specified, treating the walls simply as mirror boundary conditions. This inevitably led to Loschmidt's paradox. However, if the stochastic behavior of the molecules in actual walls is considered, along with the randomizing effect of the ambient, background thermal radiation, Boltzmann’s assumption of molecular chaos can be justified.

It is important to note that isolated systems are not equivalent to closed systems. Closed systems cannot exchange matter with the surroundings, but can exchange energy. Isolated systems can exchange neither matter nor energy with their surroundings, and as such are only theoretical and do not exist in reality (except, possibly, the entire universe).

Thermodynamic equilibrium

In thermodynamics, a thermodynamic system is said to be in **thermodynamic equilibrium** when it is in thermal equilibrium, mechanical equilibrium, radiative equilibrium, and chemical equilibrium. The word equilibrium means a state of balance. In an equilibrium state, there are no unbalanced potentials (or driving forces) with the system. A system that is in equilibrium experiences no changes when it is isolated from its surroundings.

The opposite of equilibrium systems are nonequilibrium systems that are instantaneously off balance.

Overview

Classical thermodynamics deals with dynamic equilibrium states. The local state of a system at thermodynamic equilibrium is determined by the values of its intensive parameters, such as pressure or temperature. Specifically, thermodynamic equilibrium is characterized by the minimum of a thermodynamic potential, such as the Helmholtz free energy, i.e. systems at constant temperature and volume:

$$A = U - TS;$$

Or as the Gibbs free energy, i.e. systems at constant pressure and temperature:

$$G = H - TS.$$

where T = temperature, S = entropy, p = pressure, V = volume. The Helmholtz free energy is often denoted by the symbol F, but the use of A is preferred by IUPAC .

The process that leads to a thermodynamic equilibrium is called thermalization. An example of this is a system of interacting particles that is left undisturbed by outside influences. By interacting, they will share energy/momentum among themselves and reach a state where the global statistics are unchanging in time.

Conditions for equilibrium

By considering the differential form of thermodynamic potentials, the following relationships can be derived:

- For a completely isolated system, $\Delta S = 0$ at equilibrium.
- For a system at constant temperature and volume, $\Delta A = 0$ at equilibrium.
- For a system at constant temperature and pressure, $\Delta G = 0$ at equilibrium.

The various types of equilibriums are achieved as follows:

- Two systems are in *thermal equilibrium* when their temperatures are the same.
- Two systems are in *mechanical equilibrium* when their pressures are the same.
- Two systems are in *diffusive equilibrium* when their chemical potentials are the same.

Local and global equilibrium

It is useful to distinguish between global and local thermodynamic equilibrium. In thermodynamics, exchanges within a system and between the system and the outside are controlled by intensive parameters. As an example, temperature controls heat exchanges. *Global thermodynamic equilibrium* (GTE) means that those intensive parameters are homogeneous throughout the whole system, while *local thermodynamic equilibrium* (LTE) means that those intensive parameters are varying in space and time, but are varying so slowly that for any point, one can assume thermodynamic equilibrium in some neighborhood about that point.

If the description of the system requires variations in the intensive parameters that are too large, the very assumptions upon which the definitions of these intensive parameters are based will break down, and the system will be in neither global nor local equilibrium. For example, it takes a certain number of collisions for a particle to equilibrate to its surroundings. If the average distance it has moved during these collisions removes it from the neighborhood it is equilibrating to, it will never equilibrate, and there will be no LTE. Temperature is, by definition, proportional to the average internal energy of an equilibrated neighborhood. Since there is no equilibrated neighborhood, the concept of temperature breaks down, and the temperature becomes undefined.

It is important to note that this local equilibrium applies only to massive particles. In a radiating gas, the photons being emitted and absorbed by the gas need not be in thermodynamic equilibrium with each other or with the massive particles of the gas in order for LTE to exist.

As an example, LTE will exist in a glass of water which contains a melting ice cube. The temperature inside the glass can be defined at any point, but it is colder near the ice cube than far away from it. If energies of the molecules located near a given point are observed, they will be distributed according to the Maxwell-Boltzmann distribution for a certain temperature. If the energies of the molecules located near another point are observed, they will be distributed according to the Maxwell-Boltzmann distribution for another temperature.

Local thermodynamic equilibrium is not a stable state, unless it is maintained by exchanges between the system and the outside. For example, it could be maintained inside the glass of water by regularly adding ice into it in order to compensate for the melting. Transport phenomena are processes which lead a system from local to global thermodynamic equilibrium. Going back to our example, the diffusion of heat will lead our glass of water toward global thermodynamic equilibrium, a state in which the temperature of the glass is completely homogeneous.

Types of equilibrium

Thermal equilibrium

Thermal equilibrium is achieved when two systems in thermal contact with each other cease to have a net exchange of energy. It follows that if two systems are in thermal equilibrium, then their temperatures are the same.

Thermal equilibrium occurs when a system's macroscopic thermal observables have ceased to change with time. For example, an ideal gas whose distribution function has stabilised to a specific Maxwell-Boltzmann distribution would be in thermal equilibrium. This outcome allows a single temperature and pressure to be attributed to the whole system. Thermal equilibrium of a system does not imply absolute uniformity within a system; for example, a river system can be in thermal equilibrium when the macroscopic temperature distribution is stable and not changing in time, even though the spatial temperature distribution reflects thermal pollution inputs.

Quasistatic equilibrium

Quasistatic equilibrium (also known as **quasi-equilibrium**) is the quasi-balanced state of a thermodynamic system near to thermodynamic equilibrium in some sense or degree. A process is called quasi-static when it follows a succession of equilibrium states; the surroundings may be irreversibly altered during the process so that after a return path, the system ends up in a final state which differs from its initial state.

The quasistatic equilibrium model facilitates or justifies the use of Gibbsian thermodynamic applications, i.e. equations of state, to systems characterized by slow change if measured on the adjunct time scale. In short, the quasistatic equilibrium model approximates change as a series of equilibrium processes.

In a quasistatic process, or equilibrium process, a sufficiently slow transition of a thermodynamic system from one equilibrium state to another occurs such that at every moment in time the state of the system is close to an equilibrium state. During a quasistatic process, the system reaches equilibrium much faster, almost instantaneously, than its physical parameters vary. A quasistatic process is not necessarily a reversible one.

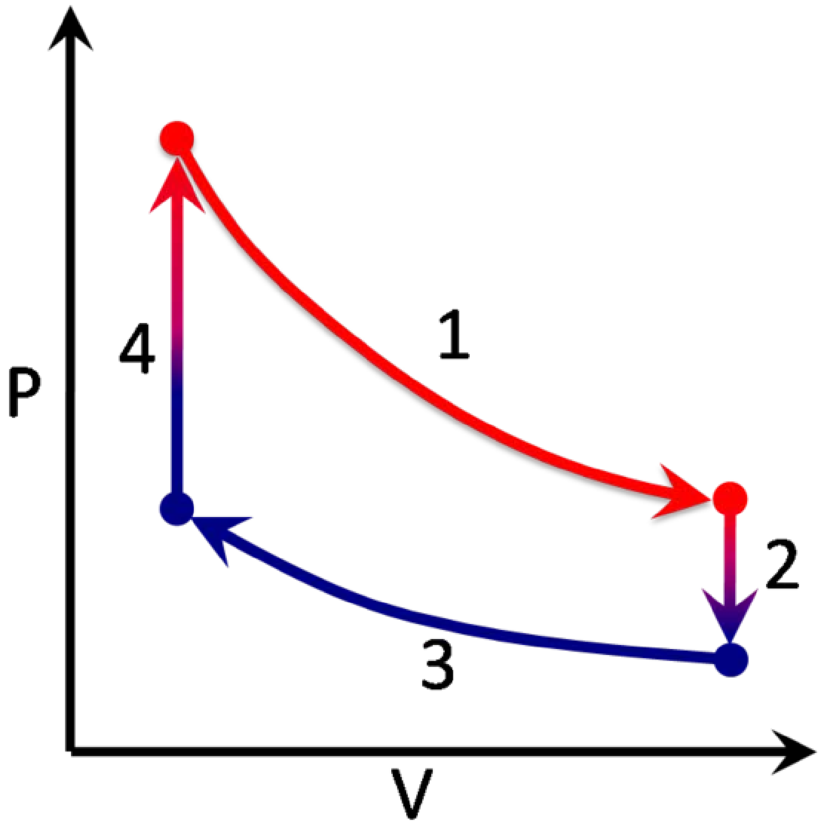
For **quasi-equilibrium**, it is only required that the properties of the system be uniform at any instant during a process.

Chapter- 5

Thermodynamic Process

A **thermodynamic process** may be defined as the energetic evolution of a thermodynamic system proceeding from an initial state to a final state. Paths through the space of thermodynamic variables are often specified by holding certain thermodynamic variables constant. A state function is a thermodynamic variable which depends only on the current state of the system, not the path taken to reach that state. Conversely a process function does depend on the path.

Overview



An example of a series of thermodynamic processes which make up the Stirling cycle

A thermodynamic process can be visualized by graphically plotting the changes to the system's state variables. In the example, four processes are shown. Each process has a well-defined start and end point in the pressure-volume state space. In this particular example, processes 1 and 3 are isothermal, whereas processes 2 and 4 are isochoric. The PV diagram is a particularly useful visualization of a process, because the area under the curve of a process is the amount of work done by the system during that process. Thus work is considered to be a process variable, as its exact value depends on the particular path taken between the start and end points of the process. Similarly, heat may be transferred during a process, and it too is a process variable. In contrast, pressure and volume (as well as numerous other other properties) are considered state variables because their values depend only on the position of the start and end points, not the particular path between them.

Conjugate variable processes

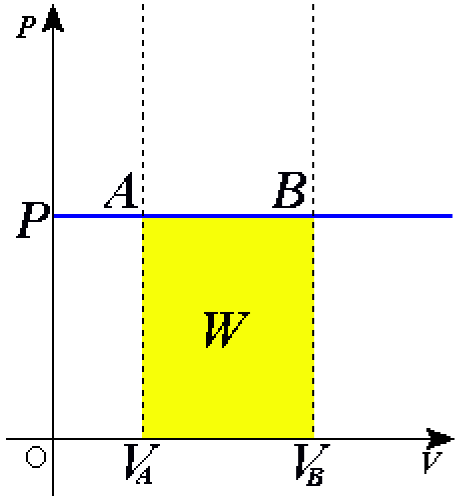
It is often useful to group processes into pairs, in which each variable held constant is one member of a conjugate pair.

Pressure - volume

The pressure-volume conjugate pair is concerned with the transfer of mechanical or dynamic energy as the result of work.

Isobaric process

An **isobaric process** is a thermodynamic process in which the pressure stays constant. The term derives from the Greek *isos,* (equal), and *barus,* (heavy). The heat transferred to the system does work but also changes the internal energy of the system:



The yellow area represents the work done

$$Q = \Delta U + W$$

According to the first law of thermodynamics, where W is work done by the system, U is internal energy, and Q is heat. Pressure-volume work by the closed system is defined as:

$$W = \int p \, dV$$

where Δ means change over the whole process, whereas d denotes a differential. Since pressure is constant, this means that

$$W = p\Delta V.$$

Applying the ideal gas law, this becomes

$$W = n \, R \, \Delta T$$

assuming that the quantity of gas stays constant, e.g., there is no phase change during a chemical reaction. According to the equipartition theorem, the change in internal energy is related to the temperature of the system by

$$\Delta U = n \, c_V \, \Delta T,$$

where c_V is specific heat at a constant volume.

Substituting the last two equations into the first equation produces:

$$\begin{aligned} Q &= n \, c_V \, \Delta T + n \, R \, \Delta T \\ &= n \, (c_V + R) \, \Delta T \\ &= n \, c_P \, \Delta T, \end{aligned}$$

where c_P is specific heat at a constant pressure.

Specific heat capacity

To find the molar specific heat capacity of the gas involved, the following equations apply for any general gas that is calorically perfect. The property γ is either called the adiabatic index or the heat capacity ratio. Some published sources might use k instead of γ.

Molar isochoric specific heat:

$$c_V = \frac{R}{\gamma - 1}.$$

Molar isobaric specific heat:

$$c_p = \frac{\gamma R}{\gamma - 1}.$$

The values for γ are γ = 1.4 for diatomic gasses like air and its major components, and $\gamma = \frac{5}{3}$ for monatomic gasses like the noble gasses. The formulas for specific heats would reduce in these special cases:

Monatomic:

$$c_V = \frac{3R}{2} \text{ and } c_P = \frac{5R}{2}$$

Diatomic:

$$c_V = \frac{5R}{2} \text{ and } c_P = \frac{7R}{2}$$

An isobaric process is shown on a P-V diagram as a straight horizontal line, connecting the initial and final thermostatic states. If the process moves towards the right, then it is an expansion. If the process moves towards the left, then it is a compression.

Sign convention for work

The motivation for the specific sign conventions of thermodynamics comes from early development of heat engines. When designing a heat engine, the goal is to have the system produce and deliver work output. The source of energy in a heat engine, is a heat input.

If the volume compresses (delta V = final volume - initial volume < 0), then W < 0. That is, during isobaric compression the gas does negative work, or the environment does positive work. Restated, the environment does positive work on the gas.

If the volume expands (delta V = final volume - initial volume > 0), then W > 0. That is, during isobaric expansion the gas does positive work, or equivalently, the environment does negative work. Restated, the gas does positive work on the environment.

If heat is added to the system, then Q > 0. That is, during isobaric expansion/heating, positive heat is added to the gas, or equivalently, the environment receives negative heat. Restated, the gas receives positive heat from the environment.

If the system rejects heat, then Q < 0. That is, during isobaric compression/cooling, negative heat is added to the gas, or equivalently, the environment receives positive heat. Restated, the environment receives positive heat from the gas.

Defining enthalpy

An isochoric process is described by the equation $Q = \Delta U$. It would be convenient to have a similar equation for isobaric processes. Substituting the second equation into the first yields

$$Q = \Delta U + \Delta(pV) = \Delta(U + pV)$$

The quantity $U + p\,V$ is a state function so that it can be given a name. It is called enthalpy, and is denoted as H. Therefore an isobaric process can be more succinctly described as

$$Q = \Delta H.$$

Enthalpy and isobaric specific heat capacity are very useful mathematical constructs, since when analyzing a process in an open system, the situation of zero work occurs when the fluid flows at constant pressure. In an open system, enthalpy is the quantity which is useful to use to keep track of energy content of the fluid.

Variable density viewpoint

A given quantity (mass m) of gas in a changing volume produces a change in density ρ. In this context the ideal gas law is written

$$\mathrm{R}(T\,\rho) = \mathrm{M}\,P$$

where T is thermodynamic temperature. When R and M are taken as constant, then pressure P can stay constant as the density-temperature quadrant (ρ, T) undergoes a squeeze mapping.

Isochoric process

An **isochoric process**, also called a **constant-volume process**, an **isovolumetric process**, or an **isometric process**, is a thermodynamic process during which the volume of the closed system undergoing such a process remains constant. In nontechnical terms, an isochoric process is exemplified by the heating or the cooling of the contents of a sealed non-deformable container: The thermodynamic process is the addition or removal of heat; the isolation of the contents of the container establishes the closed system; and the inability of the container to deform imposes the constant-volume condition.

Formalism

An isochoric thermodynamic process is characterized by constant volume, i.e. $\Delta V = 0$. The process does no pressure-volume work, since such work is defined by

$$\Delta W = P\Delta V,$$

where P is pressure. The sign convention is such that positive work is performed by the system on the environment.

For a reversible process, the first law of thermodynamics gives the change in the system's internal energy:

$$dU = dQ - dW$$

Replacing work with a change in volume gives

$$dU = dQ - PdV$$

Since the process is isochoric, $dV = 0$, the previous equation now gives

$$dU = dQ$$

Using the definition of specific heat capacity at constant volume,

$$C_v = dU / dT,$$

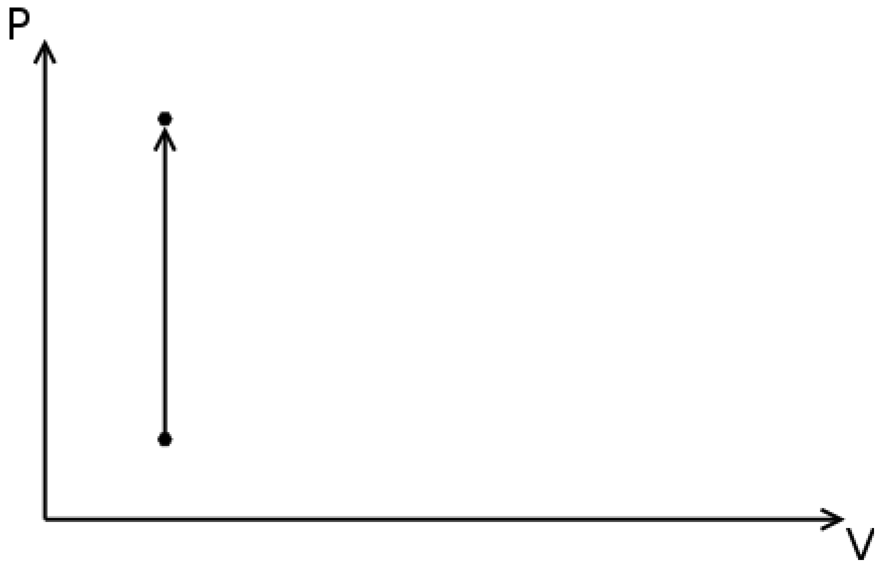
$$dQ = nC_v dT$$

Integrating both sides yields

$$Q = n \int_a^b C \, dT.$$

Where C is the specific heat capacity at constant volume, a is initial temperature and b is final temperature. We conclude with:

$$Q = nC_v \Delta T$$



Isochoric Process in the Pressure volume diagram. In this diagram, pressure increases, but volume remains constant.

On a pressure volume diagram, an isochoric process appears as a straight vertical line. Its thermodynamic conjugate, an isobaric process would appear as a straight horizontal line.

Ideal gas

If an ideal gas is used in an isochoric process, and the quantity of gas stays constant, then the increase in energy is proportional to an increase in temperature and pressure. Take for example a gas heated in a rigid container: the pressure and temperature of the gas will increase, but the volume will remain the same.

Ideal Otto cycle

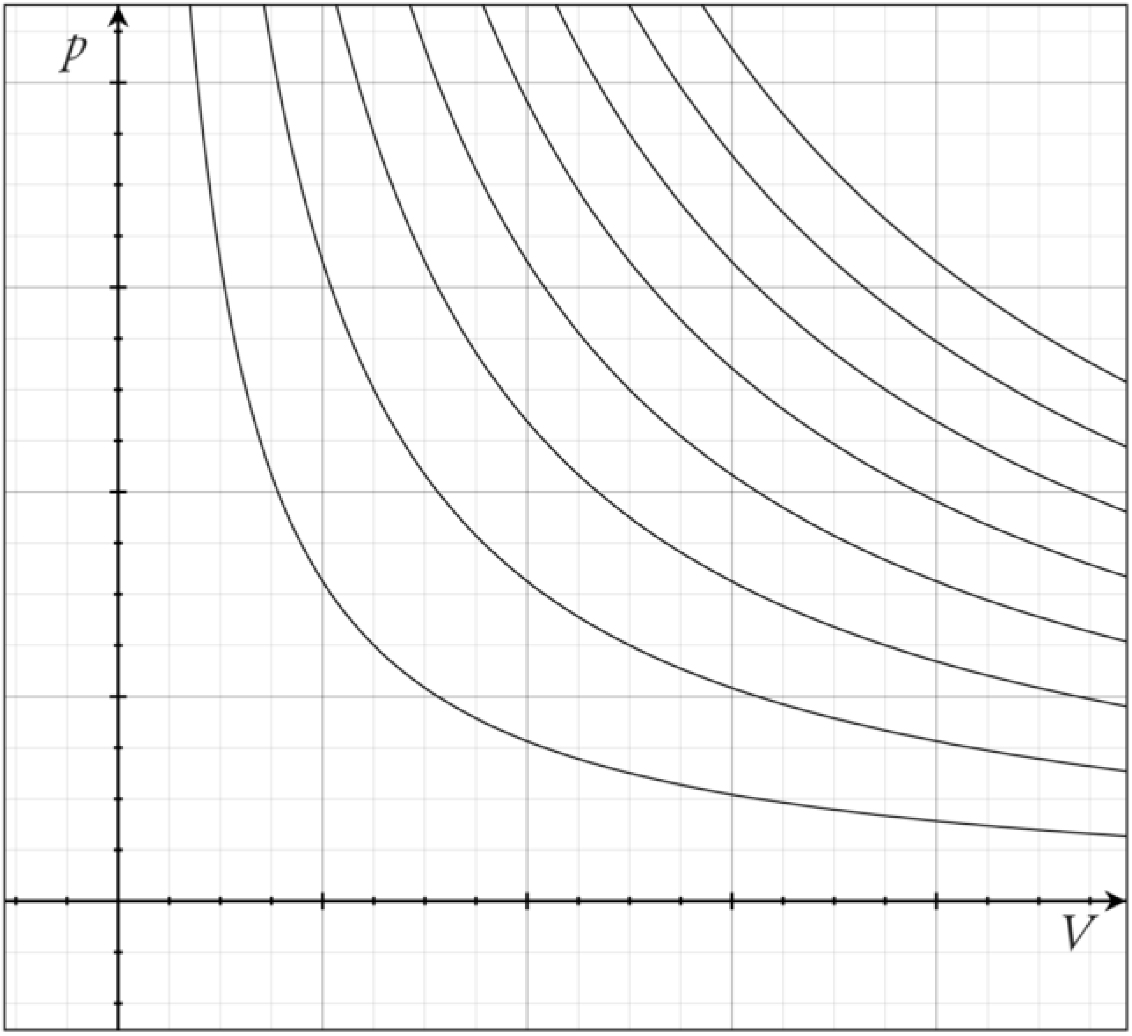
The ideal Otto cycle is an example of an isochoric process when it is assumed that the burning of the gasoline-air mixture in an internal combustion engine car is instantaneous. There is an increase in the temperature and the pressure of the gas inside the cylinder while the volume remains the same.

Temperature - entropy

Isothermal process

An **isothermal process** is a change of a system, in which the temperature remains constant: $\Delta T = 0$. This typically occurs when a system is in contact with an outside thermal reservoir (heat bath), and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange. In contrast, an *adiabatic process* is where a system exchanges no heat with its surroundings ($Q = 0$). In other words, in an isothermal process, the value $\Delta T = 0$ but $Q \neq 0$, while in an adiabatic process, $\Delta T \neq 0$ but $Q = 0$.

Details for an ideal gas



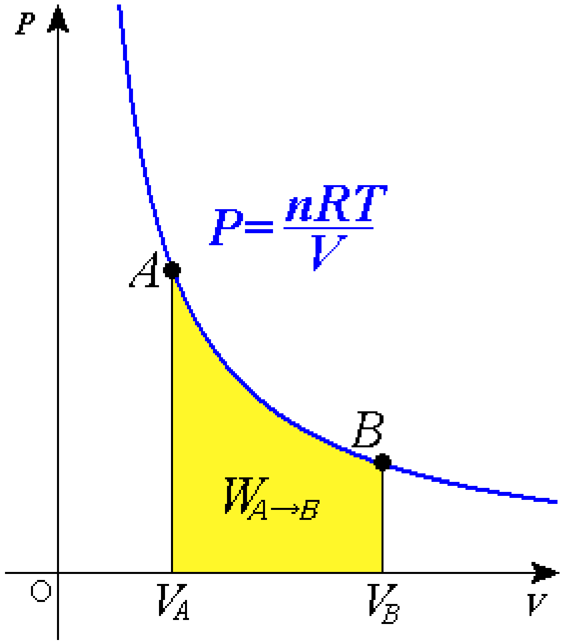
Several isotherms of an ideal gas on a p-V diagram

For the special case of a gas to which Boyle's law applies, the product pV is a constant if the gas is kept at isothermal conditions. The value of the constant is nRT, where n is the number of moles of gas present and R is the ideal gas constant. In other words, the ideal gas law $pV = nRT$ applies. This means that

$$p = \frac{nRT}{V} = \frac{constant}{V}$$

holds. The family of curves generated by this equation is shown in the graph presented here. Each curve is called an isotherm. Such graphs are termed indicator diagrams and were first used by James Watt and others to monitor the efficiency of engines. The temperature corresponding to each curve in the figure increases from the lower left to the upper right.

Calculation of work



The yellow area represents "work" for this isothermal change

In thermodynamics, the work involved when a gas changes from state A to state B is simply

$$W_{A\to B} = \int_{V_A}^{V_B} p\,dV$$

For an isothermal, reversible process, this integral equals the area under the relevant pressure-volume isotherm, and is indicated in yellow in the figure at right for an ideal gas. Again p = nRT / V applies and with T being a constant (as this is an isothermal process), we have:

$$W_{A\to B} = \int_{V_A}^{V_B} p\,dV = \int_{V_A}^{V_B} \frac{nRT}{V} dV = nRT \int_{V_A}^{V_B} \frac{1}{V} dV = nRT \ln \frac{V_B}{V_A} = nRT \ln \frac{P_A}{P_B}$$

By convention work is defined as the work the system does on the surroundings.

It is also worth noting that, for many systems, if the temperature is held constant then the internal energy of the system also is constant, and so $\Delta U = 0$. From First Law of Thermodynamics, $Q = \Delta U + W$, so it follows that $Q = W$ for this same isothermal process.

Applications

Isothermal processes can occur in any kind of system, including highly-structured machines, and even living cells. Various parts of the cycles of some heat engines are carried out isothermally and may be approximated by a Carnot cycle. Phase changes, such as melting or evaporation, are also isothermal processes.

Adiabatic process

In thermodynamics, an **adiabatic process** or an **isocaloric process** is a thermodynamic process in which no heat is transferred to or from the working fluid. The term "adiabatic" literally means impassable, coming from the Greek roots ἀ- ("not"), διὰ- ("through"), and βαῖνειν ("to pass"); this etymology corresponds here to an absence of heat transfer. Conversely, a process that involves heat transfer (addition or loss of heat to the surroundings) is generally called **diabatic**. Although the terms adiabatic and isocaloric can often be interchanged, adiabatic processes may be considered a subset of isocaloric processes; the remaining complement subset of isocaloric processes being processes where net heat transfer does not diverge regionally such as in an idealized case with mediums of infinite thermal conductivity or non-existent thermal capacity.

In an adiabatic irreversible process, dQ=0 is not equal to TdS (TdS>0). dQ=TdS=0 holds for reversible processes only. For example, an **adiabatic boundary** is a boundary that is impermeable to heat transfer and the system is said to be adiabatically (or thermally) insulated; an insulated wall approximates an adiabatic boundary. Another example is the adiabatic flame temperature, which is the temperature that would be achieved by a flame in the absence of heat loss to the surroundings. An adiabatic process that is reversible is also called an isentropic process. Additionally, an adiabatic process that is irreversible and extracts no work is in an isenthalpic process, such as viscous drag, progressing towards a nonnegative change in entropy.

One opposite extreme—allowing heat transfer with the surroundings, causing the temperature to remain constant—is known as an isothermal process. Since temperature is thermodynamically conjugate to entropy, the isothermal process is conjugate to the adiabatic process for reversible transformations.

A transformation of a thermodynamic system can be considered adiabatic when it is quick enough that no significant heat is transferred between the system and the outside. At the opposite extreme, a transformation of a thermodynamic system can be considered isothermal if it is slow enough so that the system's temperature remains constant by heat exchange with the outside.

Adiabatic heating and cooling

Adiabatic changes in temperature occur due to changes in pressure of a gas while not adding or subtracting any heat. In contrast, free expansion is an isothermal process for an ideal gas.

Adiabatic heating occurs when the pressure of a gas is increased from work done on it by its surroundings, i.e. a piston. Diesel engines rely on adiabatic heating during their compression stroke to elevate the temperature sufficiently to ignite the fuel.

Adiabatic heating also occurs in the Earth's atmosphere when an air mass descends, for example, in a katabatic wind or Foehn wind flowing downhill.

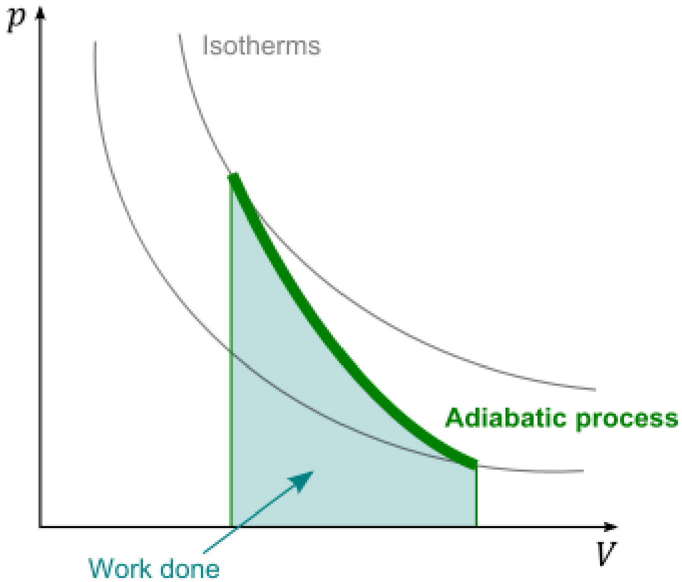
Adiabatic cooling occurs when the pressure of a substance is decreased as it does work on its surroundings. Adiabatic cooling does not have to involve a fluid. One technique used to reach very low temperatures (thousandths and even millionths of a degree above absolute zero) is adiabatic demagnetisation, where the change in magnetic field on a magnetic material is used to provide adiabatic cooling. Adiabatic cooling also occurs in the Earth's atmosphere with orographic lifting and lee waves, and this can form pileus or lenticular clouds if the air is cooled below the dew point.

Rising magma also undergoes adiabatic cooling before eruption.

Such temperature changes can be quantified using the ideal gas law, or the hydrostatic equation for atmospheric processes.

No process is truly adiabatic. Many processes are close to adiabatic and can be easily approximated by using an adiabatic assumption, but there is always some heat loss; as no perfect insulators exist.

Ideal gas (reversible process)



For a simple substance, during an adiabatic process in which the volume increases, the internal energy of the working substance must decrease

The mathematical equation for an ideal fluid undergoing a reversible (i.e., no entropy generation) adiabatic process is

$$PV^{\gamma} = \text{constant}$$

where P is pressure, V is specific or molar volume, and

$$\gamma = \frac{C_P}{C_V} = \frac{\alpha + 1}{\alpha},$$

C_P being the specific heat for constant pressure, C_V being the specific heat for constant volume, γ is the adiabatic index, and α is the number of degrees of freedom divided by 2 (3/2 for monatomic gas, 5/2 for diatomic gas).

For a monatomic ideal gas, $\gamma = 5/3$, and for a diatomic gas (such as nitrogen and oxygen, the main components of air) $\gamma = 7/5$. Note that the above formula is only applicable to classical ideal gases and not Bose-Einstein or Fermi gases.

For reversible adiabatic processes, it is also true that

$$P^{1-\gamma}T^{\gamma} = \text{constant}$$
$$VT^{\alpha} = \text{constant}$$

where *T* is an absolute temperature.

This can also be written as

$$TV^{\gamma-1} = \text{constant}$$

Example of adiabatic compression

Let's now look at a common example of adiabatic compression- the compression stroke in a gasoline engine. We will make a few simplifying assumptions: that the uncompressed volume of the cylinder is 1000cc's (one liter), that the gas within is nearly pure nitrogen (thus a diatomic gas with five degrees of freedom and so $\gamma = 7/5$), and that the compression ratio of the engine is 10:1 (that is, the 1000 cc volume of uncompressed gas will compress down to 100 cc when the piston goes from bottom to top). The uncompressed gas is at approximately room temperature and pressure (a warm room temperature of ~27 degC or 300 K, and a pressure of 1 bar ~ 100,000 Pa, or about 14.7 PSI, or typical sea-level atmospheric pressure).

$$PV^{\gamma} = \text{constant} = 100,000\text{pa} * 1000^{7/5} = 100E3 * 15.8E3 = 1.58E9$$

so our adiabatic constant for this experiment is about 1.58 billion.

The gas is now compressed to a 100cc volume (we will assume this happens quickly enough that no heat can enter or leave the gas). The new volume is 100 ccs, but the constant for this experiment is still 1.58 billion:

$$P * V^{\gamma} = \text{constant} = 1.58E9 = P * 100^{7/5}$$

so solving for P:

$$P = 1.58E9/100^{7/5} = 1.58E9/630.9 = 2.50E6\text{pa}$$

or about 362 PSI or 24.5 atm. Note that this pressure increase is more than a simple 10:1 compression ratio would indicate; this is because the gas is not only compressed, but the work done to compress the gas has also heated the gas and the hotter gas will have a greater pressure even if the volume had not changed.

We can solve for the temperature of the compressed gas in the engine cylinder as well, using the ideal gas law. Our initial conditions are 100,000 pa of pressure, 1000 cc volume, and 300 K of temperature, so our experimental constant is:

$$\frac{PV}{T} = \text{constant} = \frac{1E5 * 1E3}{300} = 3.33E5$$

We know the compressed gas has V = 100 cc and P = 2.50E6 pascals, so we can solve for temperature by simple algebra:

$$\frac{PV}{\text{constant}} = T = \frac{2.50E6 * 100}{3.33E5} = 751$$

That's 751 Kelvins, or 477 degC, or 892 degF. This is why a high compression engine requires fuels specially formulated to not self-ignite (which would cause engine knocking when operated under these conditions of temperature and pressure), or that a supercharger and intercooler to provide a lower temperature at the same pressure would be advantageous. A diesel engine operates under even more extreme conditions, with compression ratios of 20:1 or more being typical, in order to provide a very high gas temperature which insures immediate ignition of injected fuel.

Derivation of continuous formula

The definition of an adiabatic process is that heat transfer to the system is zero, $\delta Q = 0$. Then, according to the first law of thermodynamics,

$$(1) \qquad dU + \delta W = \delta Q = 0,$$

where dU is the change in the internal energy of the system and δW is work done *by* the system. Any work (δW) done must be done at the expense of internal energy U, since no heat δQ is being supplied from the surroundings. Pressure-volume work δW done *by* the system is defined as

$$(2) \qquad \delta W = P\,dV.$$

However, P does not remain constant during an adiabatic process but instead changes along with V.

It is desired to know how the values of dP and dV relate to each other as the adiabatic process proceeds. For an ideal gas the internal energy is given by

$$(3) \qquad U = \alpha n R T,$$

where R is the universal gas constant and n is the number of moles in the system (a constant).

Differentiating Equation (3) and use of the ideal gas law, $PV = nRT$, yields

$$(4) \qquad dU = \alpha n R\,dT = \alpha\,d(PV) = \alpha(P\,dV + V\,dP).$$

Equation (4) is often expressed as $dU = nC_V\,dT$ because $C_V = \alpha R$.

Now substitute equations (2) and (4) into equation (1) to obtain

$$-P\,dV = \alpha P\,dV + \alpha V\,dP,$$

simplify:

$$-(\alpha+1)P\,dV = \alpha V\,dP,$$

and divide both sides by *PV*:

$$-(\alpha+1)\frac{dV}{V} = \alpha\frac{dP}{P}.$$

After integrating the left and right sides from V_0 to V and from P_0 to P and changing the sides respectively,

$$\ln\left(\frac{P}{P_0}\right) = -\frac{\alpha+1}{\alpha}\ln\left(\frac{V}{V_0}\right).$$

Exponentiate both sides,

$$\left(\frac{P}{P_0}\right) = \left(\frac{V}{V_0}\right)^{-\frac{\alpha+1}{\alpha}},$$

and eliminate the negative sign to obtain

$$\left(\frac{P}{P_0}\right) = \left(\frac{V_0}{V}\right)^{\frac{\alpha+1}{\alpha}}.$$

Therefore,

$$\left(\frac{P}{P_0}\right)\left(\frac{V}{V_0}\right)^{\frac{\alpha+1}{\alpha}} = 1$$

and

$$PV^{\frac{\alpha+1}{\alpha}} = P_0V_0^{\frac{\alpha+1}{\alpha}} = PV^\gamma = \text{constant}.$$

Derivation of discrete formula

The change in internal energy of a system, measured from state 1 to state 2, is equal to

$$(1) \qquad \Delta U = \alpha R n_2 T_2 - \alpha R n_1 T_1 = \alpha R (n_2 T_2 - n_1 T_1)$$

At the same time, the work done by the pressure-volume changes as a result from this process, is equal to

$$(2) \qquad W = \int_{V_1}^{V_2} P\,dV$$

Since we require the process to be adiabatic, the following equation needs to be true

$$(3) \qquad \Delta U + W = 0$$

By the previous derivation,

$$(4) \qquad PV^{\gamma} = \text{constant} = P_1 V_1^{\gamma}$$

Rearranging (4) gives

$$P = P_1 \left(\frac{V_1}{V}\right)^{\gamma}$$

Substituting this into (2) gives

$$W = \int_{V_1}^{V_2} P_1 \left(\frac{V_1}{V}\right)^{\gamma} dV$$

Integrating,

$$W = P_1 V_1^{\gamma} \frac{V_2^{1-\gamma} - V_1^{1-\gamma}}{1-\gamma}$$

Substituting $\gamma = \frac{\alpha + 1}{\alpha}$,

$$W = -\alpha P_1 V_1^{\gamma} \left(V_2^{1-\gamma} - V_1^{1-\gamma}\right)$$

Rearranging,

$$W = -\alpha P_1 V_1 \left(\left(\frac{V_2}{V_1}\right)^{1-\gamma} - 1\right)$$

Using the ideal gas law and assuming a constant molar quantity (as often happens in practical cases),

$$W = -\alpha nRT_1 \left(\left(\frac{V_2}{V_1} \right)^{1-\gamma} - 1 \right)$$

By the continuous formula,

$$\frac{P_2}{P_1} = \left(\frac{V_2}{V_1} \right)^{-\gamma}$$

Or,

$$\left(\frac{P_2}{P_1} \right)^{\frac{-1}{\gamma}} = \frac{V_2}{V_1}$$

Substituting into the previous expression for *W*,

$$W = -\alpha nRT_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

Substituting this expression and (1) in (3) gives

$$\alpha nR(T_2 - T_1) = \alpha nRT_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

Simplifying,

$$T_2 - T_1 = T_1 \left(\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)$$

Simplifying,

$$\frac{T_2}{T_1} - 1 = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1$$

Simplifying,

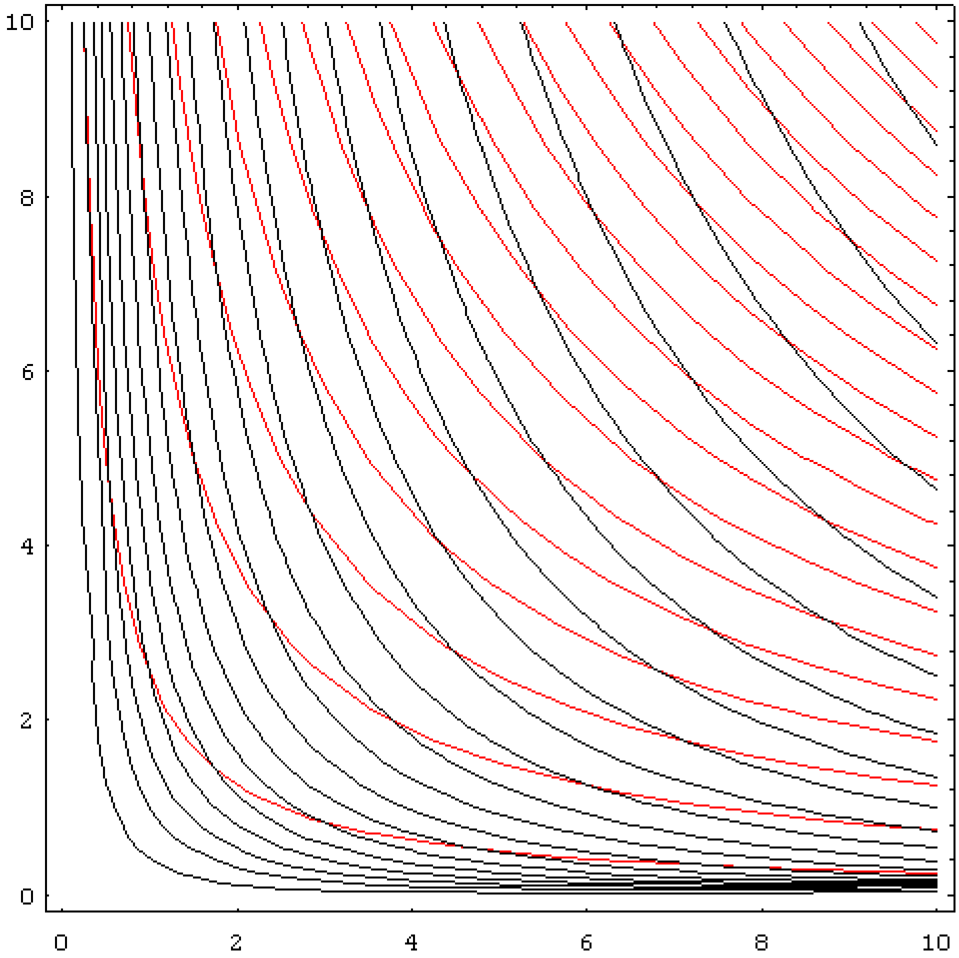
$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}}$$

Graphing adiabats

An adiabat is a curve of constant entropy on the P-V diagram. Properties of adiabats on a P-V diagram are:

1. Every adiabat asymptotically approaches both the V axis and the P axis (just like isotherms).
2. Each adiabat intersects each isotherm exactly once.
3. An adiabat looks similar to an isotherm, except that during an expansion, an adiabat loses more pressure than an isotherm, so it has a steeper inclination (more vertical).
4. If isotherms are concave towards the "north-east" direction (45 °), then adiabats are concave towards the "east north-east" (31 °).
5. If adiabats and isotherms are graphed severally at regular changes of entropy and temperature, respectively (like altitude on a contour map), then as the eye moves towards the axes (towards the south-west), it sees the density of isotherms stay constant, but it sees the density of adiabats grow. The exception is very near absolute zero, where the density of adiabats drops sharply and they become rare.

The following diagram is a P-V diagram with a superposition of adiabats and isotherms:



The isotherms are the red curves and the adiabats are the black curves

The adiabats are isentropic.

Volume is the horizontal axis and pressure is the vertical axis.

Isentropic process

In thermodynamics, an **isentropic process** or **isoentropic process** (*ισον* = "equal" (Greek); *εντροπία* entropy = "disorder"(Greek)) is one in which for purposes of engineering analysis and calculation, one may assume that the process takes place from initiation to completion without an increase or decrease in the entropy of the system, i.e., the entropy of the system remains constant. It can be proved that any reversible adiabatic process is an isentropic process.

Background

Second law of thermodynamics states that,

$$\delta Q \leq TdS$$

where δQ is the amount of energy the system gains by heating, T is the temperature of the system, and dS is the change in entropy. The equal sign will hold for a reversible process. For a reversible isentropic process, there is no transfer of heat energy and therefore the process is also adiabatic. For an irreversible process, the entropy will increase. Hence removal of heat from the system (cooling) is necessary to maintain a constant internal entropy for an irreversible process in order to make it isentropic. Thus an irreversible isentropic process is not adiabatic.

For reversible processes, an isentropic transformation is carried out by thermally "insulating" the system from its surroundings. Temperature is the thermodynamic conjugate variable to entropy, thus the conjugate process would be an isothermal process in which the system is thermally "connected" to a constant-temperature heat bath.

Isentropic flow

An **isentropic flow** is a flow that is both adiabatic and reversible. That is, no heat is added to the flow, and no energy transformations occur due to friction or dissipative effects. For an isentropic flow of a perfect gas, several relations can be derived to define the pressure, density and temperature along a streamline.

Note that energy **can** be exchanged with the flow in an isentropic transformation, as long as it doesn't happen as heat exchange. An example of such an exchange would be an isentropic expansion or compression, with entail work done on or by the flow.

Derivation of the isentropic relations

For a closed system, the total change in energy of a system is the sum of the work done and the heat added,

$$dU = dW + dQ$$

The work done on a system by changing the volume is,

$$dW = -pdV$$

where p is the pressure and V is the volume. The change in enthalpy ($H = U + pV$) is given by,

$$dH = dU + pdV + Vdp = nC_p dT$$

Since a reversible process is adiabatic (i.e. no heat transfer occurs), so $dQ = 0, dS = 0$. This leads to two important observations,

$dU = -pdV$, and
$dH = Vdp$ or $dQ = dH - Vdp = 0$
$dQ = TdS$ => $dS = (1/T)dH - (V/T)dp$

The heat capacity ratio can be written as,

$$\gamma = \frac{C_p}{C_V} = -\frac{dp/p}{dV/V}$$

For an ideal gas γ is constant. Hence on integrating the above equation, assuming a perfect gas, we get

$pV^{\gamma} = \text{constant}$ i.e.

$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

Using the equation of state for an ideal gas, $pV = nRT$,

$$TV^{\gamma-1} = \text{constant}$$
$$\frac{p^{\gamma-1}}{T^{\gamma}} = \text{constant}$$

also, for constant $C_p = C_v + R$ (per mole),

$\frac{V}{T} = \frac{nR}{p}$ and $p = \frac{nRT}{V}$

$$S_2 - S_1 = nC_p \ln\left(\frac{T_2}{T_1}\right) - nR \ln\left(\frac{p_2}{p_1}\right)$$
$$\frac{S_2 - S_1}{n} = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{T_2V_1}{T_1V_2}\right) = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right)$$

Thus for isentropic processes with an ideal gas,

$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{(R/C_v)}$ or $V_2 = V_1 \left(\frac{T_1}{T_2}\right)^{(C_v/R)}$

Table of isentropic relations for an ideal gas

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}} = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}} = \left(\frac{\rho_2}{\rho_1}\right)^{(\gamma-1)} = \left(\frac{V_1}{V_2}\right)^{(\gamma-1)}$$

$$\frac{\rho_2}{\rho_1} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}} = \left(\frac{p_2}{p_1}\right)^{\frac{1}{\gamma}} = \frac{V_1}{V_2}$$

$$\frac{V_2}{V_1} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} = \frac{\rho_1}{\rho_2} = \left(\frac{p_1}{p_2}\right)^{\frac{1}{\gamma}}$$

Derived from:

$$pV^{\gamma} = \text{constant}$$
$$pV = mR_sT$$
$$p = \rho R_sT$$

Where:
p= Pressure
V= Volume
γ= Ratio of specific heats = C_p/C_v
T= Temperature
m= Mass
R_s= Gas constant for the specific gas = R/M
R= Universal gas constant
M= Molecular weight of the specific gas
ρ= Density
C_p= Specific heat at constant pressure
C_v= Specific heat at constant volume

Thermodynamic potentials

Isenthalpic process

An **isenthalpic process** or **isoenthalpic process** is a process that proceeds without any change in enthalpy, *H*; or specific enthalpy, *h*.

In a steady-state, steady-flow process, significant changes in pressure and temperature can occur to the fluid and yet the process will be isenthalpic if there is no transfer of heat to or from the surroundings, no work done on or by the surroundings, and no change in the kinetic energy of the fluid. (If a steady-state, steady-flow process is analysed using a control volume everything outside the control volume is considered to be the **surroundings.**)

The throttling process is a good example of an isenthalpic process. Consider the lifting of a relief valve or safety valve on a pressure vessel. The specific enthalpy of the fluid inside the pressure vessel is the same as the specific enthalpy of the fluid as it escapes from the valve. With a knowledge of the specific enthalpy of the fluid, and the pressure outside the pressure vessel, it is possible to determine the temperature and speed of the escaping fluid.

In an isenthalpic process:

- $h_1 = h_2$
- $dh = 0$

Isenthalpic processes on an ideal gas follow isotherms since $dh = 0 = c_p dT$.

Chemical potential - particle number

The processes above have all implicitly assumed that the boundaries are also impermeable to particles. We may assume boundaries that are both rigid and thermally insulating, but are permeable to one or more types of particle. Similar considerations then hold for the chemical potential-particle number conjugate pair, which is concerned with the transfer of energy via this transfer of particles.

- In a constant chemical potential process the system is *particle-transfer connected*, by a particle-permeable boundary, to a constant-μ reservoir.
- In a constant particle number process there is no energy added or subtracted from the system by particle transfer. We may say that the system is *particle-transfer-insulated* from its environment by a boundary that is impermeable to particles.

Polytropic processes

A **polytropic process** is a thermodynamic process that obeys the relation:

$$pV^n = C$$

where p is the pressure, V is volume, n, the **polytropic index**, is any real number, and C is a constant. This equation can be used to accurately characterize processes of certain systems, notably the compression or expansion of a gas and in some cases liquids and solids.

Applicability

The equation is a valid characterization of a thermodynamic process assuming that the process is quasistatic and the values of the heat capacities, C_p and C_V, are almost constant when n is not zero or infinity. (In reality, C_p and C_V are actually functions of temperature, but are nearly constant within small changes of temperature).

Under standard conditions, most gases can be accurately characterized by the ideal gas law. This construct allows for the pressure-volume relationship to be defined for essentially all ideal thermodynamic cycles, such as the well-known Carnot cycle. Note however that there may also be instances where a polytropic process occurs in a non-ideal gas.

Relationship to ideal processes

For certain values of the polytropic index, the process will be synonymous with other common processes. Some examples of the effects of varying index values are given in the table.

Variation of polytropic index n

Polytropic index	**Relation**	**Effects**
$n < 0$	—	An explosion occurs
$n = 0$	$pV^0 = p$ (constant)	Equivalent to an isobaric process (constant pressure)
$n = 1$	$pV = NkT$ (constant)	Equivalent to an isothermal process (constant temperature)
$1 < n < \gamma$	—	A quasi-adiabatic process such as in an internal combustion engine during expansion, or in vapor compression refrigeration during compression
$n = \gamma$	—	$\gamma = \frac{C_p}{C_V}$ is the adiabatic index, yielding an adiabatic process (no heat transferred)
$n = \infty$	—	Equivalent to an isochoric process (constant volume)

When the index n is between any two of the former values (0, 1, gamma, or infinity), it means that the polytropic curve will bounded by the curves of the two corresponding indices.

Note that 1 < γ < 2, since $\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} = \frac{C_p}{C_p - R}$.

Notation

In the case of an isentropic ideal gas, γ is the ratio of specific heats, known as the adiabatic index or as adiabatic exponent.

An isothermal ideal gas is also a polytropic gas. Here, the polytropic index is equal to one, and differs from the adiabatic index γ.

In order to discriminate between the two gammas, the polytropic gamma is sometimes capitalized, Γ.

To confuse matters further, some authors refer to Γ as the polytropic index, rather than *n*. Note that

$$n = \frac{1}{\Gamma - 1}.$$

Other

A solution to the Lane-Emden equation using a polytropic fluid is known as a polytrope.

Quasistatic process

In thermodynamics, a **quasistatic process** is a thermodynamic process that happens infinitely slowly. However, it is very important of note that *no* real process is quasistatic. Therefore in practice, such processes can only be approximated by performing them *infinitesimally* slowly.

A quasistatic process often ensures that the system will go through a sequence of states that are infinitesimally close to equilibrium (so the system remains in quasistatic equilibrium), in which case the process is typically reversible. An example of a quasistatic process that is not reversible is the slow heat exchange between two bodies at two finitely different temperatures, where the heat exchange rate is controlled by an approximately adiabatic partition between the two bodies (Sears and Salinger, 1986) — in this case, no matter how slowly the process takes place, the states of the two bodies are never infinitesimally close to equilibrium, since thermal equilibrium requires that the two bodies be at precisely the same temperature.

Some ambiguity exists in the literature concerning the distinction between quasistatic and reversible processes, as these are sometimes taken as synonyms (Lavenda, 1978). The above definition is closer to the intuitive understanding of the word "quasi-" (almost) "static", while remaining technically different from reversible processes.

Chapter- 6

Thermal Conductivity

In physics, **thermal conductivity**, *k*, is the property of a material that indicates its ability to conduct heat. It appears primarily in Fourier's Law for heat conduction. Thermal conductivity is measured in watts per kelvin per metre ($W \cdot K^{-1} \cdot m^{-1}$). Multiplied by a temperature difference (in kelvins, K) and an area (in square metres, m^2), and divided by a thickness (in metres, m) the thermal conductivity predicts the rate of energy loss (in watts, W) through a piece of material.

The reciprocal of thermal conductivity is *thermal resistivity*.

Measurement

There are a number of possible ways to **measure thermal conductivity**, each of them suitable for a limited range of materials, depending on the thermal properties and the medium temperature. Two classes of methods exist to measure the thermal conductivity of a sample: steady-state and non-steady-state methods.

Steady-state methods

In general, steady-state techniques perform a measurement when the temperature of the material measured does not change with time. This makes the signal analysis straightforward (steady state implies constant signals). The disadvantage is that a well-engineered experimental setup is usually needed.

In geology and geophysics, the most common method for consolidated rock samples is the divided bar. There are various modifications to these devices depending on the temperatures and pressures needed as well as sample sizes. A sample of unknown conductivity is placed between two samples of known conductivity (usually brass plates). The setup is usually vertical with the hot brass plate at the top, the sample in between then the cold brass plate at the bottom. Heat is supplied at the top and made to move downwards to stop any convection within the sample. Measurements are taken after the sample has attained equilibrium (same heat over entire sample), this usually takes about 10 minutes.

Transient methods

The transient techniques perform a measurement during the process of heating up. The advantage is that measurements can be made relatively quickly. Transient methods are usually carried out by needle probes.

Non-steady-state methods to measure the thermal conductivity do not require the signal to obtain a constant value. Instead, the signal is studied as a function of time. The advantage of these methods are that they can in general be performed more quickly, since there is no need to wait for a steady-state situation. The disadvantage is that the mathematical analysis of the data is in general more difficult.

Transient plane source method

Example of probe used for transient plane source measurements. Photo shows a Hotdisk sensor

Transient Plane Source Method is also called the Hot disk method. A plane sensor, a special mathematical model describing the heat conductivity, combined with precise electronics, enables the method to be used to measure Thermal Transport Properties. It covers a thermal conductivity range of 4–5 orders of magnitude and can be used for measuring various kinds of materials, such as solids, powder, liquid, paste and thin films etc. In 2008 it was approved as an ISO-standard for measuring thermal transport properties of polymers (November 2008).

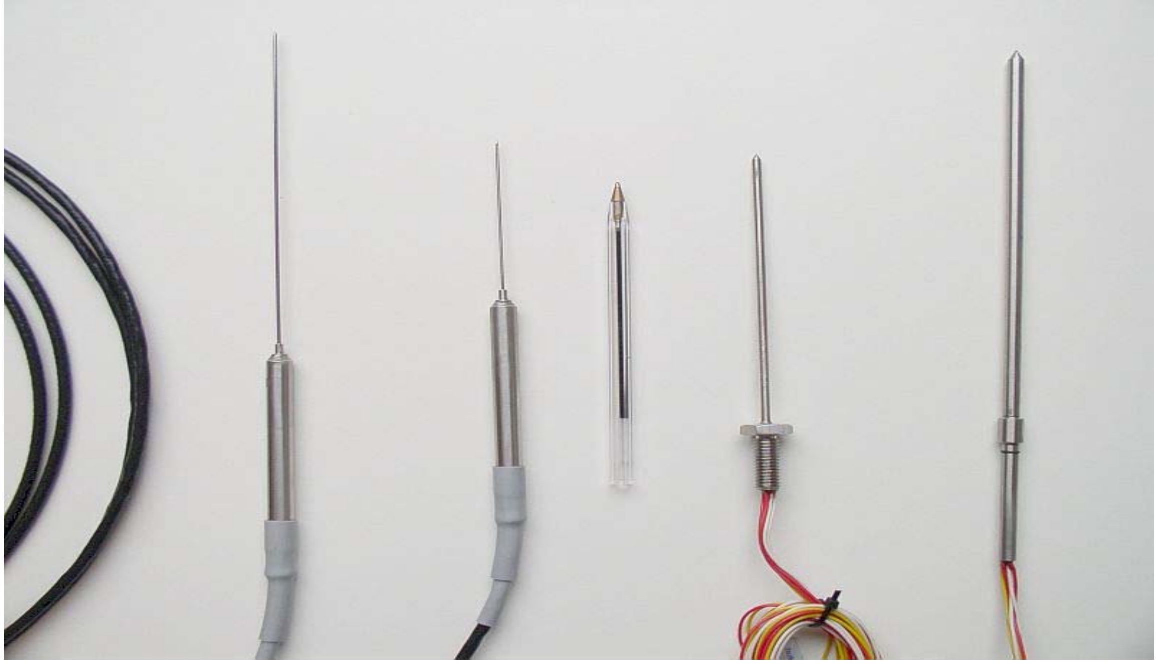
The method was developed by Dr Silas Gustavsson at Chalmers University of technology, Sweden, and is sometimes referred to as”the Gustavsson Probe”.

The probe is a flat sensor with a continuous double spiral of electrically conducting nickel (Ni) metal etched out of thin foil and clad between two layers of Kapton. The thin Kapton provides electrical insulation and mechanical stability to the sensor. The sensor is placed between the surfaces of two sample pieces of the sample to be measured. During the measurement a current passes through the nickel and creates an increase in temperature. The heat generated dissipates through the sample on either side of the sensor at a rate depending on the thermal transport characteristics of the material. By recording temperature vs. time response in the sensor, the characteristics of the material can be calculated.

Modified transient plane source (MTPS) method

A variation of the above method is the Modified Transient Plane Source Method (MTPS) developed by Nancy Mathis of the University of New Brunswick and commercialized through her company Mathis Instruments Ltd (now C-Therm Technologies Ltd.). The device uses a one-sided, interfacial, heat reflectance sensor that applies a momentary, constant heat source to the sample. The difference between this method and traditional transient plane source technique described above is that the heating element is supported on a backing, which provides mechanical support, electrical insulation and thermal insulation. This modification provides a one-sided interfacial measurement in offering maximum flexibility in testing liquids, powders, pastes and solids.

Transient line source method



Series of needle probes used for transient line source measurements. Photo shows, from left to right, models TP02, TP08, a ballpoint for purposes of size comparison, TP03 and TP09

The physical model behind this method is the infinite line source with constant power per unit length. The temperature profile *T*(*t*,*r*) at a distance *r* at time *t* is as follows

$$T(t,r) = \frac{Q}{4\pi k}\mathrm{Ei}\left(\frac{r^2}{4at}\right)$$

where

Q is the power per unit length, in [W·m^{-1}]
k is the thermal conductivity of the sample, in [W·m^{-1}·K^{-1}]
Ei(x) is the exponential integral, a transcendent mathematical function
r is the radial distance to the line source
a is the thermal diffusivity, in [m^2·s^{-1}]
t is the amount of time that has passed since heating has started, in [s]

When performing an experiment, one measures the temperature at a point at fixed distance, and follows that temperature in time. For large times, the exponential integral can be approximated by making use of the following relation

$$\mathrm{Ei}(x) = -\gamma - \ln(x) + O(x)$$

where

$\gamma \approx 0.577$ is the Euler gamma constant

This leads to the following expression

$$T(t,r) = \frac{Q}{4\pi k}\left\{-\gamma - \ln\left(\frac{r^2}{4at}\right) + \ln(t)\right\}$$

Note that the first term in the brackets on the RHS is a constant, while the second term goes as the inverse of time and therefore drops out fairly quickly. Thus if the probe temperature is plotted versus the natural logarithm of time, the thermal conductivity can be determined from the slope given knowledge of Q, if the initial data, before the diffusivity term becomes negligible, are ignored. Typically this means ignorming the first 60 to 120 seconds of data and measuring for 600 to 1200 seconds.

Other methods

For good conductors of heat, Searle's bar method can be used. For poor conductors of heat, Lees' disc method can be used.

Thermoreflectance

Thermoreflectance is a method by which the thermal properties of a material can be measured, most importantly thermal conductivity. This method can be applied most notably to thin film materials (up to hundreds of nanometers thick), which have properties that vary greatly when compared to the same materials in bulk. The idea behind this technique is that once a material is heated up, the change in the reflectance of the surface can be utilized to derive the thermal properties. The reflectivity is measured with respect to time, and the data received can be matched to a model which contain coefficients that correspond to thermal properties.

Measuring devices

A thermal conductance tester, one of the instruments of gemology, determines if gems are genuine diamonds using diamond's uniquely high thermal conductivity.

Standards

- IEEE Standard 442-1981, "IEEE guide for soil thermal resistivity measurements", ISBN 0-7381-0794-8.
- IEEE Standard 98-2002, "Standard for the Preparation of Test Procedures for the Thermal Evaluation of Solid Electrical Insulating Materials", ISBN 0-7381-3277-2
- ASTM Standard D5334-08, "Standard Test Method for Determination of Thermal Conductivity of Soil and Soft Rock by Thermal Needle Probe Procedure"
- ASTM Standard D5470-06, "Standard Test Method for Thermal Transmission Properties of Thermally Conductive Electrical Insulation Materials"
- ASTM Standard E1225-04, "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique"
- ASTM Standard D5930-01, "Standard Test Method for Thermal Conductivity of Plastics by Means of a Transient Line-Source Technique"
- ASTM Standard D2717-95, "Standard Test Method for Thermal Conductivity of Liquids"
- ISO 22007-2:2008 "Plastics -- Determination of thermal conductivity and thermal diffusivity -- Part 2: Transient plane heat source (hot disc) method"
- Note: What is called the k-value of construction materials (e.g. window glass) in the U.S., is called λ-value in Europe. What is called U-value (= the inverse of R-value) in the U.S., used to be called k-value in Europe, but is now also called U-value in Europe.

Definitions

The reciprocal of thermal conductivity is *thermal resistivity*, usually measured in kelvin-metres per watt ($K \cdot m \cdot W^{-1}$). When dealing with a known amount of material, its *thermal* *conductance* and the reciprocal property, *thermal resistance*, can be described. Unfortunately, there are differing definitions for these terms.

Conductance

For general scientific use, *thermal conductance* is the quantity of heat that passes in unit time through a plate of *particular area and thickness* when its opposite faces differ in temperature by one kelvin. For a plate of thermal conductivity k, area A and thickness L this is kA/L, measured in $W \cdot K^{-1}$ (equivalent to: W/°C). Thermal conductivity and conductance are analogous to electrical conductivity ($A \cdot m^{-1} \cdot V^{-1}$) and electrical conductance ($A \cdot V^{-1}$).

There is also a measure known as heat transfer coefficient: the quantity of heat that passes in unit time through *unit area* of a plate of particular thickness when its opposite faces differ in temperature by one kelvin. The reciprocal is *thermal insulance*. In summary:

- *thermal conductance* = kA/L, measured in $W \cdot K^{-1}$
    - *thermal resistance* = $L/(kA)$, measured in $K \cdot W^{-1}$ (equivalent to: °C/W)
- *heat transfer coefficient* = k/L, measured in $W \cdot K^{-1} \cdot m^{-2}$
    - *thermal insulance* = L/k, measured in $K \cdot m^2 \cdot W^{-1}$.

The heat transfer coefficient is also known as *thermal admittance*

Resistance

When thermal resistances occur in series, they are additive. So when heat flows through two components each with a resistance of 1 °C/W, the total resistance is 2 °C/W.

A common engineering design problem involves the selection of an appropriate sized heat sink for a given heat source. Working in units of thermal resistance greatly simplifies the design calculation. The following formula can be used to estimate the performance:

$$R_{hs} = \frac{\Delta T}{P_{th}} - R_s$$

where:

- R_{hs} is the maximum thermal resistance of the heat sink to ambient, in °C/W
- ΔT is the temperature difference (temperature drop), in °C
- P_{th} is the thermal power (heat flow), in watts
- R_s is the thermal resistance of the heat source, in °C/W

For example, if a component produces 100 W of heat, and has a thermal resistance of 0.5 °C/W, what is the maximum thermal resistance of the heat sink? Suppose the maximum temperature is 125 °C, and the ambient temperature is 25 °C; then the ΔT is 100 °C. The heat sink's thermal resistance to ambient must then be 0.5 °C/W or less.

Transmittance

A third term, *thermal transmittance*, incorporates the thermal conductance of a structure along with heat transfer due to convection and radiation. It is measured in the same units as thermal conductance and is sometimes known as the *composite thermal conductance*. The term *U-value* is another synonym.

Summary

In summary, for a plate of thermal conductivity k (the *k value*), area A and thickness t:

- *thermal conductance* = k/t, measured in $W \cdot K^{-1} \cdot m^{-2}$;
- *thermal resistance* (*R-value*) = t/k, measured in $K \cdot m^2 \cdot W^{-1}$;
- *thermal transmittance* (*U-value*) = $1/(\Sigma(t/k))$ + convection + radiation, measured in $W \cdot K^{-1} \cdot m^{-2}$.
- *K-value* refers in Europe to the total insulation value of a building. K-value is obtained by multiplying the form factor of the building (= the total inward surface of the outward walls of the building divided by the total volume of the building) with the average U-value of the outward walls of the building. K value is therefore expressed as $(m^2 \cdot m^{-3}) \cdot (W \cdot K^{-1} \cdot m^{-2}) = W \cdot K^{-1} \cdot m^{-3}$. A house with a volume of 400 m^3 and a K-value of 0.45 (the new European norm. It is commonly referred to as K45) will therefore theoretically require 180 W to maintain its interior temperature 1 K above exterior temperature. So, to maintain the house at 20 °C when it is freezing outside (0 °C), 3600 W of continuous heating is required.

Examples

In metals, thermal conductivity approximately tracks electrical conductivity according to the Wiedemann-Franz law, as freely moving valence electrons transfer not only electric current but also heat energy. However, the general correlation between electrical and thermal conductance does not hold for other materials, due to the increased importance of phonon carriers for heat in non-metals. As shown in the table below, highly electrically conductive silver is less thermally conductive than diamond, which is an electrical insulator.

Thermal conductivity depends on many properties of a material, notably its structure and temperature. For instance, pure crystalline substances exhibit very different thermal conductivities along different crystal axes, due to differences in phonon coupling along a given crystal axis. Sapphire is a notable example of variable thermal conductivity based on orientation and temperature, with 35 W/(m·K) along the c-axis and 32 W/(m·K) along the a-axis.

Air and other gases are generally good insulators, in the absence of convection. Therefore, many insulating materials function simply by having a large number of gas-filled pockets which prevent large-scale convection. Examples of these include expanded and extruded polystyrene (popularly referred to as "styrofoam") and silica aerogel. Natural, biological insulators such as fur and feathers achieve similar effects by dramatically inhibiting convection of air or water near an animal's skin.

Ceramic is used for its low thermal conductivity on exhaust systems to prevent heat from reaching sensitive components

Light gases, such as hydrogen and helium typically have high thermal conductivity. Dense gases such as xenon and dichlorodifluoromethane have low thermal conductivity. An exception, sulfur hexafluoride, a dense gas, has a relatively high thermal conductivity due to its high heat capacity. Argon, a gas denser than air, is often used in insulated glazing (double paned windows) to improve their insulation characteristics.

Thermal conductivity is important in building insulation and related fields. However, materials used in such trades are rarely subjected to chemical purity standards. Several construction materials' *k* values are listed below. These should be considered approximate due to the uncertainties related to material definitions.

The following table is meant as a small sample of data to illustrate the thermal conductivity of various types of substances.

Experimental values

This is a list of approximate values of thermal conductivity, *k*, for some common materials. Please consult the list of thermal conductivities for more accurate values, references and detailed information.

Material	Thermal conductivity W/(m·K)
Silica Aerogel	0.004 - 0.04
Air	0.025
Wood	0.04 - 0.4
Hollow Fill Fibre Insulation Polartherm	0.042
Alcohols and oils	0.1 - 0.21
Polypropylene	0.25
Mineral oil	0.138
Rubber	0.16
LPG	0.23 - 0.26
Cement, Portland	0.29
Epoxy (silica-filled)	0.30
Epoxy (unfilled)	0.59
Water (liquid)	0.6
Thermal grease	0.7 - 3
Thermal epoxy	1 - 7
Glass	1.1
Soil	1.5
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminium	237 (pure) 120—180 (alloys)
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)

Physical origins

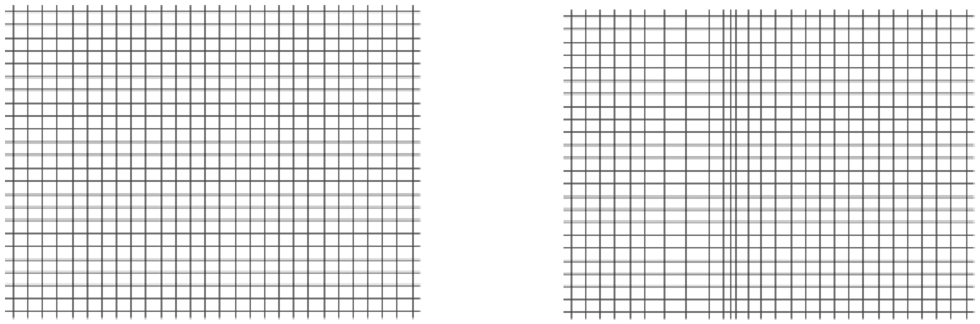
Heat flux is exceedingly difficult to control and isolate in a laboratory setting. Thus at the atomic level, there are no simple, correct expressions for thermal conductivity. Atomically, the thermal conductivity of a system is determined by how atoms composing the system interact. There are two different approaches for calculating the thermal conductivity of a system.

- The first approach employs the Green-Kubo relations. Although this employs analytic expressions which in principle can be solved, in order to calculate the thermal conductivity of a dense fluid or solid using this relation requires the use of molecular dynamics computer simulation.

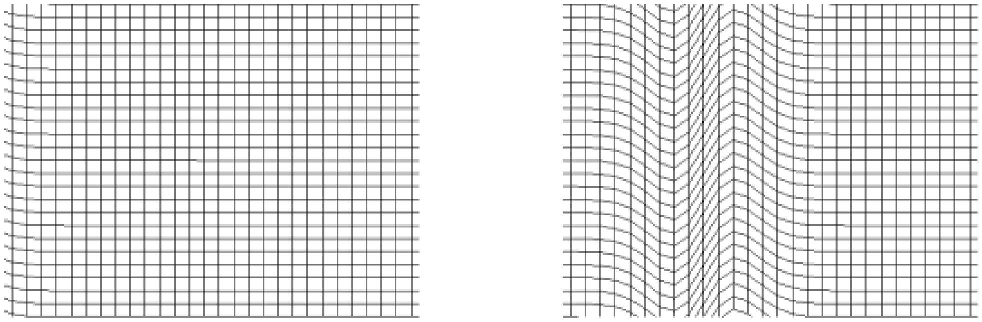
- The second approach is based upon the relaxation time approach. Due to the anharmonicity within the crystal potential, the phonons in the system are known to scatter. There are three main mechanisms for scattering:
    - Boundary scattering, a phonon hitting the boundary of a system;
    - Mass defect scattering, a phonon hitting an impurity within the system and scattering;
    - Phonon-phonon scattering, a phonon breaking into two lower energy phonons or a phonon colliding with another phonon and merging into one higher energy phonon.

Lattice waves

A kinetic theory of solids follows naturally from the standpoint of the normal modes of vibration in an elastic crystalline solid – from the longest wavelength (or fundamental frequency of the body) to the highest Debye frequency (that of a single particle). There are simple equations derived to describe the relationship of these normal modes to the mechanisms of thermal phonon wave propagation as represented by the superposition of elastic waves—both longitudinal (acoustic) and transverse (optical) waves of atomic displacement.



Longitudinal compression (or acoustic or pressure) wave oscillating within the dimensions of a 2-dimensional lattice.



Transverse (shear) wave in a 2-dimensional lattice, oscillating in the 3rd spatial dimension.

The velocities of longitudinal acoustic phonons in condensed matter are directly responsible for the **thermal conductivity** which levels out temperature differentials between compressed and expanded volume elements. For example, the thermal properties of glass are interpreted in terms of an approximately constant mean free path for lattice phonons. Furthermore, the value of the mean free path is of the order of magnitude of the scale of structural (dis)order at the atomic or molecular level.

Thus, heat transport in both glassy and crystalline dielectric solids occurs through elastic vibrations of the lattice. This transport is limited by elastic scattering of acoustic phonons by lattice defects. These predictions were confirmed by the experiments of Chang and Jones on commercial glasses and glass ceramics, where mean free paths were limited by "internal boundary scattering" to length scales of 10^{-2} cm to 10^{-3} cm.

The phonon mean free path has been associated directly with the effective relaxation length for processes without directional correlation. Thus, if V_g is the group velocity of a phonon wave packet, then the relaxation length l is defined as:

$$l = V_g t$$

where t is the characteristic relaxation time. Now, since longitudinal waves have a much greater group or "phase velocity" than that of transverse waves, V_{long} is much greater than V_{trans}, the relaxation length or mean free path of longitudinal phonons will be much greater. Thus, thermal conductivity will be largely determined by the speed of longitudinal phonons.

Regarding the dependence of wave velocity on wavelength or frequency (aka "dispersion"), low-frequency phonons of long wavelength will be limited in relaxation length by elastic Rayleigh scattering. This type of light scattering form small particles is proportional to the fourth power of the frequency. For higher frequencies, the power of the frequency will decrease until at highest frequencies scattering is almost frequency independent. Similar arguments were subsequently generalized to many glass forming substances using Brillouin scattering.

Controlling resistance

Often in heat transfer the concept of controlling resistance is used to determine how to either increase or decrease heat transfer. Heat transfer coefficients represent how much heat is able to transfer through a defined region of a heat transfer area. The inverse of these coefficients are the resistances of those areas. If a wall can be considered, it would have a heat transfer coefficient representing convection on each side of the wall, and one representing conduction through the wall. To obtain an overall heat transfer coefficient, the resistances need to be summed up.

$$\frac{1}{U}=\sum_i\frac{1}{h_i}+\sum_i R_i=\frac{1}{h_1}+\frac{1}{h_2}+\frac{1}{h_3}+\cdots+R_1+R_2+R_3+\cdots$$

Due to the nature of the above reciprocal relation, the smallest heat transfer coefficient (h) or the largest resistance is generally the controlling resistance as it dominates the other terms to the point that varying the other resistances will have little impact on the overall resistance:

$$\frac{1}{U}\approx\frac{1}{h_i}\text{ or } R_i$$

Thus the controlling resistance can be used to both simplify heat transfer calculations and manipulate a system to a desired resistance value.

- Note: In the textile industry, a tog value may be quoted as a measure of thermal resistance in place of a measure in SI units.

Equations

First, we define heat conduction, H:

$$H=\frac{\Delta Q}{\Delta t}=kA\frac{\Delta T}{x}$$

where $\frac{\Delta Q}{\Delta t}$ is the rate of heat flow, k is the thermal conductivity, A is the total cross sectional area of conducting surface, ΔT is temperature difference, and x is the thickness of conducting surface separating the 2 temperatures. Dimension of thermal conductivity = $M^1L^1T^{-3}K^{-1}$

Rearranging the equation gives thermal conductivity:

$$k = \frac{\Delta Q}{\Delta t}\frac{1}{A}\frac{x}{\Delta T}$$

(Note: $\Delta T / x$ is the temperature gradient)

I.E. It is defined as the quantity of heat, ΔQ, transmitted during time Δt through a thickness x, in a direction normal to a surface of area A, per unit area of A, due to a temperature difference ΔT, under steady state conditions and when the heat transfer is dependent only on the temperature gradient.

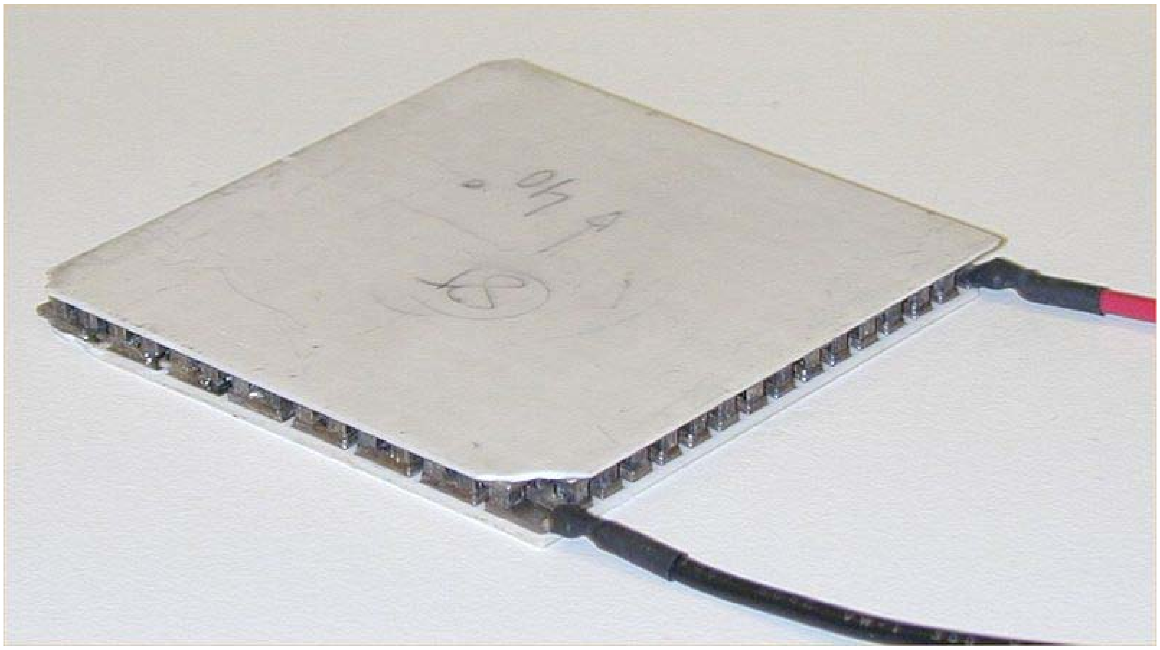
Alternatively, it can be thought of as a flux of heat (energy per unit area per unit time) divided by a temperature gradient (temperature difference per unit length)

$$k = \frac{\Delta Q}{A\Delta t}\frac{x}{\Delta T}$$

Typical units are SI: W/(m·K) and English units: Btu/(h·ft·°F). To convert between the two, use the relation 1 Btu/(h·ft·°F) = 1.730735 W/(m·K). [Perry's Chemical Engineers' Handbook, 7th Edition, Table 1-4]

Chapter- 7

Thermoelectric Effect



Thermoelectric effect

The **thermoelectric effect** is the direct conversion of temperature differences to electric voltage and vice versa. A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely when a voltage is applied to it, it creates a temperature difference (known as the Peltier effect). At atomic scale (specifically, charge carriers), an applied temperature gradient causes charged carriers in the material, whether they are electrons or electron holes, to diffuse from the hot side to the cold side, similar to a classical gas that expands when heated; hence, the thermally induced current.

This effect can be used to generate electricity, to measure temperature, to cool objects, or to heat them or cook them. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices make very convenient temperature controllers.

Traditionally, the term *thermoelectric effect* or *thermoelectricity* encompasses three separately identified effects, the **Seebeck effect**, the **Peltier effect**, and the **Thomson**

effect. In many textbooks, thermoelectric effect may also be called the **Peltier–Seebeck effect**. This separation derives from the independent discoveries of French physicist Jean Charles Athanase Peltier and Estonian-German physicist Thomas Johann Seebeck. Joule heating, the heat that is generated whenever a voltage is applied across a resistive material, is somewhat related, though it is not generally termed a thermoelectric effect (and it is usually regarded as being a loss mechanism due to non-ideality in thermoelectric devices). The Peltier–Seebeck and Thomson effects can in principle be thermodynamically reversible, whereas Joule heating is not.

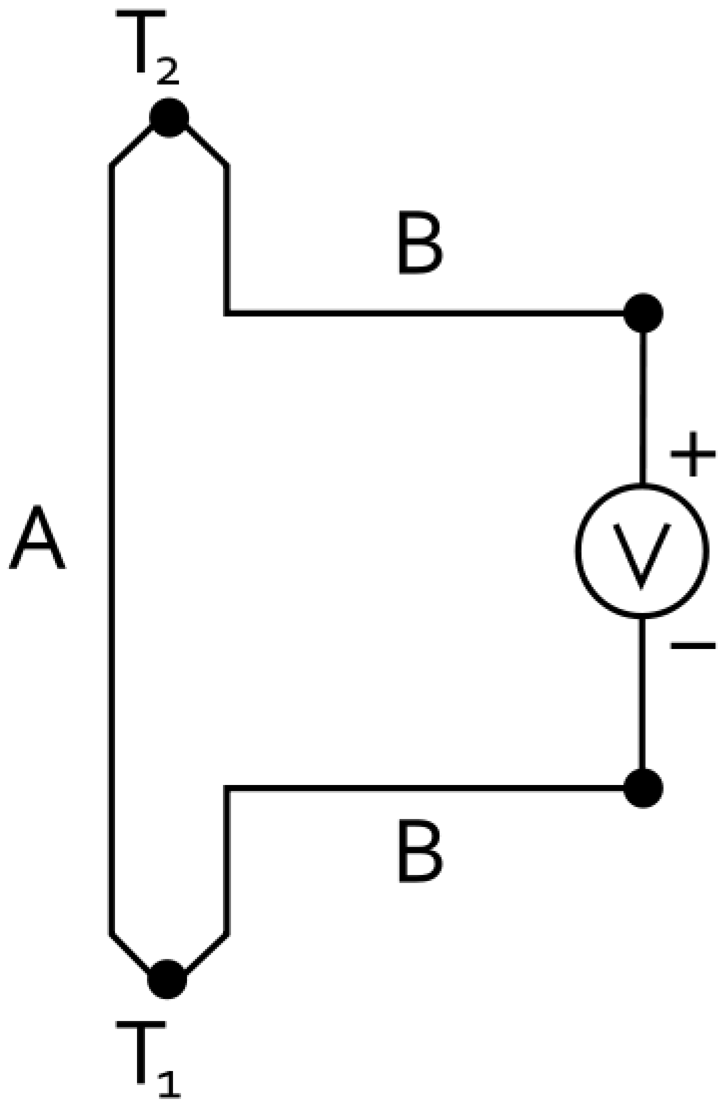
Seebeck effect

The **Seebeck effect** is the conversion of temperature differences directly into electricity.

Seebeck discovered that a compass needle would be deflected when a closed loop was formed of two metals joined in two places with a temperature difference between the junctions. This is because the metals respond differently to the temperature difference, which creates a current loop, which produces a magnetic field. Seebeck, however, at this time did not recognize there was an electric current involved, so he called the phenomenon the thermomagnetic effect, thinking that the two metals became magnetically polarized by the temperature gradient. The Danish physicist Hans Christian Ørsted played a vital role in explaining and conceiving the term "thermoelectricity".

The effect is that a voltage, the thermoelectric EMF, is created in the presence of a temperature difference between two different metals or semiconductors. This causes a continuous current in the conductors if they form a complete loop. The voltage created is of the order of several microvolts per kelvin difference. One such combination, copper-constantan, has a Seebeck coefficient of 41 microvolts per kelvin at room temperature.

In the circuit:



(which can be in several different configurations and be governed by the same equations), the voltage developed can be derived from:

$$V = \int_{T_1}^{T_2} \left(S_{\mathrm{B}}(T) - S_{\mathrm{A}}(T) \right) dT.$$

S_{A} and S_{B} are the Seebeck coefficients (also called *thermoelectric power* or *thermopower*) of the metals A and B as a function of temperature, and T_1 and T_2 are the temperatures of the two junctions. The Seebeck coefficients are non-linear as a function of temperature, and depend on the conductors' absolute temperature, material, and molecular structure. If the Seebeck coefficients are effectively constant for the measured temperature range, the above formula can be approximated as:

$$V = (S_{\mathrm{B}} - S_{\mathrm{A}}) \cdot (T_2 - T_1).$$

The Seebeck effect is commonly used in a device called a thermocouple (because it is made from a coupling or junction of materials, usually metals) to measure a temperature difference directly or to measure an absolute temperature by setting one end to a known temperature. A metal of unknown composition can be classified by its thermoelectric effect if a metallic probe of known composition, kept at a constant temperature, is held in contact with it. Industrial quality control instruments use this Seebeck effect to identify metal alloys. This is known as thermoelectric alloy sorting.

Several thermocouples connected in series are called a thermopile, which is sometimes constructed in order to increase the output voltage since the voltage induced over each individual couple is small.

This is also the principle at work behind thermal diodes and thermoelectric generators (such as radioisotope thermoelectric generators or RTGs) which are used for creating power from heat differentials.

The Seebeck effect is due to two effects: *charge carrier diffusion* and *phonon drag* (described below). If both connections are held at the same temperature, but one connection is periodically opened and closed, an AC voltage is measured, which is also temperature dependent. This application of the Kelvin probe is sometimes used to argue that the underlying physics only needs one junction. And this effect is still visible if the wires only come close, but do not touch, thus no diffusion is needed.

Thermopower

The thermopower, thermoelectric power, or Seebeck coefficient of a material measures the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. The thermopower has units of (V/K), though in practice it is more common to use microvolts per kelvin. Values in the hundreds of μV/K, negative or positive, are typical of good thermoelectric materials. The term thermopower is a misnomer since it measures the voltage or electric field induced in response to a temperature difference, not the electric power. An applied temperature difference causes charged carriers in the material, whether they are electrons or holes, to diffuse from the hot side to the cold side, similar to a classical gas that expands when heated. Mobile charged carriers migrating to the cold side leave behind their oppositely charged and immobile nuclei at the hot side thus giving rise to a thermoelectric voltage (thermoelectric refers to the fact that the voltage is created by a temperature difference). Since a separation of charges also creates an electric potential, the buildup of charged carriers onto the cold side eventually ceases at some maximum value since there exists an equal amount of charged carriers drifting back to the hot side as a result of the electric field at equilibrium. Only an increase in the temperature difference can resume a buildup of more charge carriers on the cold side and thus lead to an increase in the thermoelectric voltage. Incidentally the thermopower also measures the entropy per charge carrier in the material. To be more specific, the partial molar electronic entropy is said to equal the absolute thermoelectric power multiplied by the negative of Faraday's constant.

The thermopower of a material, represented by *S* (or sometimes by α), depends on the material's temperature and crystal structure. Typically metals have small thermopowers because most have half-filled bands. Electrons (negative charges) and holes (positive charges) both contribute to the induced thermoelectric voltage thus canceling each other's contribution to that voltage and making it small. In contrast, semiconductors can be doped with excess electrons or holes, and thus can have large positive or negative values of the thermopower depending on the charge of the excess carriers. The sign of the thermopower can determine which charged carriers dominate the electric transport in both metals and semiconductors.

If the temperature difference ΔT between the two ends of a material is small, then the thermopower of a material is defined (approximately) as:

$$S = \frac{\Delta V}{\Delta T}$$

and a thermoelectric voltage ΔV is seen at the terminals.

This can also be written in relation to the electric field *E* and the temperature gradient ∇T, by the approximate equation:

$$S = \frac{E}{\nabla T}.$$

In practice one rarely measures the absolute thermopower of the material of interest. This is because electrodes attached to a voltmeter must be placed onto the material in order to measure the thermoelectric voltage. The temperature gradient then also typically induces a thermoelectric voltage across one leg of the measurement electrodes. Therefore the measured thermopower includes a contribution from the thermopower of the material of interest and the material of the measurement electrodes.

The measured thermopower is then a contribution from both and can be written as:

$$S_{AB} = S_B - S_A = \frac{\Delta V_B}{\Delta T} - \frac{\Delta V_A}{\Delta T}.$$

Superconductors have zero thermopower since the charged carriers produce no entropy. This allows a direct measurement of the absolute thermopower of the material of interest, since it is the thermopower of the entire thermocouple as well. In addition, a measurement of the Thomson coefficient, μ, of a material can also yield the thermopower through the relation: $S = \int \frac{\mu}{T} dT.$

The thermopower is an important material parameter that determines the efficiency of a thermoelectric material. A larger induced thermoelectric voltage for a given temperature gradient will lead to a larger efficiency. Ideally one would want very large thermopower values since only a small amount of heat is then necessary to create a large voltage. This voltage can then be used to provide power.

Charge-carrier diffusion

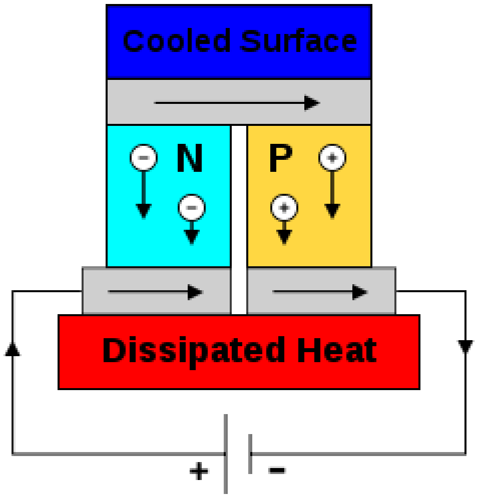
Charge carriers in the materials (electrons in metals, electrons and holes in semiconductors, ions in ionic conductors) will diffuse when one end of a conductor is at a different temperature to the other. Hot carriers diffuse from the hot end to the cold end, since there is a lower density of hot carriers at the cold end of the conductor. Cold carriers diffuse from the cold end to the hot end for the same reason.

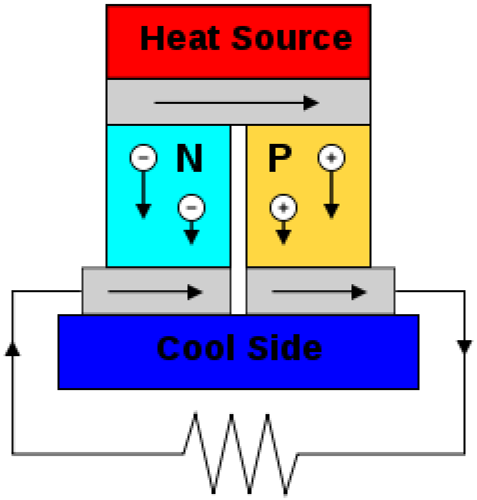
If the conductor were left to reach thermodynamic equilibrium, this process would result in heat being distributed evenly throughout the conductor. The movement of heat (in the form of hot charge carriers) from one end to the other is called a heat current. As charge carriers are moving, it is also an electric current.

In a system where both ends are kept at a constant temperature difference (a constant heat current from one end to the other), there is a constant diffusion of carriers. If the rate of diffusion of hot and cold carriers in opposite directions were equal, there would be no net change in charge. However, the diffusing charges are scattered by impurities, imperfections, and lattice vibrations (phonons). If the scattering is energy dependent, the hot and cold carriers will diffuse at different rates. This creates a higher density of carriers at one end of the material, and the distance between the positive and negative charges produces a potential difference; an electrostatic voltage.

This electric field, however, opposes the uneven scattering of carriers, and an equilibrium is reached where the net number of carriers diffusing in one direction is canceled by the net number of carriers moving in the opposite direction from the electrostatic field. This means the thermopower of a material depends greatly on impurities, imperfections, and structural changes (which often vary themselves with temperature and electric field), and the thermopower of a material is a collection of many different effects.

Early thermocouples were metallic, but many more recently developed thermoelectric devices are made from alternating p-type and n-type semiconductor elements connected by metallic interconnects as pictured in the figures below. Semiconductor junctions are especially common in power generation devices, while metallic junctions are more common in temperature measurement. Charge flows through the n-type element, crosses a metallic interconnect, and passes into the p-type element. If a power source is provided, the thermoelectric device may act as a cooler, as in the figure to the left below. This is the Peltier effect, described below. Electrons in the n-type element will move opposite the direction of current and holes in the p-type element will move in the direction of current, both removing heat from one side of the device. If a heat source is provided, the thermoelectric device may function as a power generator, as in the figure to the right below. The heat source will drive electrons in the n-type element toward the cooler region, thus creating a current through the circuit. Holes in the p-type element will then flow in the direction of the current. The current can then be used to power a load, thus converting the thermal energy into electrical energy.





Phonon drag

Phonons are not always in local thermal equilibrium; they move against the thermal gradient. They lose momentum by interacting with electrons (or other carriers) and imperfections in the crystal. If the phonon-electron interaction is predominant, the phonons will tend to push the electrons to one end of the material, losing momentum in the process. This contributes to the already present thermoelectric field. This contribution is most important in the temperature region where phonon-electron scattering is predominant. This happens for

$$T \approx \frac{1}{5}\theta_{\mathrm{D}}$$

where θ_D is the Debye temperature. At lower temperatures there are fewer phonons available for drag, and at higher temperatures they tend to lose momentum in phonon-phonon scattering instead of phonon-electron scattering.

This region of the thermopower-versus-temperature function is highly variable under a magnetic field.

Spin Seebeck Effect and Magnetic Batteries

Physicists have recently discovered that heating one side of a magnetized nickel-iron rod causes electrons to rearrange themselves according to their spins. This so-called "spin

Seebeck effect" could lead to batteries that generate magnetic currents, rather than electric currents. A source of magnetic currents could be especially useful for the development of spintronics devices, which use magnetic currents in order to reduce overheating in computer chips, since, unlike electric currents, steady magnetic currents do not generate heat.

Peltier effect

The **Peltier effect** bears the name of Jean-Charles Peltier, a French physicist who in 1834 discovered the calorific effect of an electric current at the junction of two different metals. When a current is made to flow through the circuit, heat is evolved at the upper junction (at T_2), and absorbed at the lower junction (at T_1). The Peltier heat absorbed by the lower junction per unit time, $\dot{Q}$is equal to

$$\dot{Q} = \Pi_{\mathrm{AB}} I = \left(\Pi_{\mathrm{B}} - \Pi_{\mathrm{A}}\right) I$$

where π is the **Peltier coefficient** Π_{AB} of the entire thermocouple, and Π_A and Π_B are the coefficients of each material. p-type silicon typically has a positive Peltier coefficient (though not above ~550 K), and n-type silicon is typically negative.

The Peltier coefficients represent how much heat current is carried per unit charge through a given material. Since charge current must be continuous across a junction, the associated heat flow will develop a discontinuity if Π_A and Π_B are different. This causes a non-zero divergence at the junction and so heat must accumulate or deplete there, depending on the sign of the current. Another way to understand how this effect could cool a junction is to note that when electrons flow from a region of high density to a region of low density, this "expansion" causes cooling (as with an ideal gas).

The carriers are attempting to return to the electron equilibrium that existed before the current was applied by absorbing energy at one connector and releasing it at the other. The individual couples can be connected in series to enhance the effect.

An interesting consequence of this effect is that the direction of heat transfer is controlled by the polarity of the current; reversing the polarity will change the direction of transfer and thus the sign of the heat absorbed/evolved.

A **Peltier cooler**/heater or thermoelectric heat pump is a solid-state active heat pump which transfers heat from one side of the device to the other. Peltier cooling is also called *thermo-electric cooling* (TEC).

Thomson effect

The **Thomson effect** was predicted and subsequently experimentally observed by William Thomson (Lord Kelvin) in 1851. It describes the heating or cooling of a current-carrying conductor with a temperature gradient.

Any current-carrying conductor (except for a superconductor), with a temperature difference between two points, will either absorb or emit heat, depending on the material.

If a current density J is passed through a homogeneous conductor, heat production per unit volume is:

$$q = \rho J^2 - \mu J \frac{dT}{dx}$$

where

ρ is the resistivity of the material

dT/dx is the temperature gradient along the wire

μ is the Thomson coefficient.

The first term ρJ^2 is simply the Joule heating, which is not reversible.

The second term is the Thomson heat, which changes sign when J changes direction.

In metals such as zinc and copper, which have a hotter end at a higher potential and a cooler end at a lower potential, when current moves from the hotter end to the colder end, it is moving from a high to a low potential, so there is an evolution of heat. This is called the **positive Thomson effect**.

In metals such as cobalt, nickel, and iron, which have a cooler end at a higher potential and a hotter end at a lower potential, when current moves from the hotter end to the colder end, it is moving from a low to a high potential, there is an absorption of heat. This is called the **negative Thomson effect**.

The Thomson coefficient is unique among the three main thermoelectric coefficients because it is the only thermoelectric coefficient directly measurable for individual materials. The Peltier and Seebeck coefficients can only be determined for pairs of materials. Thus, there is no direct experimental method to determine an absolute Seebeck coefficient (i.e. thermopower) or absolute Peltier coefficient for an individual material. However, as mentioned elsewhere here there are two equations, the Thomson relations, also known as the Kelvin relations (see below), relating the three thermoelectric coefficients. Therefore, only one can be considered unique.

If the Thomson coefficient of a material is measured over a wide temperature range, including temperatures close to zero, one can then integrate the Thomson coefficient over the temperature range using the Kelvin relations to determine the absolute (i.e. single-material) values for the Peltier and Seebeck coefficients. In principle, this need only be done for one material, since all other values can be determined by measuring pairwise

Seebeck coefficients in thermocouples containing the reference material and then adding back the absolute thermoelecric power (thermopower) of the reference material.

It is commonly asserted that lead has a zero Thomson effect. While it is true that the thermoelectric coefficients of lead are small, they are in general non-zero. The Thomson coefficient of lead has been measured over a wide temperature range and has been integrated to calculate the absolute thermoelectric power (thermopower) of lead as a function of temperature.

Unlike lead, the thermoelectric coefficients of all known superconductors are zero.

The Thomson relationships

The Seebeck effect is actually a combination of the Peltier and Thomson effects. In fact, in 1854 Thomson found two relationships, now called the Thomson or Kelvin relationships, between the corresponding coefficients. The absolute temperature T, the Peltier coefficient Π and Seebeck coefficient S are related by the second Thomson relation

$$\Pi = S \cdot T$$

which predicted the Thomson effect before it was actually formalized. These are related to the Thomson coefficient μ by the first Thomson relation

$$\mu = TdS/dT.$$

Thomson's theoretical treatment of thermoelectricity is remarkable in the fact that it is probably the first attempt to develop a reasonable theory of irreversible thermodynamics (non-equilibrium thermodynamics). This occurred at about the time that Clausius, Thomson, and others were introducing and refining the concept of entropy.

Figure of merit

The *figure of merit* for thermoelectric devices is defined as

$$Z = \frac{\sigma S^2}{\kappa},$$

where σ is the electrical conductivity, κ is the thermal conductivity, and S is the Seebeck coefficient or thermopower (conventionally in μV/K). This is more commonly expressed as the *dimensionless figure of merit ZT* by multiplying it with the average temperature ($(T_2 + T_1) / 2$). Greater values of ZT indicate greater thermodynamic efficiency, subject to certain provisions, particularly the requirement that the two materials of the couple have similar Z values. ZT is therefore a very convenient figure for comparing the potential efficiency of devices using different materials. Values of ZT=1 are considered good, and values of at least the 3–4 range are considered to be essential for thermoelectrics to compete with mechanical generation and refrigeration in efficiency. To date, the best reported *ZT* values have been in the 2–3 range. Much research in thermoelectric materials has focused on increasing the Seebeck coefficient and reducing the thermal conductivity, especially by manipulating the nanostructure of the materials.

Device efficiency

The efficiency of a thermoelectric device for electricity generation is given by η, defined as

$$\eta = \frac{\text{energy provided to the load}}{\text{heat energy absorbed at hot junction}}$$, and

$$\eta_{max} = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+Z\bar{T}}-1}{\sqrt{1+Z\bar{T}}+\frac{T_C}{T_H}}$$

where T_H is the temperature at the hot junction and T_C is the temperature at the surface being cooled. $Z\bar{T}$is the modified dimensionless figure of merit which now takes into consideration the thermoelectric capacity of both thermoelectric materials being used in the power generating device, and is defined as

$$Z\bar{T} = \frac{(S_p - S_n)^2 \bar{T}}{[(\rho_n \kappa_n)^{1/2} + (\rho_p \kappa_p)^{1/2}]^2}$$

where ρ is the electrical resistivity, $\bar{T}$is the average temperature between the hot and cold surfaces, and the subscripts n and p denote properties related to the n- and p-type semiconducting thermoelectric materials, respectively. It is worthwhile to note that the efficiency of a thermoelectric device is limited by the Carnot efficiency (hence the T_H and T_C terms in Φ_{max}), since thermoelectric devices are still inherently heat engines.

The COP of current commercial thermoelectric refrigerators ranges from 0.3 to 0.6, only about one-sixth the value of traditional vapor-compression refrigerators.

Uses

Seebeck effect

The Seebeck effect can be used to turn any heat source into electrical power. These devices, called thermoelectric generators (or "thermogenerators") function like a heat engine, but less bulky, with no moving parts, and typically more expensive and less efficient.

Any power plant produces waste heat, which can be used to generate additional power using a thermoelectric generator (a form of energy recycling). This is potentially an enormous market.

Automobiles also produce waste heat, and harvesting it could increase fuel efficiency.

Space probes often use Radioisotope thermoelectric generators.

Solar cells use only the high frequency part of the radiation, while the low frequency heat energy is wasted. Several patents about the use of thermoelectric devices in tandem with solar cells have been filed. The idea is to increase the efficiency of the combined solar/thermoelectric system to convert the solar radiation into useful electricity.

Peltier effect

The Peltier effect can be used to create a refrigerator which is compact and has no circulating fluid or moving parts.

Temperature measurement

Thermocouples and thermopiles are commonly used to measure temperatures. They use the Seebeck effect. More precisely, they do not directly measure temperature, they measure temperature *differences* between the probe and the voltmeter at the other end of the wires. The temperature of the voltmeter, usually the same as room temperature, can be measured separately using "cold junction compensation" techniques.

Thermoelectric generator

Thermoelectric generators (also called **thermogenerators**) are devices which convert heat (temperature differences) directly into electrical energy, using a phenomenon called the "Seebeck effect" (or "thermoelectric effect"). Their typical efficiencies are around 5-10%. Older Seebeck-based devices used bimetallic junctions and were bulky while more recent devices use bismuth telluride (Bi_2Te_3) semiconductor p-n junctions and can have thicknesses in the millimeter range. These are solid state devices and unlike dynamos have no moving parts, with the occasional exception of a fan.

Radioisotope thermoelectric generators can provide electric power for spacecraft. Automotive thermoelectric generators are proposed to recover usable energy from automobile waste heat.

Uses

Thermoelectric generators can be applied in a variety of situations. Usually, thermoelectric generators are used for small applications where heat engines (which are bulkier but more efficient) such as Stirling engines would not be possible.

The use of waste heat in combustion engines promises to be a high volume application field. Not only the exhaust but also cooling agents are targeted.

Two general problems exist in such devices: high output resistance and adverse thermal characteristics. In order to get a significant output voltage a very high Seebeck coefficient is needed (high V/°C). A common approach is to place many thermo-elements in series, causing the effective output resistance of a generator to be very high (>10kOhm). Thus power is only efficiently transferred to loads with high resistance; power is lost across the output resistance otherwise. A generator with very high output impedance is effectively a temperature sensor, not a generator. Secondly, because low thermal conductivity is required for a good TEG, this can severely dampen the heat dissipation of such a device (i.e. TEG's serve as poor heat sinks). For example it is not generally considered wise to place a TEG on an essential IC chip that requires cooling. Because of the low thermal conductivity of a TEG device, that IC is cooled at a slower rate.

Cars produce waste heat, and harvesting it can increase the fuel efficiency of the car. Space probes to the outer solar system make use of the effect in radioisotope thermoelectric generators for electrical power.

Solar cells use only the high frequency part of the radiation, while the low frequency heat energy is wasted. Several patents about the use of thermoelectric devices in tandem with solar cells have been filed. The idea is to increase the efficiency of the combined solar/thermoelectric system to convert the solar radiation into useful electricity.

Thermoelectric modules can be used for energy recovery of otherwise wasted heat.

The modules are efficient in use when collecting heat between 250 and 280 degrees Celsius and can convert 7.2 percent of the available heat into electricity. Currently, each device can produce 24 watts of energy though developments by the scientists at UC Berkeley suggest the output will improve. Choice in material may also change as availability and cost escalation of bismuth telluride may lead to the use of gallium arsenide for cars or silicon, which is under study by mechanical engineering professor, Agnes Maynard at UC Berkeley.

Several companies have begun projects in installing large quantities of these thermoelectric devices.