

# Notes on Thermal Physics

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## 1 What is Thermodynamics?

Thermodynamics is a branch of physics that deals with heat, work, and temperature, and their relation to energy, radiation, and physical properties of matter. The behavior of these quantities is governed by the four laws of thermodynamics which convey a quantitative description using measurable macroscopic physical quantities.

## 2 Thermodynamic Processes

1. asdfkjsadfkjshd fuck me harder
  - asdfasdf yeah daddy
  - Defined by change in a system, a thermodynamic process is a passage of a thermodynamic system from an initial to a final state of thermodynamic equilibrium.
  - The initial and final states are the defining elements of the process. The actual course of the process is not the primary concern, and thus often is ignored. This is the customary default meaning of the term 'thermodynamic process'.
  - In general, during the actual course of a thermodynamic process, the system passes through physical states which are not describable as thermodynamic states, because they are far from internal thermodynamic equilibrium.

### 2.1 Isothermal Processes

- 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 in the system will occur slowly enough to allow the system to continue to 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  $\Delta T = 0$  and therefore the change in internal energy  $\Delta U = 0$  (only for an ideal gas) but  $Q \neq 0$ , while in an adiabatic process,  $\Delta T \neq 0$  but  $Q = 0$ .
- Simply, we can say that in an isothermal process:
  - $T = \text{constant}$
  - $dt = \Delta T = 0$

### 2.1.1 Examples

- Isothermal processes can occur in any kind of system that has some means of regulating the temperature, including highly structured machines, and even living cells. Some parts of the cycles of some heat engines are carried out isothermally (for example, in the Carnot cycle).
- In the thermodynamic analysis of chemical reactions, it is usual to first analyze what happens under isothermal conditions and then consider the effect of temperature. Phase changes, such as melting or evaporation, are also isothermal processes when, as is usually the case, they occur at constant pressure.
- Isothermal processes are often used as a starting point in analyzing more complex, non-isothermal processes.
- Isothermal processes are of special interest for ideal gases.
- This is a consequence of Joule's second law which states that the internal energy of a fixed amount of an ideal gas depends only on its temperature.
- Thus, in an isothermal process the internal energy of an ideal gas is constant. This is a result of the fact that in an ideal gas there are no intermolecular forces. Note that this is true only for ideal gases; the internal energy depends on pressure as well as on temperature for liquids, solids, and real gases.
- In the isothermal compression of a gas there is work done on the system to decrease the volume and increase the pressure.
- Doing work on the gas increases the internal energy and will tend to increase the temperature. To maintain the constant temperature energy must leave the system as heat and enter the environment.
- If the gas is ideal, the amount of energy entering the environment is equal to the work done on the gas, because internal energy does not change. For isothermal expansion, the energy supplied to the system does work on the surroundings.

- In either case, with the aid of a suitable linkage the change in gas volume can perform useful mechanical work. For details of the calculations, see calculation of work.
- For an adiabatic process, in which no heat flows into or out of the gas because its container is well insulated,  $Q = 0$ .
- If there is also no work done, i.e. a free expansion, there is no change in internal energy. For an ideal gas, this means that the process is also isothermal.
- Thus, specifying that a process is isothermal is not sufficient to specify a unique process.

## 2.2 Adiabatic Process

- A process without transfer of heat or matter to or from a system, so that  $Q = 0$ , is called adiabatic, and such a system is said to be adiabatically isolated.
- The assumption that a process is adiabatic is a frequently made simplifying assumption.
- For example, the compression of a gas within a cylinder of an engine is assumed to occur so rapidly that on the time scale of the compression process, little of the system's energy can be transferred out as heat to the surroundings.
- Even though the cylinders are not insulated and are quite conductive, that process is idealized to be adiabatic. The same can be said to be true for the expansion process of such a system.

### 2.2.1 Examples

For a closed system, one may write the first law of thermodynamics as :  $\Delta U = Q - W$ , where  $\Delta U$  denotes the change of the system's internal energy,  $Q$  the quantity of energy added to it as heat, and  $W$  the work done by the system on its surroundings.

- If the system has such rigid walls that work cannot be transferred in or out ( $W = 0$ ), and the walls are not adiabatic and energy is added in the form of heat ( $Q > 0$ ), and there is no phase change, then the temperature of the system will rise.
- If the system has such rigid walls that pressure-volume work cannot be done, but the walls are adiabatic ( $Q = 0$ ), and energy is added as isochoric work in the form of friction or the stirring of a viscous fluid within the system ( $W < 0$ ), and there is no phase change, then the temperature of the system will rise.

- If the system walls are adiabatic ( $Q = 0$ ) but not rigid ( $W \neq 0$ ), and, in a fictive idealized process, energy is added to the system in the form of frictionless, non-viscous pressure–volume work ( $W < 0$ ), and there is no phase change, then the temperature of the system will rise.
- Such a process is called an isentropic process and is said to be "reversible". Fictively, if the process were reversed the energy could be recovered entirely as work done by the system.
- If the system contains a compressible gas and is reduced in volume, the uncertainty of the position of the gas is reduced, and seemingly would reduce the entropy of the system, but the temperature of the system will rise as the process is isentropic ( $\Delta S = 0$ ).
- Should the work be added in such a way that friction or viscous forces are operating within the system, then the process is not isentropic, and if there is no phase change, then the temperature of the system will rise, the process is said to be "irreversible", and the work added to the system is not entirely recoverable in the form of work.
- If the walls of a system are not adiabatic, and energy is transferred in as heat, entropy is transferred into the system with the heat. Such a process is neither adiabatic nor isentropic, having  $Q > 0$ , and  $\Delta S > 0$  according to the second law of thermodynamics.
- Naturally occurring adiabatic processes are irreversible (entropy is produced).
- The transfer of energy as work into an adiabatically isolated system can be imagined as being of two idealized extreme kinds.
- In one such kind, no entropy is produced within the system (no friction, viscous dissipation, etc.), and the work is only pressure-volume work (denoted by  $PdV$ ).
- In nature, this ideal kind occurs only approximately because it demands an infinitely slow process and no sources of dissipation.
- The other extreme kind of work is isochoric work ( $dV = 0$ ), for which energy is added as work solely through friction or viscous dissipation within the system.
- A stirrer that transfers energy to a viscous fluid of an adiabatically isolated system with rigid walls, without phase change, will cause a rise in temperature of the fluid, but that work is not recoverable. Isochoric work is irreversible.
- The second law of thermodynamics observes that a natural process, of transfer of energy as work, always consists at least of isochoric work and often both of these extreme kinds of work.

- Every natural process, adiabatic or not, is irreversible, with  $\Delta S > 0$ , as friction or viscosity are always present to some extent.

### 3 Thermodynamic Free Energy

- The change in the free energy is the maximum amount of work that a thermodynamic system can perform in a process at constant temperature
- Its sign indicates whether a process is thermodynamically favorable or forbidden.
- Since free energy usually contains potential energy, it is not absolute but depends on the choice of a zero point.
- Therefore, only relative free energy values, or changes in free energy, are physically meaningful.
- Free energy is that portion of any first-law energy that is available to perform thermodynamic work at constant temperature, i.e., work mediated by thermal energy.
- Free energy is subject to irreversible loss in the course of such work.[1] Since first-law energy is always conserved, it is evident that free energy is an expendable, second-law kind of energy.
- Several free energy functions may be formulated based on system criteria. Free energy functions are Legendre transforms of the internal energy.
- The basic definition of "energy" is a measure of a body's (in thermodynamics, the system's) ability to cause change.
- The difference between the change in internal energy, which is  $\Delta U$ , and the energy lost in the form of heat is what is called the "useful energy" of the body, or the work of the body performed on an object. In thermodynamics, this is what is known as "free energy". In other words, free energy is a measure of work (useful energy) a system can perform at constant temperature.

#### 3.1 Gibbs free energy

- In thermodynamics, the Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure.
- The Gibbs free energy  $\Delta G = \Delta H - T\Delta S$ , measured in joules in SI) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (can exchange heat and work with its surroundings, but not matter).

- This maximum can be attained only in a completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces

### 3.2 Grand potential

- The grand potential is a quantity used in statistical mechanics, especially for irreversible processes in open systems. The grand potential is the characteristic state function for the grand canonical ensemble.
- A grand canonical ensemble is the statistical ensemble that is used to represent the possible states of a mechanical system of particles that are in thermodynamic equilibrium with a reservoir
- It is defined as:

$$\phi_G = U - TS - \mu N$$

- where  $U$  is the internal energy,  $T$  is the temperature of the system,  $S$  is the entropy,  $\mu$  is the chemical potential, and  $N$  is the number of particles in the system.

### 3.3 Helmholtz free energy

- In thermodynamics, the Helmholtz free energy is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume (isothermal, isochoric).
- The negative of the change in the Helmholtz energy during a process is equal to the maximum amount of work that the system can perform in a thermodynamic process in which volume is held constant. If the volume were not held constant, part of this work would be performed as boundary work.
- This makes the Helmholtz energy useful for systems held at constant volume. Furthermore, at constant temperature, the Helmholtz free energy is minimized at equilibrium.
- The Helmholtz energy is defined as:

$$F = U - TS$$

- where:
  - $F$  is the Helmholtz free energy (sometimes also called "A") (SI: joules, CGS: ergs),
  - $U$  is the internal energy of the system (SI: joules, CGS: ergs),

- $T$  is the absolute temperature (kelvins) of the surroundings, modelled as a heat bath,
- $S$  is the entropy of the system (SI: joules per kelvin, CGS: ergs per kelvin).
- The Helmholtz energy is the Legendre transformation of the internal energy  $U$ , in which temperature replaces entropy as the independent variable

## 4 Thermodynamic Equilibrium

Thermodynamic equilibrium is an axiomatic concept of thermodynamics. It is an internal state of a single thermodynamic system, or a relation between several thermodynamic systems connected by more or less permeable or impermeable walls. In thermodynamic equilibrium there are no net macroscopic flows of matter or of energy, either within a system or between systems.

### 4.1 Conditions for Thermodynamic Equilibrium

- For a completely isolated system,  $S$  is maximum at thermodynamic equilibrium.
- For a system with controlled constant temperature and volume,  $A$  is minimum at thermodynamic equilibrium.
- For a system with controlled constant temperature and pressure,  $G$  is minimum at thermodynamic 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.
- All forces are balanced and there is no significant external driving force.

## Footnote

In thermodynamics, **chemical potential** of a species is energy that can be absorbed or released due to a change of the particle number of the given species, e.g. in a chemical reaction or phase transition.