
Basic Thermodynamics

Handout 1

Definitions

System = whatever part of the Universe we select.

Open systems can exchange particles with their surroundings. **Closed** systems cannot.

An **isolated** system is not influenced from outside its boundaries.

A **Thermodynamic process** is when a system undergoes a series of changes.

A **quasistatic** process is one carried out so slowly that the system passes throughout by a series of equilibrium states so is always in equilibrium. A process which is quasistatic and has no hysteresis is said to be **reversible**.

An **irreversible** process involves friction (i.e. dissipation).

Isothermal = at constant temperature.

Isentropic = at constant entropy.

Isovolumetric = at constant volume.

Isobaric = at constant pressure.

Adiathermal = without flow of heat. A system bounded by adiathermal walls is **thermally isolated**. Any work done on such a system produces an adiathermal change.

Diathermal walls allow flow of heat. Two systems separated by diathermal walls are said to be **in thermal contact**.

Adiabatic = adiathermal and reversible.

Put a system in thermal contact with some new surroundings. Heat flows and/or work is done. Eventually no further change takes place: the system is said to be in a state of **thermal equilibrium**.

Thermodynamic state: a system is in a “thermodynamic state” if macroscopic observable properties have fixed, definite values, independent of ‘how you got there’. These properties are **variables of state** or **functions of state**. Examples are volume, pressure, temperature etc. In thermal equilibrium these variables of state have no time dependence.

Functions of state can be:

- (a) **Extensive** (proportional to system size) e.g. energy, volume, magnetization, mass;
- (b) **Intensive** (independent of system size) e.g. temperature, pressure, magnetic field, density.

Total work done on a system and total heat put into a system are **not** functions of state — you cannot say a system has a certain amount of heat, or a certain amount of work.

Equation of state = an equation which connects functions of state: for a gas this takes the form $f(p, V, T) = 0$. An example is the equation of state for an ideal gas: $pV = nRT$.

First Law of Thermodynamics (reminder)

Basically a statement of conservation of energy which includes heat as a form of energy:

$$dU = dQ + dW,$$

where dQ is **heat absorbed** by the system, and dW is **work done on** the system. U is a function of state called **internal energy**.

Second Law of Thermodynamics

Clausius' statement:

No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

Kelvin's statement:

No process is possible whose sole result is the complete conversion of heat into work.

Heat engine: cyclic process which converts heat into work. The efficiency of a heat engine is

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1},$$

where Q_1 = heat in, Q_2 = heat out, and W = work out.

Exact differentials

An expression such as $F_1(x, y) dx + F_2(x, y) dy$ is known as an **exact differential** if it can be written as the differential

$$df = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy,$$

of a differentiable single-valued function $f(x, y)$. This implies that

$$F_1 = \left(\frac{\partial f}{\partial x}\right) \quad F_2 = \left(\frac{\partial f}{\partial y}\right),$$

or in vector form $\mathbf{F} = \nabla f$. Hence the integral of an exact differential is path-independent so that [where 1 and 2 are shorthands for (x_1, y_1) and (x_2, y_2)]

$$\int_1^2 F_1(x, y) dx + F_2(x, y) dy = \int_1^2 \mathbf{F} \cdot d\mathbf{r} = \int_1^2 df = f(2) - f(1),$$

and the answer depends only on the initial and final states of the system. For an **inexact differential** this is not true and knowledge of the initial and final states is not sufficient to evaluate the integral: you have to know which path was taken.

For an exact differential the integral round a closed loop is zero:

$$\oint F_1(x, y) dx + F_2(x, y) dy = \oint \mathbf{F} \cdot d\mathbf{r} = \oint df = 0,$$

which implies $\nabla \times \mathbf{F} = 0$ (by Stokes' theorem) and hence

$$\left(\frac{\partial F_2}{\partial x}\right) = \left(\frac{\partial F_1}{\partial y}\right) \quad \text{or} \quad \left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right).$$

Functions of state have exact differentials with respect to each other.