1.1: Definitions

Thermodynamic Coordinates

The macroscopically and directly observable quantities for any state of a physical system are the thermodynamic coordinates of that state. As an example, the pressure p and volume V of a gas can be taken as thermodynamic coordinates. In more general situations, other coordinates, such as magnetization and magnetic field, surface tension and area, may be necessary. The point is that the thermodynamic coordinates uniquely characterize the macroscopic state of the system.

Thermal Contact

Two bodies are in thermal contact if there can be free flow of heat between the two bodies.

Adiabatic Isolation

A body is said to be in adiabatic isolation if there can be no flow of heat energy into the body or out of the body into the environment. In other words, there is no exchange of heat energy with the environment.

Thermodynamic Equilibrium

A body is said to be in thermodynamic equilibrium if the thermodynamic coordinates of the body do not change with time.

Two bodies are in thermal equilibrium with each other if on placing them in thermal contact, the thermodynamic coordinates do not change with time.

Quasistatic Changes

The thermodynamic coordinates of a physical can change due to any number of reasons, due to compression, magnetization, supply of external heat, work done by the system, etc. A change is said to be quasistatic if the change in going from an initial state of equilibrium to a final state of equilibrium is carried out through a sequence of intermediate states which are all equilibrium states. The expectation is that such quasistatic changes can be achieved by changes which are slow on the time-scale of the molecular interactions.

Since thermodynamics is the description of equilibrium states, the changes considered in thermodynamics are all quasistatic changes.

Work done by a System

It is possible to extract work from a thermodynamic system or work can be done by external agencies on the system, through a series of quasistatic changes. The work done by a system is denoted by W. The amount of work done between two equilibrium states of a system will depend on the process connecting them. For example, for the expansion of a gas, the work done by the system is

$$dW = p\,dV \tag{1.1.1}$$

Exact Differentials

Consider a differential form defined on some neighborhood of an n-dimensional manifold which may be written explicitly as

$$A = \sum_i f_i dx^i \tag{1.1.2}$$

where f_i are functions of the coordinates x^i. A is an exact differential form if we can integrate A along any curve C between two points, say, $\vec{x} = (x^1, x^2, \cdots, x^n)$ and $\vec{x'} = (x^{1'}, x^{2'}, \cdots, x^{n'})$ and the result depends only on the two end-points and is independent of the path C. This means that there exists a function F in the neighborhood under consideration such that $A = d\,F$. A necessary condition for exactness of A is

$$\frac{\partial f_j}{\partial x^i} - \frac{\partial f_i}{\partial x^j} = 0 \tag{1.1.3}$$

Conversely, if the conditions Equation 1.1.3 are satisfied, then one can find a function F such that $A = dF$ in a star-shaped neighborhood of the points $\vec{x}$ and $\overrightarrow{x'}$.

The differential forms we encounter in thermodynamics are not necessarily exact. For example, the work done by a system, say, dW is not an exact differential. Thus the work done in connecting two states α and β, which is given by $\int_{\alpha}^{\beta} dW$, will depend on the path, i.e., the process involved in going from state α to state β.