Thermodynamics of materials

01. Thermodynamic System

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Thermodynamic Systems

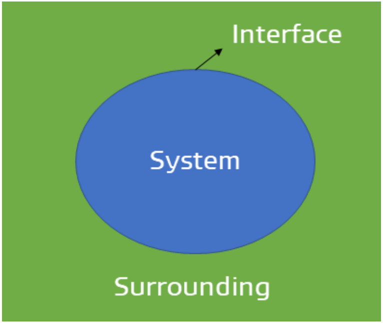
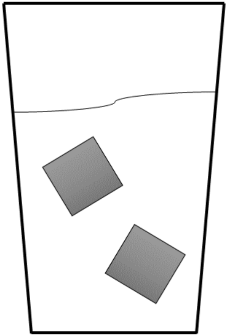


Figure: System of the thermodynamics and rest of them is considered as the surrounding.

Thermodynamic Systems



- The system can be the cup and the inside, and the surroundings can be the outside of the cup.
- The system can be the water and the ice, then the outside includes the cup is assumed as surrounding.

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Thermodynamic Variables

- Three categories of basic thermodynamic variables to describe a system:
  1. Total energy of the system.
  2. The amounts of different types of matter inside the system.
  3. The levels of potentials representing the intensities of the different forms of energy.

Thermodynamic Variables

- A simple system, a homogeneous system disregarding surface and gravitational effects and so on.
- For a simple system, three basic variables to represent the matter in the system: thermal, mechanical, and chemical:
  1. S-Entropy representing the amount of thermal matter in the system.
  2. V-Volume representing the amount of mechanical matter in the system.
  3. N-The number of moles representing the amount of chemical matter in the system.

Thermodynamic Variables

- For each type of matter, we define a corresponding potential measuring its thermodynamic stability, so we also have three types of potentials: thermal, mechanical, and chemical:
  1. T-Temperature representing the thermal potential and thus the thermodynamic stability of entropy in the system.
  2. p-Pressure representing the mechanical potential and thus the thermodynamic stability of volume.
  3. μ-Chemical potential representing the thermodynamic stability of chemical matter.

Thermodynamic Variables

- We can also define three forms of energy
  1. Thermal energy (U_{T})
  2. Mechanical energy (U_{M})
  3. Chemical energy (U_{C})
- Gibbs employed the internal energy U as the basic thermodynamic variable to represent the total energy of a system, and there are seven basic thermodynamic variables to quantify a simple system:

$$U, S, V, N, T, p, \mu$$

- All other thermodynamic quantities of a simple system can be expressed in terms of these seven basic variables.

Thermodynamic Variables of Simple System

- For a simple system with n chemical components, there are $2n$ chemical variables with each component i described by its amount N_i and chemical potential μ_i.
- For an n-component system. there are $2n + 5$ basic variables: U, S, V, T, p, N_i, μ_i.

Internal Energy

- The mass-energy equivalence proposed by Einstein will not be discussed in this lesson; if it is, the other items considered here will only have a marginal effect.
- Macroscopically, the internal energy of a simple system U may be considered as

$$U = U_{\mathsf{T}} + U_{\mathsf{M}} + U_{\mathsf{C}}$$

Internal Energy

- Microscopically, the internal energy of a material can be interpreted as the sum of two types of energies:
  1. The interatomic and electronic interaction potential energy or chemical bonding energy E_p
  2. The kinetic energy E_k associated with the motion of electrons, motion or vibration of atoms, or motion and rotation of molecules within a material, i.e.,

$$U = E_\mathsf{p} + E_\mathsf{k}$$

Entropy

- Macroscopically, entropy (S) is considered as the amount of thermal matter of a system.
- A system with large amount of entropy has large amount of thermal energy, i.e., internal energy, and the transfer of heat between the system and its surroundings means that entropy is transferred.
- When chemical matter is transported, entropy is always transferred.

Entropy

- Microscopically, a high entropy means that there are a large number of accessible microstates.
- An increase in entropy means that the system has an increased number of accessible energy states.

Volume

- Volume (V) is the amount of space occupied by a thermodynamic system, which is a mechanical matter of the system.

Amount of Chemical Substance

- Amounts $(N_1, N_2, \cdots, N_i, \cdots, N_n)$ of substances are generally measured in terms of the number of moles, N_i, for each species i. $(N_1, N_2, \cdots, N_i, \cdots, N_n)$ is a set of n thermodynamic variables.
- The mole fraction x_i is given as follows, which is a non-dimensional physical quantity.

$$x_i = \frac{N_i}{N}$$

where N is the total number of moles. $(x_1, x_2, \cdots, x_i, \cdots, x_n)$ is a set of $n-1$ thermodynamic variables, because there is one constraint

$$\sum_{i=1}^{N} x_i = 1$$

Potential Within a System

- The higher the potential, the less stable the corresponding matter is, and the lower the potential, the more stable it is.
- The amount of potential energy per unit amount of matter of a homogeneous system is

$$\text{potential} = \frac{\text{energy}}{\text{matter}}$$

- For example, the electric potential, ϕ, is the amount of electrostatic potential energy, U_{E}, per unit amount of electric matter, i.e., the charge, q,

$$\text{electric potential}(\phi) = \frac{\text{electric energy}(U_{\mathsf{E}})}{\text{electric matter}(q)}$$

For infinitesimal amount of charge dq,

$$d\phi = \frac{dU_{\mathsf{E}}}{dq}$$

Potential Within a System

- The gravitational potential gz is the amount of gravitational potential energy U_G per unit mass, m.

$$gz = \frac{U_\mathsf{G}}{m} = \frac{mgz}{m}$$

- An object sitting at a high gravitational potential position is less stable than at a lower one position.

Potential Within a System

- The internal energy and variation of internal energy ΔU is divided into

$$U = U_{\mathsf{T}} + U_{\mathsf{M}} + U_{\mathsf{C}}$$

$$\Delta U = \Delta U_{\mathsf{T}} + \Delta U_{\mathsf{M}} + \Delta U_{\mathsf{C}}$$

we can define thermal potential, temperature T, a mechanical potential, pressure p, and a chemical potential μ:

$$T = \frac{U_{\mathsf{T}}}{S} \qquad p = -\frac{U_{\mathsf{M}}}{V} \qquad \mu = \frac{U_{\mathsf{C}}}{N}$$

- The negative sign for pressure is due to fact that if volume is added to a system, the mechanical energy and this the internal energy of the system decrease. For infinitesimal system,

$$T = \frac{dU_{\mathsf{T}}}{dS} \qquad p = -\frac{dU_{\mathsf{M}}}{dV} \qquad \mu = \frac{dU_{\mathsf{C}}}{dN}$$

Potential Within a System

- The infinitesimal internal energy is

$$dU = dU_{\mathsf{T}} + dU_{\mathsf{M}} + dU_{\mathsf{C}} = TdS - pdV + \mu dN \tag{1}$$

therefore,

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

Temperature

- Amount of thermal potential energy

$$U_{\mathsf{T}} = TS = U + pV - \mu N$$

- Temperature has the unit of Kelvin (K).

$$T(\mathsf{K}) = T(^{\circ}\mathsf{C}) + 273.15$$

The lowest theoretical temperature is absolute $0\,\mathsf{K}$, at which the atoms and molecules are static.

Pressure

- The mechanical potential or pressure p represents the amount of mechanical potential energy, U_{M}, stored per unit volume, V, measure of mechanical energy intensity.

$$U_{\mathsf{M}} = -pV = U - TS - \mu N$$

- Pressure is defined as the normal force per unit area and has the unit of Pa.

$$1\,\text{bar} = 10^5\text{Pa}$$

Chemical Potential

- The chemical potential of a chemical species or component of a phase, μ is the amount of chemical energy (U_{C}) per mole, or chemical energy intensity of a species or component of a phase.
- The chemical energy (U_{C}), also known as Gibbs free energy G, is given by

$$U_{\text{C}} = G = \mu N = U - TS + pV$$

- The magnitude of chemical potential is the same as the thermodynamic chemical energy or Gibbs free energy for one mole of a substance.
- Chemical potential was introduced by Gibbs more than 100 years ago and is a key concept in chemistry, materials science, physics, and more.

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Densities

- There are two types of density quantities:
  1. The amount of matter per mole or molar quantities
  2. The amount of matter per unit volume
- Typically, lowercase letters represent the molar quantities, For a simple system,

$$u = \frac{U}{N} \qquad s = \frac{S}{N} \qquad v = \frac{V}{N}$$

- For an infinitesimal system with volume dV

$$u = \frac{dU}{dN} \qquad s = \frac{dS}{dN} \qquad v = \frac{dV}{dN}$$

- The densities representing the amount of matter per unit volume

$$u_v = \frac{U}{V} \qquad s_v = \frac{S}{V} \qquad c = \frac{N}{V} \qquad c_i = \frac{N_i}{V}$$

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Extensive and Intensive Variables

- Thermodynamic properties that are proportional to the system size are called extensive properties.
- The examples of the extensive properties are entropy S, volume V, chemical substances $N_1, N_2, \cdots, N_n$ etc.
- When the size of a system increases, the magnitudes of all the extensive properties increase proportionally.
- A property of variable of a system is called intensive if it is independent of the size of the system.
- The examples of the intensive properties are T, p, μ_i etc.

Extensive and Intensive Variables

- Intensive variables can be expressed as a ratio of two extensive variables.

$$v = \frac{V}{N} \qquad \mu = \frac{G}{N}$$

- An intensive property can be expressed as the derivative of one extensive variable with respect to another extensive variable. For example, T, p and μ can be defined as

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad -p = \left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

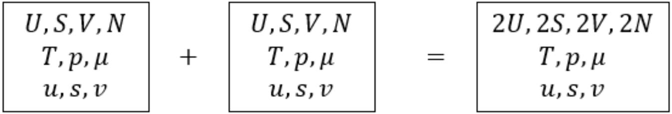

Figure: Illustration of the changes in extensive and intensive properties when a system size is doubled.

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Conjugate Variable Pairs

- A pair of variables whose product is quantity that represents a form of energy(energy density) is called a conjugate variable pair.
- Conjugate variable pairs always appear together in the same term in thermodynamic energy functions.

Thermal energy U_{T}	Mechanical Energy U_{M}	Chemical Energy U_{C}
$U_{\mathsf{T}} = TS$	$U_{\mathsf{M}} = -pV$	$U_{\mathsf{C}} = \mu_i N_i$
$dU_{\mathsf{T}} = TdS$	$dU_{\mathsf{M}} = -pdV$	$dU_{\mathsf{C}} = \mu_i dN_i$
(T, S)	$(-p, V)$	(μ_i, N_i)

Table: Basic conjugate variable pairs with their products having the unit of molar energy.