Thermodynamics of materials

02. First Law of Thermodynamics

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Thermodynamic States and State Variables

- A given thermodynamic state is described by a specific set of values of

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

- Figure in next slide is an example of plotting internal U as a function of entropy S at fixed values of volume V and fixed number of moles N.
- The information about the temperature of the state is embedded in the slope

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

Thermodynamic States and State Variables

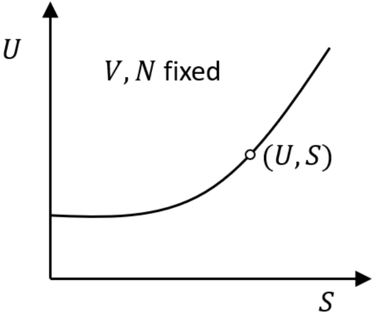

Figure: Illustration of a thermodynamic state which represented by a point in a plot of internal U as a function of S.

Thermodynamic States and State Variables

- A state is considered uniform if all thermodynamic variables have uniform values throughout the system. A state consisting of regions of homogeneous states with different uniform thermodynamic properties is called a heterogeneous state.
- An equilibrium state is a stationary state at which the properties of a system or the state variables no longer change with time, and there are no fluxes of matter, e.g., chemical species, entropy, and electric charges, going through the system.

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Thermodynamic Processes

- A process in thermodynamics refers to the change of a system from one state described by one set of values for the thermodynamic variables to another state with another set of thermodynamic variables arising from the exchange of entropy, volume, and chemical matter with its surrounding.
- The changes in state variables depend only on the values of state variables at the initial state and the final state and are independent of the process path that a system takes.
- Figure in next slide illustrates a process from state 1 to state 2 leading to finite changes in internal energy ΔU and entropy ΔS at fixed volume and fixed number of moles.

Thermodynamic Processes

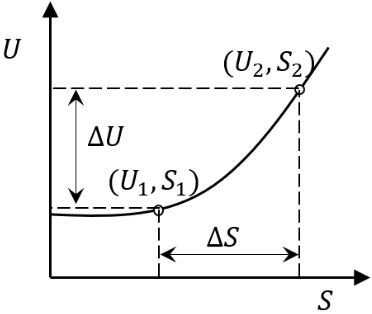

Figure: Illustration of a finite process through which the state of the system is changed from state 1 to 2.

Thermodynamic Processes

- Processes taking place within a system leading to a change of state are called internal processes.
- Some processes involve interaction between the system and its surrounding, e.g., heat conduction and mass transfer across the boundary. We may call such processes exchange process.

Spontaneous, Irreversible Processes

- A process that involves the spontaneous movement of a system from an unstable state to an equilibrium state is a spontaneous or irreversible process.
- The driving force for an irreversible process, for example a chemical potential difference between initial state and transformed state in a phase transition is finite.

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Thermodynamic Systems

- A thermodynamic system is classified according to how it interacts with its surrounding.
- An isolated system has no interactions with its surroundings.
  - No entropy exchange, $dS^{\mathrm{e}} = 0$
  - No volume exchange, $dV^{\mathrm{e}} = 0$
  - No mass exchange, $dN^{\mathrm{e}} = 0$
- For a closed system,
  - Entropy exchange, $dS^{\mathrm{e}} \neq 0$
  - Volume exchange, $dV^{\mathrm{e}} \neq 0$
  - No mass exchange, $dN^{\mathrm{e}} = 0$
- For an open system,
  - Entropy exchange, $dS^{\mathrm{e}} \neq 0$
  - Volume exchange, $dV^{\mathrm{e}} \neq 0$
  - Mass exchange, $dN^{\mathrm{e}} \neq 0$
- The 'e' subscript indicates the amount supplied to the system from the surroundings.

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First Law of Thermodynamics

- The first law of thermodynamics is about the conservation of energy.
- The main application of the first law of thermodynamics is to determine the change in the internal energy of a system dU or ΔU for a given process.
- By first law, the total energy of the whole universe (system+surrounding) is conserved

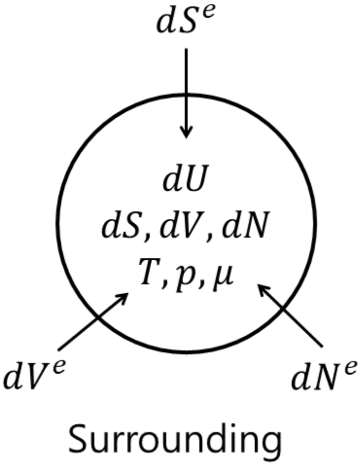
  $$U_{\text{tot}} = U + U_{\text{sur}} = \text{constant}$$

  therefore,

  $$dU_{\text{tot}} = dU + dU_{\text{sur}} = 0$$

- Energy can only be exchanged between the system and its surrounding or between two different systems, but it cannot be destroyed or created.

First Law of Thermodynamics



First Law of Thermodynamics

- Under constant T, p, μ, the increase in the internal energy is

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

- For a closed system, neglecting exchange of chemical energy transfer $dU_{\mathsf{C}}^{\mathsf{e}} = 0$, the exchange of thermal internal energy is also called by heat transfer,

$$dU_{\mathsf{T}}^{\mathsf{e}} = dQ$$

  the exchange of mechanical internal energy is also called by work done,

$$dU_{\mathsf{M}}^{\mathsf{e}} = dW$$

- It should be emphasized that the amount of thermal energy or mechanical energy or chemical energy transfer to system is necessarily equal to the respective amount of increase in the thermal energy or mechanical energy or chemical energy of the system.

First Law of Thermodynamics

- For an open system with transfer of substance,

$$dU_{\mathsf{T}}^{\mathsf{e}} = dQ + TsdN^{\mathsf{e}}$$

- The corresponding amount of entropy entering the system at temperature T from its surrounding is

$$dS^{\mathsf{e}} = \frac{dU_{\mathsf{T}}^{\mathsf{e}}}{T} = dS^{\mathsf{Q}} + sdN^{\mathsf{e}}$$

- dW represent the amount of mechanical energy exchange purely due to the volume change,

$$dU_{\mathsf{M}}^{\mathsf{e}} = dW - pvdN^{\mathsf{e}}$$

- The corresponding amount of volume exchange between the system and its surrounding is

$$dV^{\mathsf{e}} = -\frac{dU_{\mathsf{M}}^{\mathsf{e}}}{p} = -\frac{dW}{p} + vdN^{\mathsf{e}} = dV^{\mathsf{M}} + vdN^{\mathsf{e}}$$

First Law of Thermodynamics

- Therefore, the first law for an open system can be written as

$$\begin{aligned} dU &= TdS^{\mathsf{e}} - pdV^{\mathsf{e}} + \mu dN^{\mathsf{e}} \\ &= T\left(dS^{\mathsf{Q}} + sdN^{\mathsf{e}}\right) - p\left(dV^{\mathsf{M}} + vdN^{\mathsf{e}}\right) + \mu dN^{\mathsf{e}} \end{aligned}$$

In integrated form,

$$\begin{aligned} \Delta U &= T\Delta S^{\mathsf{e}} - p\Delta V^{\mathsf{e}} + \mu\Delta N^{\mathsf{e}} \\ &= \left(Q + Ts\Delta N^{\mathsf{e}}\right) + \left(W - pv\Delta N^{\mathsf{e}}\right) + \mu\Delta N^{\mathsf{e}} \end{aligned}$$

First Law of Thermodynamics for Isolated Systems

- For an isolated system, the first law of thermodynamics,

$$dU = dU^{\mathsf{e}} = -dU_{\mathsf{sys}} = dS^{\mathsf{e}} = dV^{\mathsf{e}} = dN^{\mathsf{e}} = 0$$

First Law of Thermodynamics for Closed Systems

- For a closed system, the first law of thermodynamics,

$$dN^{\mathsf{e}} = 0$$

therefore,

$$dU = TdS^{\mathsf{e}} - pdV^{\mathsf{e}}$$

Adiabatic Processes in a Closed System

- For an adiabatic process,

$$dS = dS^{\mathsf{e}} = 0$$

- For an reversible process,

$$dS^{\mathsf{ir}} = 0$$

- For a reversible adiabatic process in a closed system,

$$dU = -p^{\mathsf{ex}} dV^{\mathsf{e}} = -p dV$$

p^{ex} is external pressure.

Adiabatic Processes in a Closed System

- For an irreversible process,

$$dS^{\text{ir}} = dS \qquad dS^{\text{e}} = 0$$

- For a irreversible adiabatic expansion in a closed system,

$$p \neq p^{\text{ex}} \qquad dV = dV^{\text{e}}$$

therefore,

$$dU = TdS^{\text{e}} - p^{\text{ex}}dV^{\text{e}} = TdS - TdS^{\text{ir}} - pdV^{\text{e}} + \left(p - p^{\text{ex}}\right)dV$$

- For the same entropy change dS and volume change $dV = dV^{\text{e}}$, for reversible process, $dU = TdS - pdV$. Therefore, for irreversible process,

$$TdS^{\text{ir}} = \left(p - p^{\text{ex}}\right)dV$$

Constant Volume Processes in a Closed System

- For constant volume $dV^{\mathsf{e}} = 0$ processes in a closed simple system($dN^{\mathsf{e}} = 0$):

$$dU = TdS^{\mathsf{e}} = dQ$$

- For finite changes,

$$\Delta U = Q$$

Constant Pressure Processes in a Closed System

- For constant pressure processes in a closed system:

$$dU = TdS^{\mathsf{e}} - pdV^{\mathsf{e}}$$

$$dU + pdV^{\mathsf{e}} = TdS^{\mathsf{e}} = dQ$$

- When $dV = dV^{\mathsf{e}}$,

$$d(U + pV) = dH = dQ$$

where

$$H = U + pV$$

For finite changes,

$$\Delta H = Q$$

First Law for Reversible Processes in Open Systems

- For reversible processes in open systems,

$$dN = dN^{\mathsf{e}}$$

- Assume there is no internal chemical reaction takes place,

$$dV = dV^{\mathsf{e}} = dV^{\mathsf{M}} + v dN^{\mathsf{e}} = dV^{\mathsf{M}} + v dN$$

where v is the molar volume of the substance. For a reversible process,

$$dS = dS^{\mathsf{e}} = dS^{\mathsf{Q}} + s dN^{\mathsf{e}} = dS^{\mathsf{Q}} + s dN$$

where dS^{Q} is the amount of entropy transfer from the surrounding to the system entirely due to heat transfer.

First Law for Reversible Processes in Open Systems

- For reversible processes in an open system,

$$\begin{aligned} dU &= TdS - pdV + \mu dN \\ &= T\big(dS^{\mathsf{Q}} + sdN\big) - p\big(dV^{\mathsf{M}} + vdN\big) + \mu dN \\ &= TdS^{\mathsf{Q}} - pdV^{\mathsf{M}} + \mu dN + (Ts - pv)dN \end{aligned}$$

- Since

$$u = Ts - pv + \mu$$

therefore,

$$\begin{aligned} dU &= TdS^{\mathsf{Q}} - pdV^{\mathsf{M}} + \mu dN + (u - \mu)dN \\ &= TdS^{\mathsf{Q}} - pdV^{\mathsf{M}} + udN \end{aligned}$$

Reversible Constant S, V Processes an in Open System

- The first law yields

$$dU = \mu dN$$

- For isentropic process

$$dS = dS^{\mathsf{Q}} + sdN = 0 \to dS^{\mathsf{Q}} = -sdN$$

- The corresponding amount of heat exchange between the system and its surrounding is then

$$dQ = TdS^{\mathsf{Q}} = -TsdN$$

which implies that dQ amount of heat must be removed from the system in order to keep its entropy constant.

Reversible Constant S, V Processes an in Open System

- The constant volume condition $dV = 0$ implies,

  $$dV^{\mathsf{M}} = -v dN$$

  therefore, the amount of work done on the system is then given by

  $$dW = -p dV^{\mathsf{M}} = p v dN$$

- Therefore, $TsdN$ is the amount of heat flow from the system to the surrounding, and $pvdN$ is the amount of work done on the system by the surrounding during the reversible transfer of dN amount of substance from the surrounding to the system.

Reversible Constant S and p Processes in an Open System

- At constant entropy and pressure,

$$dU + pdV = dH = \mu dN$$

- Therefore, the amount of increase in the enthalpy of the system dH at constant S and p is equal to the chemical energy transfer μdN, and $dS = 0$,

$$dS^{\mathsf{Q}} = -sdN$$

- Hence, the corresponding amount of heat exchange between the system and its surrounding is then

$$dQ = TdS^{\mathsf{Q}} = -TsdN$$

- The volume change of the system is

$$dV = dV^{\mathsf{M}} + vdN$$

- The reversible work done on the system

$$dW = -pdV^{\mathsf{M}} = -p\big(dV - vdN\big)$$

Reversible Constant T and V Processes in an Open System

- For constant temperature and volume processes,

$$dU - TdS = dF = \mu dN$$

  where

$$F = U - TS$$

  is called the Helmholtz free energy.

- At constant temperature and volume, the change in the Helmholtz free energy is

$$dF = \mu dN$$

- The corresponding amount of heat transfer is

$$dQ = TdS - TsdN = T\big(dS - sdN\big)$$

- The amount of work interaction to keep constant volume is

$$dW = -pdV^{\mathsf{M}} = pvdN$$

Reversible Constant T and p Processes in an Open System

- For constant temperature and pressure processes,

  $$dU - TdS + pdV = dG = \mu dN$$

  where

  $$G = U - TS + pV$$

  is called the Gibbs free energy.

- At constant temperature and pressure, the change in the Gibbs free energy is

  $$dG = \mu dN$$

- The corresponding amount of heat transfer is

  $$dQ = TdS - TsdN = T\big(dS - sdN\big)$$

- The amount of work done on the system is

  $$dW = -pdV^{\mathsf{M}} = -p\big(dV - vdN\big)$$