Thermodynamics of materials

03. Second Law of Thermodynamics

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Second Law of Thermodynamics

- The second law of thermodynamics is about entropy conservation and creation. The second law of thermodynamics states that the total entropy of the universe is conserved during reversible processes and increases during irreversible processes.
- If the system never leaves equilibrium as the exchange takes place

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

  and the amount of entropy change for the system, dS, is the same as the amount of the entropy exchange dS^{e} between the system and its surrounding.
- In general,

  $$dS = dS^{\text{e}} + dS^{\text{ir}}$$

Second Law of Thermodynamics

- For an open system, dS^{e} includes the total entropy transfer due to heat transfer and the entropy carried by the chemical substance transferred to the system.
- Considering processes taking place withing the system, the corresponding entropy change for the surrounding is simply

$$dS_{\mathsf{sur}} = -dS^{\mathsf{e}}$$

- The total entropy change of the whole universe due to the processes

$$dS_{\mathsf{tot}} = dS + dS_{\mathsf{sur}} = dS - dS^{\mathsf{e}} = dS^{\mathsf{ir}}$$

- The amount of internal entropy production dS^{ir}, or total entropy change dS_{tot} for the system and surrounding, is always positive for irreversible processes and zero for reversible processes, i.e.,

$$dS_{\mathsf{tot}} = dS^{\mathsf{ir}} \geq 0$$

Second Law of Thermodynamics

- The total entropy is conserved for all reversible processes, and dS^{ir} is positive for irreversible process.
- If the processes within the system are reversible,

$$dS = dS^{\text{e}}$$

- It should be reminded that the entropy of a system is a state function; thus, the change in entropy of a system is independent of the path taken by the system between a set of specified initial and final states, regardless of whether the process is reversible or irreversible.
- A system at equilibrium has higher entropy than the same system out of equilibrium under the same thermodynamic conditions.

Quantifying Second Law of Thermodynamics

- To quantify the second law of thermodynamics, we compute the total amount of entropy produced in the process. With assumption

  $$dV^{\mathsf{e}} = dV \qquad dN^{\mathsf{e}} = dN \qquad dS^{\mathsf{e}} = dS - dS^{\mathsf{ir}}$$

  we have

  $$dU = T\left(dS - dS^{\mathsf{ir}}\right) - pdV + \mu dN = TdS - pdV + \mu dN - TdS^{\mathsf{ir}} \quad (1)$$

  where dS^{ir} is the amount of entropy produced due to one or more internal processes within the system.

Quantifying Second Law of Thermodynamics

- The last term in Eq. 1 can be quantified

$$TdS^{\mathrm{ir}} = Dd\xi$$

- D measures the amount of internal energy dissipation for the entire process or called the driving force for the process,

$$D = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N} \begin{cases} = 0 & \text{for reversible processes} \\ > 0 & \text{for irreversible processes} \end{cases}$$

and ξ measures the extent of process,

$$\xi = \begin{cases} 0 \quad \text{or} \quad \xi_i & \text{at the start of the process} \\ 1 \quad \text{or} \quad \xi_f & \text{at the end of the process} \end{cases}$$

where ξ_i and ξ_f represent the extent of the process in the initial and final states.

Quantifying Second Law of Thermodynamics

- To make a connection between the thermodynamic driving force and kinetics of a phase transition, ξ can also be regarded as an order parameter or a phase field in the phase-field method of microstructure evolution.
- For example, in the phase-field method or phase transitions,

$$\begin{cases} \xi = 0 & \text{represents the original, parent phase} \\ 0 < \xi < 1 & \text{represents a mixture of parent and new phases} \\ \xi = 1 & \text{represents the transformed, new phase} \end{cases}$$

- During a process, the amount of chemical energy $Dd\xi$ is dissipated and transforms to TdS^{ir} amount of thermal energy and produces dS^{ir} amount of entropy. The total entropy produced in a process is then

$$\Delta S^{\text{ir}} = \int_{\text{i}}^{\text{f}} dS^{\text{ir}} = \int_{\xi_i}^{\xi_f} \frac{D}{T} d\xi$$

Isolated Systems

- The second law for a process in an isolated system becomes

$$dS^{\mathrm{ir}} = dS = \frac{D d\xi}{T}$$

  i.e., the amount of entropy produced can simply be determined by the change in the entropy of the system or the driving force and the extent of the evolution process from the initial nonequilibrium state to the final equilibrium state.

- For an isolated system, we can write the driving force for a process as

$$D = T\left(\frac{\partial S}{\partial \xi}\right)_{U,V,N} = T\left(\frac{\partial S^{\mathrm{ir}}}{\partial \xi}\right)_{U,V,N}$$

$$D \begin{cases} = 0 & \text{For an initially equilibrium state} \\ > 0 & \text{For an initially nonequilibrium state} \end{cases}$$

Constant S Processes in a Closed System

- The amount of entropy produced during a constant entropy process in a closed system depend on the pressure difference between the external pressure and internal pressure within the system during the volume change.
- During a reversible constant entropy process, the internal energy change of the system is
$$dU = -pdV$$
- When the external pressure is p^{ex}, the internal energy change during an irreversible constant entropy is
$$dU = -p^{\text{ex}}dV - TdS^{\text{ir}}$$
therefore,
$$dS^{\text{ir}} = \frac{\left(p - p^{\text{ex}}\right)dV}{T}$$

Constant S Processes in a Closed System

- The amount of entropy produced in a finite process can then be expressed as

$$\Delta S^{\text{ir}} = \int S^{\text{ir}} = \int \frac{(p - p^{\text{ex}})}{T} dV \geq 0$$

- It is confirmed that when

$$p = p^{\text{ex}}$$

for all over the domain,

$$\Delta S^{\text{ir}} = 0$$

Constant S and V Processes in a Closed System

- For constant S and V in a closed system,

  $$dS = dV = dN = 0$$

  the second law yields

  $$dS^{\text{ir}} = -\frac{dU}{T} = \frac{D d\xi}{T}$$

- The amount of entropy produced in a constant S and V process within a closed system is equal to the amount of dissipated internal energy $D d\xi$ or dU divided by temperature T.
- For a constant S and V process in a closed system, we can write the driving force for a process as

  $$D = -\left(\frac{\partial U}{\partial \xi}\right)_{S,V,N} = T\left(\frac{\partial S^{\text{ir}}}{\partial \xi}\right)_{S,V,N}$$

Constant T and V Processes in a Closed System

- If both the V and T of a closed system are fixed,

$$dS^{\text{ir}} = dS - \frac{dQ}{T} = dS - \frac{dU}{T} = -\frac{d\big(U - TS\big)}{T} = -\frac{dF}{T}$$

For finite change,

$$\Delta S^{\text{ir}} = \frac{D\Delta\xi}{T} = -\frac{\Delta F}{T}$$

where

$$F = U - TS$$

is the Helmholtz free energy of the system.

- For a constant T and V process in a closed system, the driving force for a process is

$$D = -\left(\frac{\partial F}{\partial \xi}\right)_{T,V,N} = T\left(\frac{\partial S^{\text{ir}}}{\partial \xi}\right)_{T,V,N}$$

Constant S and p Processes in a Closed System

- The second law of thermodynamics for a constant S and p process can be written as

$$dS^{\text{ir}} = -\frac{dQ}{T} = -\frac{dH}{T} = \frac{Dd\xi}{T}$$

- The equation demonstrates that the amount of entropy produced in a constant S and p process within a closed system is equal to dissipated enthalpy,

$$D = -\left(\frac{\partial H}{\partial \xi}\right)_{S,p,N} = T\left(\frac{\partial S^{\text{ir}}}{\partial \xi}\right)_{S,p,N}$$

Constant T and p Processes in a Closed System

- The second law of thermodynamics for a constant T and p process can be written as

  $$dS^{\text{ir}} = dS - \frac{dQ}{T} = dS - \frac{dH}{T} = -\frac{d\big(H - TS\big)}{T} = -\frac{dG}{T} = \frac{Dd\xi}{T}$$

  for finite difference,

  $$\Delta S^{\text{ir}} = -\frac{\Delta G}{T}$$

  where

  $$G = H - TS$$

  is the Gibbs free energy of the system.

- For a constant T and p process in a closed system,

  $$D = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p,N} = T\left(\frac{\partial S^{\text{ir}}}{\partial \xi}\right)_{T,p,N}$$

Open System

- An open system undergoing a constant T, V and μ, the first law yields

$$dU = TdS^{\mathrm{e}} + \mu dN^{\mathrm{e}} = TdS^{\mathrm{e}} + \mu dN$$

- The second law yields

$$dS^{\mathrm{ir}} = dS - dS^{\mathrm{e}}$$

- In sum,

$$dS^{\mathrm{ir}} = dS - \frac{\left(dU - \mu dN\right)}{T}$$

- When T and μ constant, we have

$$dS^{\mathrm{ir}} = \frac{d\left(U - TS - \mu N\right)}{T} = -\frac{d\Xi}{T}$$

for finite change

$$\Delta S^{\mathrm{ir}} = \frac{Dd\xi}{T} = -\frac{\Delta\Xi}{T}$$

Open System

- The grand potential energy of the system is defined by

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

- The amount of entropy produced in a constant T, V, μ process of an open system is dissipated grand potential

$$-\frac{\Delta \Xi}{T}$$

and the driving force for the process is

$$D = -\left(\frac{\partial \Xi}{\partial \xi}\right)_{T,V,\mu} = T\left(\frac{\partial S^{\text{ir}}}{\partial \xi}\right)_{T,V,\mu}$$