The Third Law of Thermodynamics

(Lecture 10)

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Advanced Thermodynamics (M2794.007900)

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(*) Some materials in this lecture note are borrowed from the textbook of Ashley H. Carter.

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Statements of the Third Law

- The third law of thermodynamics is concerned with the behavior of systems in equilibrium near 0 K.

  Entropy, by definition, is given by

$$S = \int_0^T \frac{\delta Q_r}{T} + S_0 \quad \text{where } S_0 : \text{entropy at 0 K}$$

In many engineering applications, we only need to know the change in entropy. However, for example, if we want to calculate the change in Gibbs function,

$$dG = -SdT + VdP$$

knowing the absolute entropy or S_0 could be important!

→ The third law enables us to determine S_0!

Statements of the Third Law

➔ Let's derive the Nernst and Planck statements of the third law.

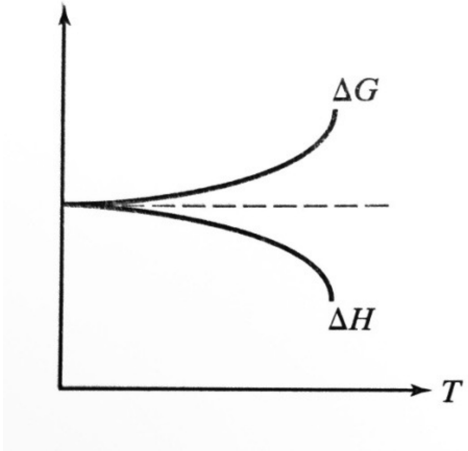
By definition,

$$G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

Gibbs-Helmholtz equation

For an isothermal process,

$$\Delta G = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T}\right]_P$$



In the vicinity of absolute zero,

$$\Delta G \cong \Delta H$$

From his experiments, Nernst also postulated that,

$$\lim_{T\to 0}\left[\frac{\partial (\Delta G)}{\partial T}\right]_P = 0 \quad \text{and} \quad \lim_{T\to 0}\left[\frac{\partial (\Delta H)}{\partial T}\right]_P = 0$$

Or,

$$\lim_{T\to 0}\left[\frac{\partial (G_2 - G_1)}{\partial T}\right]_P = \lim_{T\to 0}\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right] = \lim_{T\to 0}(S_1 - S_2) = 0$$

Statements of the Third Law

➔ Continue on.

$$\lim_{T \to 0}\left(S_1 - S_2\right) = 0$$

This is the Nernst formulation of the third law. In words,
"All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero."

Planck extended Nernst's hypothesis and proposed,

$$\lim_{T \to 0} G(T) = \lim_{T \to 0} H(T) \quad \text{and} \quad \lim_{T \to 0}\left(\frac{\partial G}{\partial T}\right)_P = \lim_{T \to 0}\left(\frac{\partial H}{\partial T}\right)_P$$

Let $\Phi \equiv G - H$, then,

$$\Phi = 0 \quad \text{and} \quad \left(\frac{\partial \Phi}{\partial T}\right)_P = 0 \ \text{ in the vicinity of } T = 0(K)$$

Statements of the Third Law

- Continue on.

$$\Phi \equiv G - H \quad \text{and} \quad G = H - TS = H + T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\rightarrow T\left(\frac{\partial G}{\partial T}\right)_P - \Phi = 0 \rightarrow T\left(\frac{\partial G}{\partial T}\right)_P - T\left(\frac{\partial H}{\partial T}\right)_P - \Phi = -T\left(\frac{\partial H}{\partial T}\right)_P$$

$$\rightarrow T\left(\frac{\partial \Phi}{\partial T}\right)_P - \Phi = -T\left(\frac{\partial H}{\partial T}\right)_P \rightarrow \left(\frac{\partial \Phi}{\partial T}\right)_P - \frac{\Phi}{T} = -\left(\frac{\partial H}{\partial T}\right)_P$$

By L'Hopital's rule,

$$\lim_{T \to 0}\left(\frac{\partial \Phi}{\partial T}\right)_P = \lim_{T \to 0}\frac{\Phi}{T}$$

Finally,

$$\lim_{T \to 0}\left(\frac{\partial H}{\partial T}\right)_P = 0 = \lim_{T \to 0}\left(\frac{\partial G}{\partial T}\right)_P = \lim_{T \to 0}(-S) = 0$$

Statements of the Third Law

- Continue on.

$$\lim_{T \to 0} S = 0$$

This is the Planck's statement of the third law. In words,

"The entropy of a true equilibrium state of a system at absolute zero is zero."

This statement is true for every pure crystalline solid. A certain glass structure has a nonvanishing entropy at absolute zero, with its disordered structure.

→ Will learn in our discussion on statistical thermodynamics!

Another statement of the third law is (unattainability principle):

"It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes."

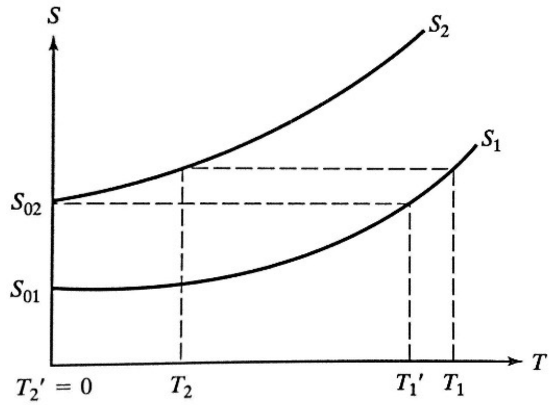
Equivalence of the Statements

- Let's prove the equivalence of the Nernst postulate and unattainability principle.

  In S-T diagram,

$$S = \int_0^T \frac{\delta Q_r}{T} + S_0 \qquad \text{where } S_0 : \text{entropy at 0K}$$

$$\text{or} \quad S = \int_0^T \frac{CdT}{T} + S_0$$



  According to the Debye law for heat capacity of a solid,

$$C_V \propto T^3$$

  Thus, S increases with T to the certain power.

Equivalence of the Statements

- Continue on.

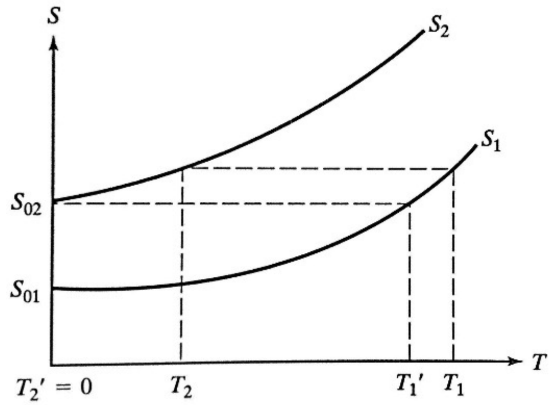
Consider a cooling process from T_1 to T_2 by an adiabatic reversible process.

Then,

$$S_2(@T_2) = S_1(@T_1)$$

$$S_{02} + \int_0^{T_2} C_2 \frac{dT}{T} = S_{01} + \int_0^{T_1} C_1 \frac{dT}{T}$$

$$\int_0^{T_2} C_2 \frac{dT}{T} = -(S_{02} - S_{01}) + \int_0^{T_1} C_1 \frac{dT}{T}$$



If $(S_{02} - S_{01}) > 0$, then, there must be certain $T_1 = T_1'$ so that

$$(S_{02} - S_{01}) = \int_0^{T_1'} C_1 \frac{dT}{T}$$

$$\text{or} \quad \int_0^{T_2'} C_2 \frac{dT}{T} = 0 \quad (\text{where } T_2' \text{: corresponding to } T_1')$$

$$\text{or} \quad T_2' = 0$$

This violates the unattainability principle! So $(S_{01} - S_{02}) \geq 0$.

Equivalence of the Statements

➔ Continue on.

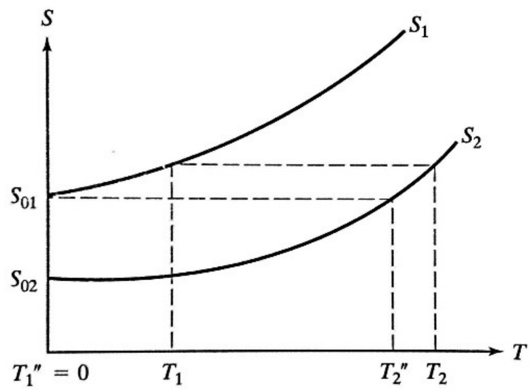
Now consider a cooling process from T_2 to T_1 by an adiabatic reversible process.

Then,

$$S_2(@T_2) = S_1(@T_1)$$

$$S_{02} + \int_0^{T_2} C_2 \frac{dT}{T} = S_{01} + \int_0^{T_1} C_1 \frac{dT}{T}$$

$$-(S_{01} - S_{02}) + \int_0^{T_2} C_2 \frac{dT}{T} = \int_0^{T_1} C_1 \frac{dT}{T}$$



If $(S_{01} - S_{02}) > 0$, then, there must be certain $T_2 = T_2''$ so that

$$(S_{01} - S_{02}) = \int_0^{T_2''} C_2 \frac{dT}{T}$$

$$\text{or} \quad \int_0^{T_1''} C_1 \frac{dT}{T} = 0 \quad (\text{where } T_1''\text{: corresponding to } T_2'')$$

$$\text{or} \quad T_1'' = 0$$

This violates the unattainability principle! So $(S_{02} - S_{01}) \geq 0$.

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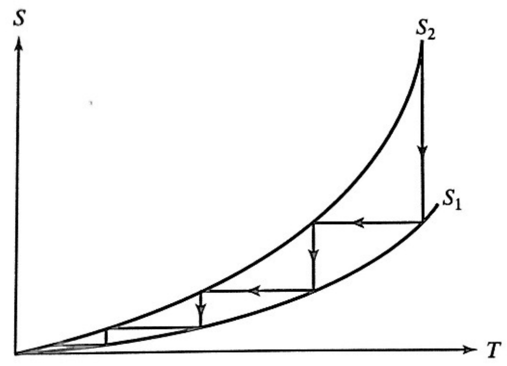
Equivalence of the Statements

➔ Continue on.

Finally, to satisfy the unattainability principle,

$$(S_{01} - S_{02}) \geq 0 \quad \text{and} \quad (S_{02} - S_{01}) \geq 0$$

$$S_{02} = S_{01}$$



Consequently, the Nernst postulate should be satisfied.

An infinite series of isothermal and adiabatic processes are required to reach absolute zero!

Consequences of the Third Law

1. Expansivity

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T$$

← Maxwell relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

$$\lim_{T\to 0}\beta = \lim_{T\to 0}\left[-\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T\right] = 0$$

← Nernst postulate

2. Slope of the phase transformation curves

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

← Clausius-Clapeyron equation

$$\lim_{T\to 0}\frac{dP}{dT} = \lim_{T\to 0}\frac{\Delta S}{\Delta V} = 0$$

← Nernst postulate

→ This has been verified for all known sublimation curves, for the vaporization curve of Helium II, and for the fusion curve of solid helium.

Consequences of the Third Law

3. Heat Capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

← Gibbs equation

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$

Integrating,

$$S - S_0 = \int_0^T C_V \frac{dT}{T} \quad \text{or} \quad S - S_0 = \int_0^T C_P \frac{dT}{T}$$

In the vicinity of absolute zero, left-hand-sides become zero by Nernst postulate. To satisfy the equation, C_V and C_P should approach zero, at least as rapidly as T (in the denominator).

$$\lim_{T\to 0} C_V = 0 \quad \text{and} \quad \lim_{T\to 0} C_P = 0$$