GENERAL PHYSICS PH1110

Nam Le, Dr.

School of Engineering Physics Hanoi University of Science and Technology

2. THERMODYNAMICS

2.3 SECOND LAW OF THERMODYNAMICS

- 1 STARTING POINTS
- 2 Postulates of the second law
- 3 HEAT ENGINE
- 4 Entropy and statement of the second law
- 5 Change in entropy of an ideal gas

1. Starting points

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- For an idealized reversible process, the entropy change obeys an equality and can be calculated. That is why it is important even though it is a hypothetical process.

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• The two postulates were shown to be equivalent by Fermi.

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- So, in the case of an ideal gas, the efficiency of a <u>reversible</u> <u>Carnot cycle</u> depends only on the temperatures of the heat source and the colder sink. However, Carnot stated that this applies for any working substance.

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• Entropy of a system is equal to the sum of entropies of all of its subsystems.

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• An arbitrary cycle corresponds to the case of $n \to \infty$:

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$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \dots + \frac{Q_n}{T_n} \le 0 \qquad \text{or} \qquad \left| \sum_{i=1}^n \frac{Q_i}{T_i} \le 0 \right|$$

• An arbitrary cycle corresponds to the case of $n \to \infty$:

$$\oint_{\widehat{1a2b1}} \frac{\delta Q}{T} \le 0$$

• According to the Carnot's theorem:

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 $\int_{\widehat{1} \circ 2} dS = \int_{\widehat{1} \circ 2} dS$ (path independent/state function)

• If the cycle is irreversible in the 1a2 process

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$$\left| \int_{\widehat{1a2}} dS = \int_{\widehat{1b2}} dS \right|$$
 (path independent/state function)

• If the cycle is irreversible in the $1a^2$ process and is reversible in the 2b1 process:

$$0 > \oint_{\widehat{1a2b1}} \frac{\delta Q}{T} = \int_{\widehat{1a2}} \frac{\delta Q}{T} + \int_{\widehat{2b1}} \frac{\delta Q}{T} = \int_{\widehat{1a2}} \left(\frac{\delta Q}{T} - dS \right)$$

▶ So, for an irreversible process: $\left| \frac{\delta Q}{T} < dS \right|$

$$\frac{\delta Q}{T} < \mathrm{d}S$$

- 4. Entropy and statement of the second law
- Summary

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- 4. Entropy and statement of the second law
- Second law of thermodynamics

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The total entropy of an isolated system can never decrease over time, and is constant if and only if all processes within the system are reversible.

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The total entropy of an isolated system can never decrease over time, and is constant if and only if all processes within the system are reversible. Isolated systems spontaneously evolve towards thermodynamic equilibrium, the state with maximum entropy.

2. THERMODYNAMICS

2.3 SECOND LAW OF THERMODYNAMICS

- 1 STARTING POINTS
- 2 Postulates of the second law
- 3 HEAT ENGINE
- 4 Entropy and statement of the second law
- 5 Change in entropy of an ideal gas

5. Change in entropy of an ideal gas

$$\delta Q = 0$$

$$\delta Q = 0 \rightarrow dS = 0$$

5. Change in entropy of an ideal gas

$$\delta Q = 0 \rightarrow dS = 0 \rightarrow S = constant$$

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• In an adiabatic process:

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5. Change in entropy of an ideal gas

• In an adiabatic process:

$$\delta Q = 0 \rightarrow dS = 0 \rightarrow S = constant$$

$$T = \text{constant} \qquad \rightarrow \qquad \Delta S = \int_1^2 dS$$

5. Change in entropy of an ideal gas

• In an adiabatic process:

$$\delta Q = 0 \rightarrow dS = 0 \rightarrow S = constant$$

$$T = \text{constant}$$
 \rightarrow $\Delta S = \int_{1}^{2} dS = \frac{1}{T} \int_{\widehat{12}} \delta Q$

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• In an isothermal process:

$$T = \text{constant}$$
 \rightarrow $\Delta S = \int_{1}^{2} dS = \frac{1}{T} \int_{\widehat{12}} \delta Q = \frac{Q}{T}$

▶ Heat added to the system in the isothermal process:

$$Q = \frac{m}{\mu} RT \ln \frac{V_2}{V_1} = \frac{m}{\mu} RT \ln \frac{p_1}{p_2}$$

▶ Therefore:

• In an adiabatic process:

$$\delta Q = 0 \rightarrow dS = 0 \rightarrow S = constant$$

• In an isothermal process:

$$T = \text{constant}$$
 \rightarrow $\Delta S = \int_{1}^{2} dS = \frac{1}{T} \int_{\widehat{12}} \delta Q = \frac{Q}{T}$

$$Q = \frac{m}{\mu} RT \ln \frac{V_2}{V_1} = \frac{m}{\mu} RT \ln \frac{p_1}{p_2}$$

► Therefore:
$$\Delta S = \frac{m}{\mu} R \ln \frac{V_2}{V_1} = \frac{m}{\mu} R \ln \frac{p_1}{p_2}$$

5. Change in entropy of an ideal gas

$$\delta Q = \mathrm{d}U - \delta W$$

$$\delta Q = dU - \delta W = \frac{m}{\mu} \frac{i}{2} R dT + p dV$$

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▶ By substituting
$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1}$$

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▶ By substituting
$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1}$$
 and $C_V + R = C_p$:

• For an arbitrary process:

$$\delta Q = dU - \delta W = \frac{m}{\mu} \frac{i}{2} R dT + p dV = \frac{m}{\mu} C_V dT + \frac{m}{\mu} RT \frac{dV}{V}$$

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▶ By substituting $\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1}$ and $C_V + R = C_p$:

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