TOPIC IV - The Second Law

Entropy in Practice (Lecture 4/4)

Contents

10. Entropy of pure substances

11. The Carnot Cycle

Objectives

Theory of entropy estimates, p, V, T relationships for isentropic processes.

One thermodynamic cycle – the Carnot Cycle.

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10. Entropy of Pure Substances

Change in dU from reversible paths. Gibbs Eqn

$$dU = dQ_{rev} + dW_{rev} = T\,dS - p\,dV \quad (11)$$

Divide by mT and rearrange to get ds,

$$ds = \frac{du}{T} + p\,\frac{dv}{T} \qquad (12)$$

For ideal gas, substitute du = c_v dT and p = RT / v and integrate.

$$s_2 - s_1 = c_v \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dV}{V} = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{V_2}{V_1}\right) \quad (13)$$

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Subst. $V_2/ V_1 = (T_2/T_1)(p_1/p_2)$

$$s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{p_1}{p_2}\right)$$

Rearrange

$$s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right) \qquad (15)$$

Isentropic means "constant entropy", $s_2 = s_1$ and,

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\gamma-1/\gamma} \qquad (16)$$

Where γ is heat capacity ratio, c_p / c_v

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Note on Pure Liquids

Incompressible, so dV = 0. Omit distinction between c_v and c_p

$$ds = \frac{du}{T} + p\,\cancel{\frac{dV}{T}} = c\,\frac{dT}{T}$$

And on integration

$$s_2 - s_1 = c\,\ln\left(\frac{T_2}{T_1}\right)$$

11. The Carnot Cycle

- Proposed 1824 as (theoretically) reversible cycle

$$\eta = 1 - T_L / T_H$$

- Piston-cylinder
- Isothermal expansion followed by isentropic expansion (1-2-3). Minimal reservoir-to-cylinder δT, followed by Q = 0
- Isothermal compression followed by isentropic compression (3-4-1)
- Can plot on p-V or T-s diagrams.

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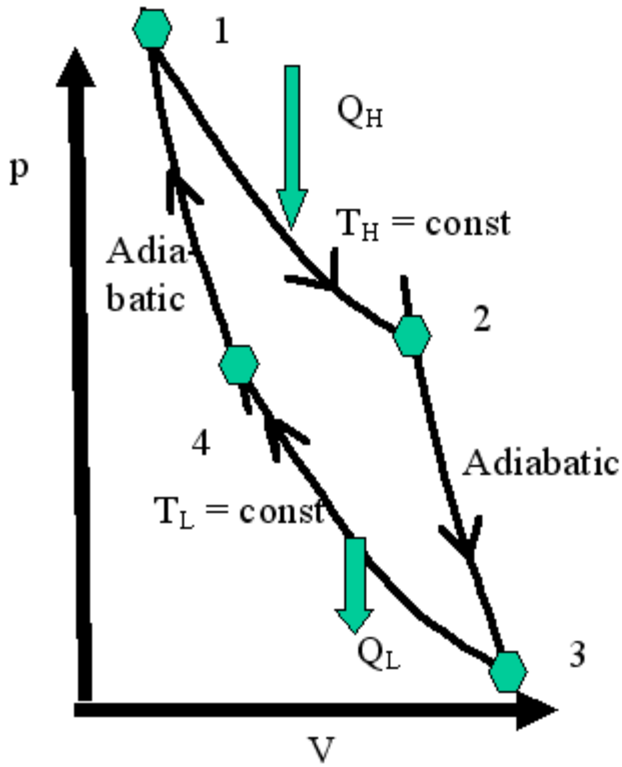
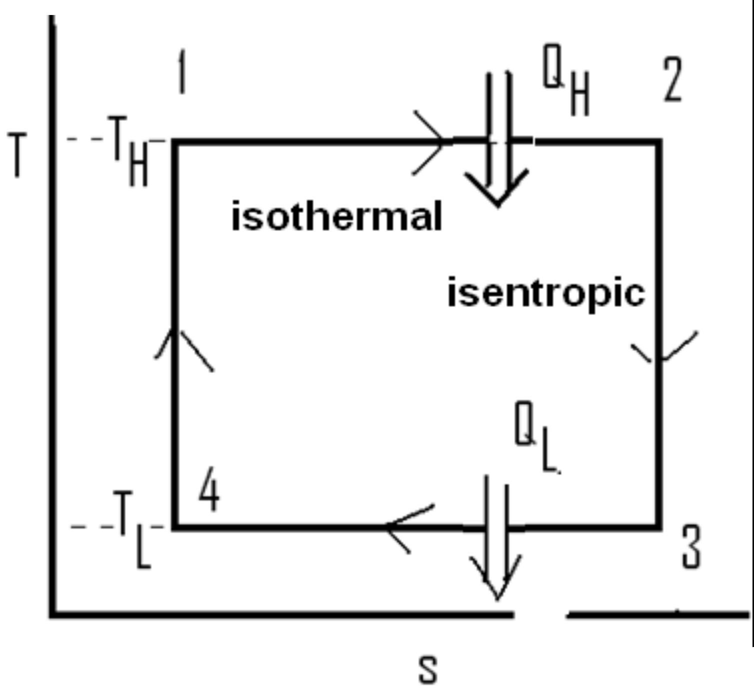


Net work = area in curve 1-2-3-4-1

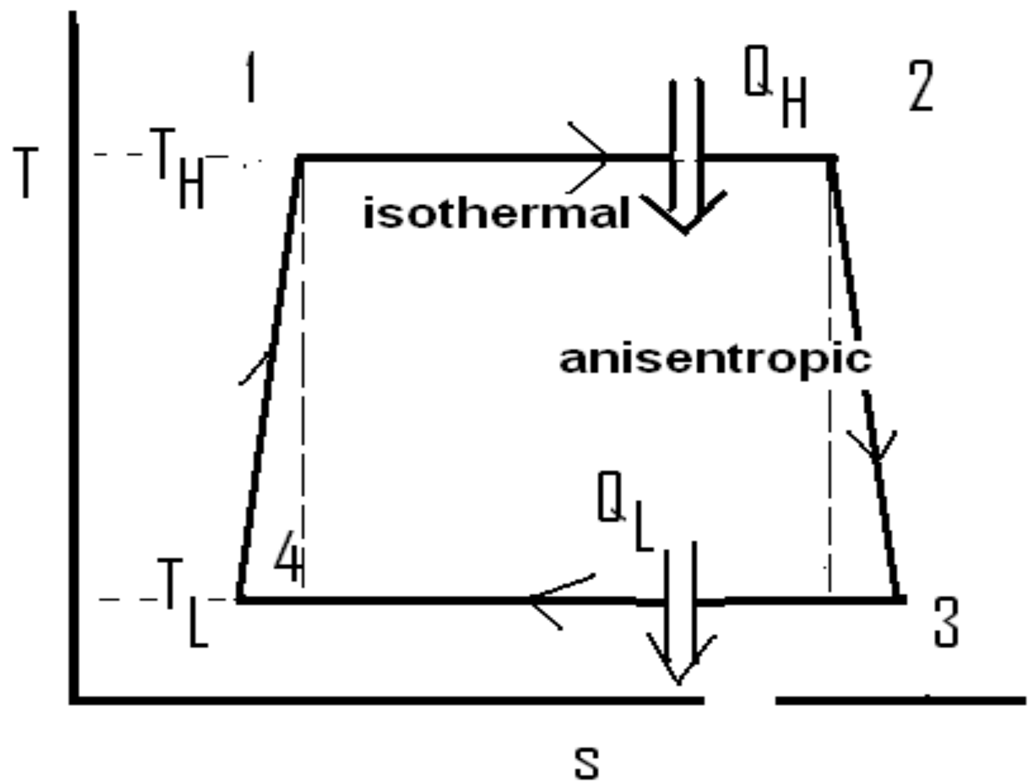


Q_H is area under 1-2.

Q_L is area under 3-4

Hence efficiency = $1 - Q_L/Q_H = 1 - T_L/T_H$

Example of irreversible compression and expansion – increased entropy



NB:Carnot cycle can be reversed to form a heat pump.

Conclusions

- The relationship $dS = (dQ/T)_{rev}$ can be integrated to give entropy, either in form of equations or tables.
- The Carnot cycle is a hypothetical reversible engine.
- Carnot (and other) cycles are usefully plotted as p-V or TS diagrams.