Any heat engine can have at most the efficiency of a Carnot engine. All Carnot engines have the same efficiency.

Efficiency of Carnot engine depends on temperatures $T_h$ and $T_c$ only.

(independent of work substance, $X, Y$)

How does it depend on $T_h$ and $T_c$?

Use an example:

work substance: ideal gas $PV = nRT$ $U = \frac{3}{2} nRT$

$x$: $V$

$y$: $-P$

**isothermal change**

$$dU = \frac{3}{2} nR dT = 0$$

$$\Rightarrow \quad dQ = dW = PdV = \frac{nRT_h}{V} dV$$

$$\Delta Q_h = nRT_h \int_{V_i}^{V_f} \frac{dU}{V} = nRT_h \ln \left( \frac{V_f}{V_i} \right)$$

$$\Delta Q_c = nRT_c \ln \left( \frac{V_f}{V_i} \right)$$

**adiabatic change**

$$dQ = 0 = dU + PdV = \frac{3}{2} nR dT + PdV$$

$$\frac{3}{2} nR dT = -PdV = -\frac{nRT}{V} dV$$

$$\Rightarrow \quad \frac{3}{2} \frac{dT}{T} = -\frac{dV}{V} \Rightarrow T^{3/2} V = \text{const.}$$

$$T_c V_{2c}^{2/3} = T_h V_{2h}^{2/3} \quad T_c V_{2c}^{2/3} = T_h V_{2h}^{2/3} \Rightarrow \frac{V_{2c}}{V_{2h}} = \frac{V_h}{V_i}$$

$$Z = \frac{\Delta Q_c}{\Delta Q_h} = 1 - \frac{T_c}{T_h} \frac{\ln \left( \frac{V_i}{V_f} \right)}{\ln \left( \frac{V_i}{V_f} \right)} = 1 - \frac{T_c}{T_h}$$
Definition of entropy

\[ \Delta Q_k - \Delta Q_c = 0 \]
\[ \frac{\Delta Q_{12}}{T_{12}} + \frac{\Delta Q_{34}}{T_{34}} = 0 \]
\[ \Delta Q_{23} = \Delta Q_{41} = 0 \]

Arbitrary reversible cycle:

An arbitrary cycle can be approximated by many constant cycle:

\[ \frac{\Delta Q_{12}}{T_{12}} + \frac{\Delta Q_{34}}{T_{34}} + \frac{\Delta Q_{56}}{T_{56}} + \ldots = 0 \]

\[ \int \frac{dQ}{T} = 0 \]

\[ \frac{dQ}{T} \] is an exact differential for reversible process.

Define state variable: \( dS = \frac{dQ}{T} \) "entropy"

What about irreversible processes?

Efficiency is smaller than (but efficiency)

\[ \int \frac{dQ}{T} \leq 0 \] (only if reversible)

\[ dS = \frac{dQ}{T} + d_i S \] with \( d_i S > 0 \)

If system is isolated:

\[ dQ = 0 \Rightarrow dS = d_i S \geq 0 \] "entropy always grows"

in equilibrium: \( dS = 0 \) "entropy is maximal"
Third law

The difference in entropy between states connected by a reversible process goes to zero in the limit \( T \to 0 \):

\[
\left( \frac{\partial S}{\partial Y} \right)_{N, T = 0} = 0 \quad \left( \frac{\partial S}{\partial X} \right)_{N, T = 0} = 0
\]

"we can measure entropy in units such that \( S = 0 \) at \( T = 0 \)"

I.3 Fundamental equation of thermodynamics

Reversible process:

\[
T dS = dU - Y dX - \sum_i \mu_i dN_i \quad (\star)
\]

\[
S = S(U, X, N, \ldots)
\]

\[
\Rightarrow \left( \frac{\partial S}{\partial U} \right)_{X, \{N_i\}} = \frac{1}{T} \quad \text{thermal}
\]

\[
\left( \frac{\partial S}{\partial X} \right)_{U, \{N_i\}} = -\frac{Y}{T} \quad \text{mechanical}
\]

\[
\left( \frac{\partial S}{\partial N_i} \right)_{U, X, \{N_i \neq 0\}} = -\frac{\mu_i}{T} \quad \text{chemical}
\]

Equation of state

Sensitivity of \( S \):

\[
\Delta S(U, X, \{N_i\}) = S(U + \Delta U, X, \{N_i\}) - S(U, X, \{N_i\})
\]
\[ \lambda = 1 + \varepsilon : \]

\[ S(U, x, y, z, v_0) + \varepsilon S(U, x, y, z, v_0) = S(U, x, y, z, v_0) + \frac{\partial S}{\partial U} U + \varepsilon \left( \frac{\partial S}{\partial x} \right) x + \varepsilon \left( \frac{\partial S}{\partial y} \right) y + \varepsilon \left( \frac{\partial S}{\partial z} \right) z + \varepsilon \left( \frac{\partial S}{\partial v_0} \right) v_0 \]

\[ \Rightarrow TS = U - xy - \sum_{i} \mu_i N_i \]

"Fundamental Equation of Thermodynamics"

"You were never to know all of the variables?"

Take differential and subtract (+):

\[ SdT + xdy + \sum_{i} \mu_i dv_i = 0 \]

"Gibbs-Duhem equation"

relate the differentials of all the intensive variables.

1.4 Thermodynamic potentials

A thermodynamic potential despite how much mechanical work can be maximally exerted by a thermodynamic system.

\[ \text{A thermodynamic potential is specific to the variable it depends on.} \]
I.4 Thermodynamic potentials

- A thermodynamic potential describes how much mechanical work can be maximally extracted by a thermodynamic system.
- Thermodynamic potentials are minimized in thermodynamic equilibrium.
- The knowledge of a thermodynamic potential as a function of its generic variables completely describes a system.
- Second derivative of thermodynamic potential gives Maxwell relation.
- First derivative of thermodynamic potentials yields equation of state.
- There is a potential for every (reasonable) set of variables. Experimental values:

I.4.1 Internal energy $U$

$$dU = dQ - dW = TdS - Td_i S + YdX + \sum \mu_i dN_i$$

$$dU \leq TdS + YdX + \sum \mu_i dN_i$$

"if process is reversible"

$$\Rightarrow U = U(S, X, \{N_i\}, Y)$$

$$\begin{align*}
\frac{\partial U}{\partial S} |_{X, \{N_i\}} &= T \\
\frac{\partial U}{\partial X} |_{S, \{N_i\}} &= Y \\
\frac{\partial U}{\partial N_i} |_{S, X, \{N_{-i}\}} &= \mu_i
\end{align*}$$
For any change of the system at constant $S, X, \Sigma N_i$:

$$\Delta U = \int dU \leq 0$$ with "" for reversible changes.

Irreversible processes at constant $S, X, \Sigma N_i$ decrease the internal energy $U$. In thermodynamic equilibrium the internal energy $U$ is minimized at fixed $S, X, \Sigma N_i$.

For reversible change $dQ = TdS = 0$

for irreversible change $dQ = TdS - Td\tilde{S}; \tilde{S} < 0$

Real heat, to be expelled by the system in order to keep entropy constant: $Q$ of $S$ made at $dQ$.

Eq. 5. $\left(\frac{\partial U}{\partial S}\right)_{X, \Sigma N_i} = T$, $\left(\frac{\partial U}{\partial X}\right)_{S, \Sigma N_i} = \Pi$, $\left(\frac{\partial U}{\partial \Sigma N_i}\right)_{S, X} = \mu_i$

Maxwell relations:

$$\left(\frac{\partial T}{\partial X}\right)_{S, \Sigma N_i} = \left(\frac{\partial Y}{\partial S}\right)_{X, \Sigma N_i}$$

$$\left(\frac{\partial T}{\partial \Sigma N_i}\right)_{S, X} = \left(\frac{\partial Y}{\partial X}\right)_{S, \Sigma N_i}$$

$$\left(\frac{\partial Y}{\partial S}\right)_{X, \Sigma N_i} = \left(\frac{\partial u_i^\prime}{\partial X}\right)_{S, \Sigma N_i}$$

$$\left(\frac{\partial u_i^\prime}{\partial \Sigma N_i}\right)_{S, X} = \left(\frac{\partial M_i^\prime}{\partial S}\right)_{S, X}$$

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