There are a "hot reservoir" and a "cold reservoir".

A B: expand isothermally (drawing heat from hot reservoir)

B C: expand adiabatically (and cool)

C D: contract isothermally (returning heat to cold reservoir)

D A: cycle contract adiabatically.

Leg AB: Heat extracted from Th: \( T_h(\delta B - \delta A) = \Delta Q_h \)

BC: No heat gained or lost

CD: Heat returned to Tc: \( T_c(\delta B - \delta A) \)

DA: No heat gained or lost

Hence, work done on some external system is

\( \Delta W = (T_h - T_c)(\delta B - \delta A) = \left(1 - \frac{T_c}{T_h}\right)\Delta Q_h \)

So cannot cycle produces optimal (thermodynamic) efficiency.

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Example: let gas be N moles of monatomic ideal gas
Example: monotonic ideal gas: calculate $\Delta Q$, $\Delta W$ in each leg of cycle:

Solution: we have

\[ U = \frac{3}{2} NRT \]
\[ S = N \sigma_0 + \frac{3}{2} N R \ln \left( \frac{T}{T_0} \right) + N R \ln \left( \frac{V}{NV_0} \right) \]

Step AB:
\[ \Delta S_{AB} = S_B - S_A = N R \ln \left( \frac{V_B}{V_A} \right) \]
\[ \Delta Q_{AB} = N R T_h \ln \left( \frac{V_B}{V_A} \right) \]
\[ \Delta U_{AB} = 0 \]
\[ \Delta W_{AB} = \text{work done on gas} \]
\[ = -N R T_h \ln \left( \frac{V_B}{V_A} \right) \quad \text{(so gas does work on RWS)} \]

Step BC
\[ \Delta S_{BC} = 0 \]
\[ \Delta Q_{BC} = 0 \]
\[ \Delta U_{BC} = \frac{3}{2} N R (T_c - T_h) = \frac{2}{3} N R \Delta W_{BC} = \text{work done on gas} \]

Also, $V_c$ is determined by
\[ \Delta S_{BC} = 0 = \frac{3}{2} N R \ln \left( \frac{T_c}{T_h} \right) + N R \ln \frac{V_c}{V_B} \]
\[ \text{or} \quad V_c = V_B \left( \frac{T_h}{T_c} \right)^{\frac{3}{2}} \]
Step CD:

\[ \Delta S_{CD} = NR \ln \frac{V_D}{V_C} \]

But \( V_D = V_A \left( \frac{T_h}{T_c} \right)^{\frac{3}{2}} \) so

\[ \Delta S_{CD} = NR \ln \left\{ \frac{V_A}{V_B} \right\} = -\Delta S_{AB} \]

\[ \Delta Q_{CD} = NRT_c \ln \left( \frac{V_A}{V_B} \right) \]

\[ \Delta U_{CD} = 0 \]

\[ \Delta W_{CD} = -NRT_c \ln \left( \frac{V_A}{V_B} \right) \]

Step DA

\[ \Delta Q_{DA} = 0 \]

\[ \Delta U_{DA} = \frac{3}{2} NR \left( T_c - T_c \right) = \Delta W_{DA} \]

\[ \Delta W_{\text{tot}} = \Delta W_{AB} + \Delta W_{BC} + \Delta W_{CD} + \Delta W_{DA} = -NR \left( T_c - T_c \right) \ln \left( \frac{V_B}{V_A} \right) \]

\[ \epsilon = -\frac{\Delta W_{\text{tot}}}{\Delta Q_{AB}} = \left( 1 - \frac{T_c}{T_h} \right) = \text{fraction of heat energy not in hot reservoir converted to work} \]

Measurement of \( T \):

(i) ratio measured by measuring Carnot efficiency (which gives \( 1 - T_c/T_h \))

(ii) let \( T \) of triple pt. of \( H_2O \) be defined as \( 273.16 \text{ K} \)

Measurement of entropy: (later)
\[ S(T, P) = S(T_0, P_0) + \int_{T_0, P_0}^{T, P} \left[ \frac{\partial S}{\partial T} \right]_P dT + \left[ \frac{\partial S}{\partial P} \right]_T dP \]

(\( \mathcal{C} = \) some specific path)

\[ \left( \frac{\partial S}{\partial T} \right)_P = \sqrt{NCP} \text{ as already shown} \]

By various derivative identities to be proved later, this becomes

\[ S(T, P) = S(T_0, P_0) + \int (\mathcal{C}) \left[ -\left( \frac{\partial P}{\partial T} \right)_S dT + dP \right] \]

Since everything in integrand is measurable, so are entropy differences. Hence, with addition of

Nernst postulate, so is entropy itself.

Some other cyclic processes:

1. Otto cycle:

   \[ \epsilon = \frac{(C_p - C_v)}{C_v} \]

   \[ \epsilon = 1 - \frac{V_B}{V_A} \]
Brayton - Joule cycle:

\[ P_A \rightarrow C \rightarrow P \rightarrow B \rightarrow P_A \]

For ideal gas: \[ \eta = 1 - \left( \frac{P_A}{P_B} \right) \]

Air-standard diesel cycle:

\[ P_C \rightarrow B \rightarrow C \rightarrow S = S_C \]

\[ V \rightarrow A \rightarrow B \rightarrow C \rightarrow S = S_A \]

Efficiency may not have simple expression
Alternative Formulations, Legendre Transformations

Original statement:
Entropy max. for given energy:
\[ \Rightarrow \text{Energy minimum for given entropy (in isolated system)} \]

Proof: Let \( S = \text{max. max.} \)
Suppose \( U \) is not min. for given \( S \)

Then could take energy out into RWS
(thereby lowering \( U \) without changing \( S \))
then add it back in form of heat
thereby increasing \( S \) for same \( U \),
contradicting max-entropy hypothesis

Conclusion: \( U \) is min. for given \( S \):

Example: diatomic wall
isolated

\[
\begin{array}{c|c|c|c}
\text{Well} & \text{Isolated} \\
\hline
U^W & S^{(1)} & V^{(1)} & N_i^{(1)} \\
S_i^{(1)} & V_i^{(1)} & N_i^{(2)} & N_i^{(2)} \\
\end{array}
\]

\[
U = U^{(1)}(S^{(1)}, V^{(1)}, N_i^{(1)}) + U^{(2)}(S^{(2)}, V^{(2)}, N_i^{(2)})
\]

\[
dU = T^{(1)}dS^{(1)} - p^{(1)}dV^{(1)} + \sum \mu_i dN_i^{(1)}
+ T^{(2)}dS^{(2)} - p^{(2)}dV^{(2)} + \sum \mu_i dN_i^{(2)} = 0
\]

Also, at fixed entropy, \( dS^{(1)} = -dS^{(2)} \)
so \( dU = 0 = (T^{(1)} - T^{(2)})dS^{(1)} = 0 \)

\[
\Rightarrow T^{(1)} = T^{(2)}
\]
Alternative potentials:

\[ F = U - TS \quad \text{Helmholtz free energy} \]
\[ H_0 = U + PV \quad \text{enthalpy} \]
\[ G = U - TS + PV \quad \text{Gibbs free energy} \]

\[ dU = TdS - PdV + \sum \mu_i dN_i \]
\[ dF = dU - TDs - TdS = -dS - PdV + \sum \mu_i dN_i \]

\[ \delta = F(T, V, N) \]

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{V, \sum \mu_i N_i} \]
\[ P = -\left( \frac{\partial F}{\partial V} \right)_{T, \sum \mu_i N_i} \]

\[ \mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T, V, \sum \mu_j N_j} \]

Similarly,

\[ dH = dU + PdV + VdP \]
\[ = TdS + VdP + \sum \mu_i dN_i \]

\[ \Rightarrow H = H(S, P, \sum \mu_i N_i) \]

\[ T \delta = \left( \frac{\partial H}{\partial S} \right)_{P, \sum \mu_i N_i} \quad V = \left( \frac{\partial H}{\partial P} \right)_{S, \sum \mu_i N_i} \]

\[ \mu_i = \left( \frac{\partial H}{\partial N_i} \right)_{S, P, \sum \mu_j N_j} \]
Finally,

\[ dG = dU - TdS - SdT + PdV + VdP \]

\[ = -SdT + VdP + \sum \mu_i dN_i \]

\[ S = -\left( \frac{\partial G}{\partial T} \right)_{V, N_i} ; \quad V = \left( \frac{\partial G}{\partial P} \right)_{T, N_i} ; \]

\[ \mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, P, N_j} . \]
Example: ideal gas in Helmholtz representation:

\[ S = N s_0 + c N R \ln \left( \frac{U}{N u_0} \right) + N R \ln \left( \frac{V}{N v_0} \right) \]

also \( U = c N R T \)

\[ \Rightarrow S = N s_0 + c N R \ln \left( \frac{T}{T_0} \right) + N R \ln \left( \frac{V}{N v_0} \right) \]

\[ c R T_0 = x s N R n_0 \]

\[ F = U - TS \]

\[ = c N R T - N T s_0 - c N R T \ln \left( \frac{T}{T_0} \right) - N R \ln \left( \frac{V}{N v_0} \right) \]

\[ = F(T, V, N) \]

Eq. of state:

\[ P = -\left( \frac{\partial F}{\partial V} \right)_{N, T} = \frac{N R T}{V} \] as known already

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{V} = -c N R + N s_0 + c N R \ln \left( \frac{T}{T_0} \right) + c N R + N R \ln \left( \frac{V}{N v_0} \right) \] as before.

So this procedure works!
Also, \[ U = F + TS \]
\[ = cNRT - NTs_0 - cNRT\ln\frac{T}{T_0} - NRT\ln\left(\frac{V}{N\bar{V}_0}\right) \]
\[ + NTs_0 + cNRT\ln\frac{T}{T_0} + NRT\ln\left(\frac{V}{N\bar{V}_0}\right) \]
\[ = cNRT \]

Eliminate \( T \) to get \( S(N, U, V) \) as before, so we have recovered the original fundamental relation.
Another example: we are given

\[
U = \frac{3}{2} PV
\]

\[
NP = AVT^4
\]

**Fundamental eq.:**

\[
p = \frac{2}{3} \frac{U}{V}
\]

\[
T = \sqrt{\frac{NP}{AV}}
\]

\[
T^4 = \frac{NP}{AV} = \frac{N}{AV} \frac{2}{3} \frac{U}{V} = \frac{2}{3} \frac{NU}{AV^2}
\]

\[
T = \left(\frac{2}{3}\right)^{\frac{1}{4}} \left(\frac{NU}{AV^2}\right)^{\frac{1}{4}}
\]

\[
\frac{1}{T} = \left(\frac{3}{2}\right)^{\frac{1}{4}} \left(\frac{AV^2}{NU}\right)^{\frac{1}{4}}
\]

\[
\text{FDS} = dU = TdS - PdV + \mu dN
\]

\[
ds = dU + PdV - \frac{\mu}{N} dN
\]

\[
\left(\frac{\partial S}{\partial U}\right) = \left(\frac{3}{2}\right)^{\frac{1}{4}} \left(\frac{AV^2}{NU}\right)^{\frac{1}{4}} = \left(\frac{3}{2}\right)^{\frac{1}{4}} \left(\frac{AV}{N}\right)^{\frac{1}{4}} U^{\frac{1}{4}}
\]

\[
S = \frac{4}{3} \left(\frac{3}{2}\right)^{\frac{1}{4}} \left(\frac{AV^2}{N}\right)^{\frac{1}{4}} U^{\frac{3}{4}} + f(V, N)
\]
\[ S = \frac{4}{3} \left( \frac{3}{2} \right)^{\frac{1}{4}} \left( \frac{AV^2}{N} \right)^{\frac{1}{4}} U^{\frac{3}{4}} + f(V, N) \]

\[ \frac{P}{T} = \frac{2}{3} \left( \frac{3}{2} \right)^{\frac{1}{4}} \left( \frac{AV^2}{NU} \right)^{\frac{1}{4}} \frac{U}{V} = \frac{2}{3} \left( \frac{3}{2} \right)^{\frac{1}{4}} A^{\frac{1}{4}} U^{\frac{3}{4}} V^{-\frac{1}{4}} N^{-\frac{1}{4}} \]

\[ S = \frac{4}{3} \left( \frac{3}{2} \right)^{\frac{1}{4}} A^{\frac{1}{4}} U^{\frac{3}{4}} V^{\frac{1}{2}} N^{-\frac{1}{4}} + g(U, N) \]

\[ \Rightarrow S = \text{const} + NK \]

Get rid of \( U \) in favor of \( T \):

\[ U = \frac{3}{2} PV \]

\[ P = \frac{AVT^4}{N} \]

So

\[ U = \frac{3}{2} A \frac{V^2}{N} T^4 \]

\[ S = \frac{4}{3} \left( \frac{3}{2} \right)^{\frac{1}{4}} A^{\frac{1}{4}} V^{\frac{1}{2}} N^{-\frac{1}{4}} \left( \frac{3}{2} \right)^{\frac{3}{4}} A^{\frac{3}{4}} \left( \frac{V^2}{N} \right)^{\frac{3}{4}} T^3 + NK \]

\[ = \frac{4}{3} \left( \frac{3}{2} \right) A \frac{V^2}{N} T^3 = 2 A \frac{V^2}{N} T^3 \]

\[ U - TS = - A \frac{V^2}{N} T^4 \]
Extremum principle for Helmholtz free energy

\[ S + S_r = \text{const} \]

\[ U + U_r = \text{min}. \]

So, the system chooses to change \( U \) so that \( \Delta U + \Delta U_r = \text{minimum} \),

where \( \Delta U = \text{change in energy from some ref. initial state} \)

\[ \Delta U_r = T_r \Delta S_r = -T_r \Delta S \]

So \( \Delta U - T_r \Delta S = \text{min} \)

or \[ \Delta F = \text{min} = F - F_{\text{ref.}} \]

or \( F \) is minimized relative to possible states at fixed temp. \( T, V, N \)

Helmholtz min. ppl.

Similarly \( G = U - TS + PV \) is min. at fixed \( (T, P, N) \)