

both eigenvalues of the matrix must be ≤ 0

That the quadratic form is always negative implies that
and so the determinant of the matrix ~~must be~~ ^{must be} positive ≥ 0

$$\frac{\partial^2 S}{\partial E^2} \frac{\partial^2 S}{\partial V^2} - \left(\frac{\partial^2 S}{\partial E \partial V} \right)^2 \geq 0$$

$$\text{Note: } \left(\frac{\partial^2 S}{\partial E^2} \right)_V = \frac{\partial}{\partial E} \left(\frac{1}{T} \right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right)_V = -\frac{1}{T^2 C_V}$$

$$\text{so } \left(\frac{\partial^2 S}{\partial E^2} \right)_V \leq 0 \Rightarrow C_V \geq 0 \quad \text{specific heat is positive}$$

Other Potentials

One can use the minimization principles of the other thermodynamic potentials, E , A , G , etc to derive other stability criteria.

Energy

S is maximum $\Rightarrow E$ is minimum

S concave $\Rightarrow E$ is convex

$$\Rightarrow E(S+\Delta S, V+\Delta V, N) + E(S-\Delta S, V-\Delta V, N) \geq 2E(S, V, N)$$

for $\Delta V = 0$ for $\Delta S = 0$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial S^2} \right)_V = \left(\frac{\partial T}{\partial S} \right)_V \geq 0 \quad \text{and} \quad \left(\frac{\partial^2 E}{\partial V^2} \right)_S = - \left(\frac{\partial P}{\partial V} \right)_S \geq 0$$

$$\text{and} \quad \left(\frac{\partial^2 E}{\partial S^2} \right)_V \left(\frac{\partial^2 E}{\partial V^2} \right)_S - \left(\frac{\partial^2 E}{\partial S \partial V} \right)^2 \geq 0$$

$$\text{or} \quad - \left(\frac{\partial T}{\partial S} \right)_V \left(\frac{\partial P}{\partial V} \right)_S - \left(\frac{\partial T}{\partial V} \right)_S^2 \geq 0$$

using $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$, $\left(\frac{\partial P}{\partial V}\right)_S = -\frac{1}{V\kappa_S}$, ~~$\left(\frac{\partial T}{\partial V}\right)_S$~~

we get

$$\frac{T}{V C_V \kappa_S} \geq \left(\frac{\partial T}{\partial V}\right)_S^2$$

Helmholtz free energy

$$A(T, V, N) = E - TS$$

$$\left(\frac{\partial A}{\partial T}\right)_{V, N} = -S$$

$$\left(\frac{\partial E}{\partial S}\right)_{V, N} = T$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V, N} = -\left(\frac{\partial S}{\partial T}\right)_{V, N}$$

$$\left(\frac{\partial^2 E}{\partial S^2}\right)_{V, N} = \left(\frac{\partial T}{\partial S}\right)_{V, N}$$

$$\text{hence } \left(\frac{\partial^2 A}{\partial T^2}\right)_{V, N} = -\frac{1}{\left(\frac{\partial^2 E}{\partial S^2}\right)_{V, N}}$$

$$\text{Since } \left(\frac{\partial^2 E}{\partial S^2}\right)_{V, N} \geq 0 \Rightarrow \left(\frac{\partial^2 A}{\partial T^2}\right)_{V, N} \leq 0$$

$$E \text{ is convex in } S \Rightarrow \underline{\underline{A \text{ is concave in } T}}$$

Consider

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V, N} = -\left(\frac{\partial S}{\partial T}\right)_{V, N} = -\frac{C_V}{T} \leq 0$$

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T, N} = -\left(\frac{\partial p}{\partial V}\right)_{T, N}$$

$$\Rightarrow C_V \geq 0$$

regard p as $p(S(T, V), V)$

$$\text{from } p = -\frac{\partial E(S, V, N)}{\partial V}$$

$$\Rightarrow \left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial p}{\partial V}\right)_S + \left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T$$

$$\text{Now } \left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial^2 A}{\partial T \partial V} = \left(\frac{\partial p}{\partial T}\right)_V = \frac{(\partial p / \partial S)_V}{(\partial T / \partial S)_V}$$

$$\text{So } \left(\frac{\partial p}{\partial v} \right)_T = \left(\frac{\partial p}{\partial v} \right)_S + \frac{\left(\frac{\partial p}{\partial s} \right)_V^2}{\left(\frac{\partial T}{\partial s} \right)_V}$$

$$= - \left(\frac{\partial^2 E}{\partial v^2} \right)_S + \frac{\left(\frac{\partial^2 E}{\partial v \partial s} \right)^2}{\left(\frac{\partial^2 E}{\partial s^2} \right)_V}$$

So

$$\left(\frac{\partial^2 A}{\partial v^2} \right)_{T,N} = - \left(\frac{\partial p}{\partial v} \right)_{T,N} = \frac{\left(\frac{\partial^2 E}{\partial v^2} \right) \left(\frac{\partial^2 E}{\partial s^2} \right) - \left(\frac{\partial E}{\partial v \partial s} \right)^2}{\left(\frac{\partial^2 E}{\partial s^2} \right)_V} \geq 0$$

since E is convex

$$\Rightarrow \left(\frac{\partial^2 A}{\partial v^2} \right)_{T,N} \geq 0 \quad \underline{\underline{A \text{ is convex in } V}}$$

$$\left(\frac{\partial^2 A}{\partial v^2} \right)_{T,N} = - \left(\frac{\partial p}{\partial v} \right)_{T,N} = \frac{1}{V \kappa_T} \geq 0 \Rightarrow \kappa_T \geq 0$$

isothermal compressibility must be positive

Gibbs free energy

$$G(T, p, N) = E - TS + pV$$

Legendre transformed from E in both S and V .

$$\Rightarrow \left(\frac{\partial^2 G}{\partial T^2} \right)_p \leq 0 \quad G \text{ concave in } T$$

$$\left(\frac{\partial^2 G}{\partial p^2} \right)_T \leq 0 \quad G \text{ concave in } p$$

(E, A, G, H, Σ)

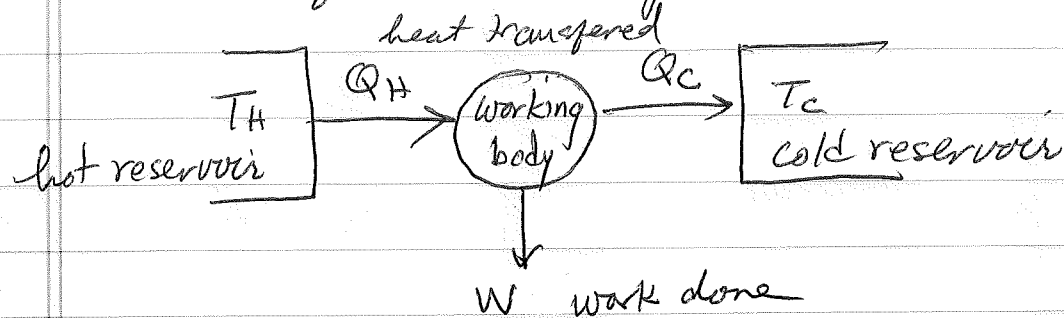
In general, the thermodynamic free energies^r for constant N (i.e. E and its Legendre transforms) are convex in their extensive variables (i.e. S, V) and concave their intensive variables (i.e. T, p).

Le Chatelier's Principle - any inhomogeneity that develops in the system should induce a process that tends to eradicate the inhomogeneity. - criterion for stability.

Heat Engines

one of the most important topics that prompted early investigations of thermodynamics was the study of heat engines - how to convert thermal energy (i.e. heat) into mechanical work.

A model for a heat engine is sketched below



Two thermal reservoirs, one hot at temperature T_H , and one cold at temperature T_C , interact with a "working body" that will convert heat flowing from hot to cold reservoir into mechanical work.

For example, the hot reservoir might be some sort of furnace burning fuel, the cold reservoir might be the ambient atmosphere, and the working body might be a chamber of gas that can push a piston.

The hot reservoir can be called the "heat source"
The cold reservoir can be called the "heat sink"

The working body is assumed to run on a "thermodynamic cycle" - it passes quasi-statically (at every moment in time it is in equilibrium) through a set of thermodynamic parameters, periodically returning to the same initial state in order to repeat the process for another cycle. This assumption of quasistatic behavior is clearly a gross simplification for a real engine, but we make it as a theoretical model.

The thermodynamic efficiency of the engine is

$$\boxed{\varepsilon = \frac{W}{Q_H} = \frac{\text{work out}}{\text{heat in}}} \quad \text{in one cycle}$$

ε measures the fraction of heat pumped into the working body that gets converted into mechanical work W done by the working body. Clearly $\varepsilon = 1$ is ideal efficiency - all heat converted to work. We will see that this ideal can never be attained,

Since the working body operates quasi-statically, changes in energy are related to changes in the thermodynamic parameters ~~by~~ (for a gas, as an example)

$$dE = TdS - pdV = \underset{\text{heat in}}{dQ} - \underset{\text{work out}}{dW}$$

Since the working body operates in a cycle, returning to its initial state, we can integrate above over one cycle of operation

$$0 = \oint_{\text{cycle}} dE = \oint_{\text{cycle}} T dS - \oint_{\text{cycle}} p dV$$

where $\oint_{\text{cycle}} dE = E_{\text{final}} - E_{\text{initial}} = 0$ since returns to initial state

Now $\oint_{\text{cycle}} p dV = \text{work done in one cycle}$

$$\oint T dS = Q_H - Q_C = Q^{\text{total}} \quad \begin{array}{l} \text{total heat} \\ \text{transferred to} \\ \text{working body in one} \\ \text{cycle} \end{array}$$

$\uparrow$ (heat pumped in from hot reservoir) $\nwarrow$ (heat released to cold reservoir)

Above $\Rightarrow 0 = Q_H - Q_C - W$

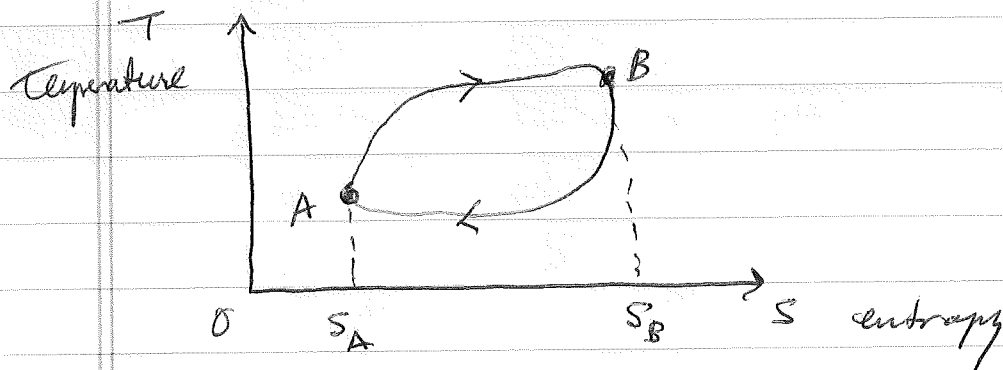
$$W = Q_H - Q_C$$

So efficiency can be written as

$$\epsilon = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

$$\boxed{\epsilon = 1 - \frac{Q_C}{Q_H}} = 1 - \frac{\text{heat released}}{\text{heat absorbed}}$$

A general engine cycle can be represented as a closed loop in the T-S plane



As the system goes from $A \rightarrow B$, the heat transferred to the working body is the area under the (top) curve

$$\Delta Q_{AB} = \int_A^B T dS > 0$$

$\Delta Q > 0 \Rightarrow$ this is heat transferred to the working body from the hot reservoir, i.e. $Q_H = \Delta Q_{AB}$

As the system goes from $B \rightarrow A$, the heat transferred from the working body is the area under the (bottom) curve.

$$\Delta Q_{BA} = \int_B^A T dS < 0$$

negative since the integral goes from S_B to smaller S_A

$\Delta Q < 0 \Rightarrow$ this is the heat released by the working body to the cold reservoir, i.e. $Q_C = -\Delta Q_{BA}$

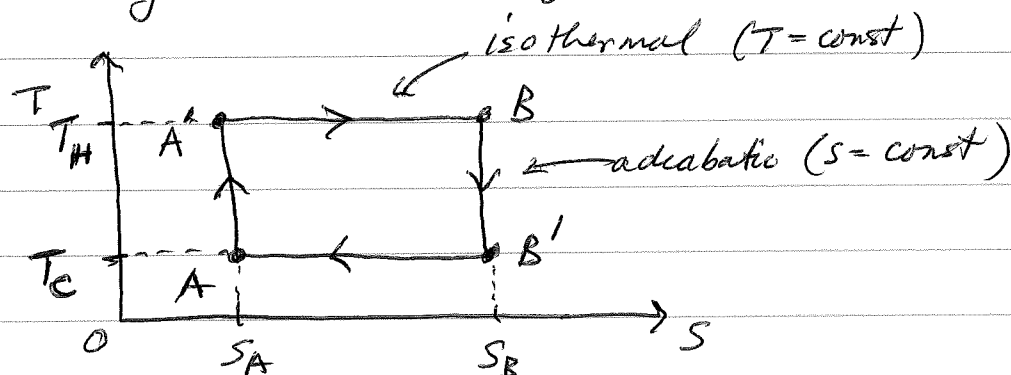
Total heat transferred $Q^{\text{tot}} = Q_H - Q_C$ is the

area bounded by the loop.

To maximize the engine efficiency, we want to maximize area under curve from A to B while minimizing the area under the curve from B to A

$$\varepsilon = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\text{area under } B \rightarrow A}{\text{area under } A \rightarrow B}$$

For an engine operating between two reservoirs of fixed temperatures T_H and T_C , the most efficient such cycle is the Carnot cycle given by the T-S diagram below



For this cycle it is easy to compute the efficiency

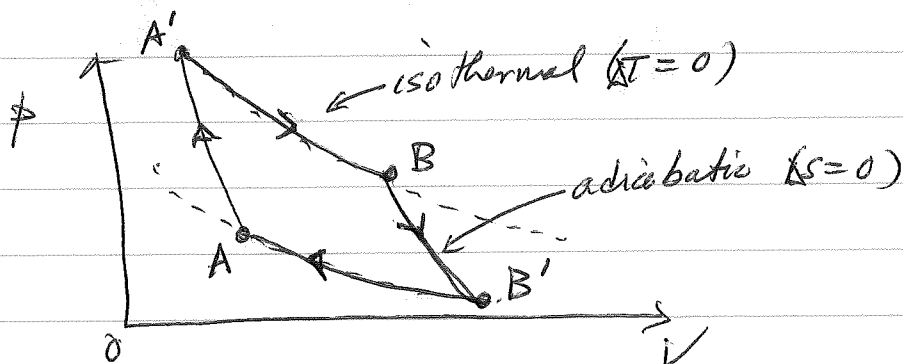
$$Q_H = T_H (S_B - S_A) \quad \text{heat absorbed}$$

$$Q_C = T_C (S_B - S_A) \quad \text{heat released}$$

$$\boxed{\varepsilon = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}}$$

Since T_C and T_H must be finite, one always has $\varepsilon < 1$.

One often sees the Carnot Cycle depicted as a loop in the p - V plane rather than the T - S plane. There it looks as sketched below



- 1) $A' \rightarrow B$ is isothermal expansion of the gas at the temperature T_H of the reservoir. Expanding gas pushes piston and does work. Working body absorbs heat $Q_H = T_H (S_B - S_A)$ from hot reservoir.
- 2) $B \rightarrow B'$ is adiabatic expansion of the gas. Working body is thermally isolated from the hot reservoir. Gas continues to do work as it expands. No heat added to gas as it expands (i.e. $\Delta Q = 0$) $\Rightarrow$ temperature of gas decreases until reaches T_C , temperature of cold reservoir.
- 3) $B' \rightarrow A$ is isothermal compression of gas. Working body is in thermal contact with the cold reservoir, maintaining temperature at T_C . Work done on the working body to compress the gas keeping T_C fixed $\rightarrow$ working body releases heat $-\Delta Q = Q_C = T_C (S_B - S_A)$ to cold reservoir.

4) $A \rightarrow A'$ is adiabatic compression of gas.

Working body is thermally isolated from reservoirs.
No heat flows in or out of working body.

Compressing gas raises its temperature back up to T_H of the hot reservoir.

isothermal segments of the cycle are curves in the p - V plane given by

$$pV = Nk_B T \rightarrow p = \frac{Nk_B T}{V}$$

with N fixed and T fixed (isothermal)

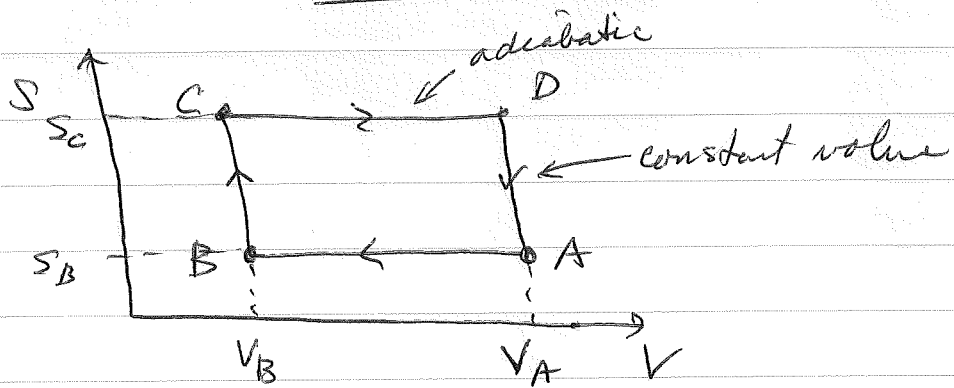
$$\Rightarrow p \propto \frac{1}{V}$$

adiabatic segments of the cycle are curves in p - V plane given by

$$p \propto \frac{1}{V^\gamma} \quad \gamma > 0$$

(see problem 11f) of Problem Set #1)

Another common thermodynamic cycle is the "Otto" cycle which consists of two adiabatics and two constant volume "strokes"



one can show that the efficiency of the Otto cycle is given by

$$\epsilon = 1 - \left(\frac{V_B}{V_A} \right)^{\frac{C_p - C_v}{C_v}}$$

where C_v and C_p are the specific heats at constant volume and pressure respectively

Note: The same cycle can be represented as a curve in either $T-S$ plane, $p-V$ plane, $S-V$ plane, or other variable choices, by the following observation.

~~A particular~~ Let us take $E(S, V)$ as ~~our~~ our thermodynamic potential. A given "stroke" of a cycle can therefore be represented as a curve in the $S-V$ plane (as in the Otto cycle diagram) that tells how S must vary as V varies during the stroke of the cycle, i.e. $S_0(V)$

But we also have ~~parameter~~

$$-\left(\frac{\partial E}{\partial V}\right)_S = p(S, V)$$

So the stroke can also be represented by the curve $p(S_0(V), V)$ in the $p-V$ plane (as in the 2nd way we drew the Carnot cycle)

Also we can invert the curve $S_0(V)$ to get $V_0(S)$ and then use

$$\left(\frac{\partial E}{\partial S}\right)_V = T(S, V)$$

to represent the stroke as the curve

$T(S, V_0(S))$ in the $T-S$ plane.

(as in our 1st way of representing the Carnot cycle)

Hence we can represent the stroke in many ~~equivalent~~ different but equivalent ways,