

Thermodynamics

1.1 Introduction

Systems can be described by a set of state variables (like U, T, N, \dots) which can be linked by an equation of state. In a closed system, there are always 2 independent variables, meaning any variable can be expressed as a function of just 2 others.

Thermodynamic processes move a system from one equilibrium state to another. State variables totally describe an equilibrium state, regardless of how they got there (entropy, temperature), and process variables are process independent (heat supplied, work done)

Variables

Internal energy This is the total energy contained in a system. The equation for U depends on the equation of state of the system considered.

Heat This is the energy transferred between objects in thermal contact which have different temperatures. Transfers of heat are associated with increase in entropy

Temperature Hotness, can be defined in terms of the average kinetic energy of a gas, or as the inverse of thermodynamic beta.

Entropy This is a measure of disorder, and of the lack of energy available to do mechanical work. In this course entropy is only considered as a macroscopic state variable.

The change in entropy can be defined as the change in reversible heat Q_R over temperature

$$\delta S = \frac{\delta Q_R}{T}$$

As the process is reversible, the entropy change of the surroundings was $-\delta Q_R/T$. The entropy change of multiple infinitesimal changes of any system can be generalised to

$$\Delta S = \int_{\text{Initial state}}^{\text{Final state}} \frac{\delta Q}{T}$$

Structure of matter

Ideal gas $PV = Nk_B T$, $U = \frac{n_d}{2} Nk_B T$

VdW gas The equation of state of an van der Waals gas is

$$\left(P - a \frac{N^2}{V^2}\right)(V - Nb) = Nk_B T$$

and its internal energy is $U = \frac{n_d}{2} Nk_B T - a \frac{N^2}{V}$

First Law

The first law states the energy change of a system dU is δ

$$dU = \delta Q - \delta W$$

where δQ is the heat supplied to the system and δW is the work done by the system. Assuming the process is quasistatic, and using the definition of entropy, we can say

$$dU = T dS - P dV$$

* Quasistatic means happening so slow it appears static

Second Law

- Kelvin statement: A perfect heat engine is impossible - so no process exists which has the sole effect of ~~the~~ taking heat energy and converting it all to work.
- Clausius statement: Heat flows from hot to cold. No process exists which has the sole purpose of moving heat from a cold reservoir to a hot one - this implies a perfect refrigerator is impossible
- Entropy statement: This is a statement that entropy must increase for non-reversible and quasistatic processes.

$$dS \begin{cases} = \frac{\delta Q}{T} & \text{if reversible} \\ > \frac{\delta Q}{T} & \text{otherwise} \end{cases}$$

Clausius Inequality & Entropy

The multistage process approach is used to derive this relationship - here a cycle is performed on N reservoirs to move energy out of them, then restore it. Note that all reservoirs have large heat capacities and their temperature stays constant as energy is transferred.

1. A system S is placed in contact with a reservoir R_i at temperature T_i and allowed to reach this temperature. This is repeated for N different reservoirs, and after it all the system S is in its original state.
2. The reservoirs R_i have all had energy removed/added to them - a Carnot heat pump comes around and adds/removes the right amount of heat to put every reservoir back at its original state (Q, U, P). This pump moves energy to/from a Carnot heat-source reservoir at temperature T^*

Lets look at how much work gets done in each step: in step 1 work is done on the reservoirs, and in step 2 work is done by the Carnot engine.

1. - In each heat exchange, work will be done - use the first law

$$\Delta U_i = \Delta Q_i - \Delta W_i$$
 - Now consider the sum over all N heat exchanges - we know $\Delta U_{\text{total}} = 0$

$$= \sum_i \Delta U_i = \sum_i \Delta Q_i - \sum_i \Delta W_i = 0 \rightarrow \text{the total work done on all reservoirs is } W_{\text{step 1}} = \sum_i \Delta W_i = \sum_i \Delta Q_i$$
2. - The Carnot engine moves heat from its (Carnot heat-source) reservoir at T^* to the individual reservoir at T_i
 - It draws ΔQ_i^* from the (Carnot heat-source) reservoir to do ΔW_i^* work, moving $\Delta Q_i = \Delta Q_i^* - \Delta W_i^*$ into the individual reservoir R_i .
 - The Carnot efficiency formula gives

$$\frac{\Delta Q_i^*}{\Delta Q_i} = \frac{T^*}{T_i} \rightarrow \Delta Q_i^* = \frac{T^*}{T_i} \Delta Q_i$$

- Then the total work done by the Carnot engine is

$$W_{\text{step 2}} = \sum_i (\Delta Q_i^* - \Delta Q_i) = \sum_i \left(\frac{T^*}{T_i} \Delta Q_i - \Delta Q_i \right)$$

From these we can see that the total work done is the sum of the work done on the systems and by the Carnot engine, which is

$$\begin{aligned} W_{\text{total}} &= W_{\text{step 1}} + W_{\text{step 2}} = \sum_i \left(\frac{T^*}{T_i} \Delta Q_i - \Delta Q_i \right) + \sum_i \Delta Q_i \\ &= T^* \sum_i \frac{\Delta Q_i}{T_i} \end{aligned}$$

In the limit of the heat transfers in each step $\Delta Q \rightarrow 0$ and the number of steps $N \rightarrow \infty$, we get the following:

$$W_{\text{total}} = T^* \oint \frac{\delta Q}{T}$$

where the path integral is over the history of temperatures caused by moving S between reservoirs.

Consider the implication of different works :

$W_{\text{total}} > 0$ Ignore this case as the second law is violated (work is done from just heat energy)

$W_{\text{tot}} = 0$ The system is reversible as no work was done — the system and everything else in the universe look the same.

$W_{\text{tot}} < 0$ There was a net flow of work into the Carnot's external reservoir, meaning it is irreversible.

This shows that :

$$\oint \frac{\delta Q}{T} \begin{cases} = 0, & \text{if reversible} \\ < 0, & \text{if irreversible} \end{cases}$$

Any reversible process satisfies $\oint_R dS = 0$, where the entropy change dS was previously defined in terms of reversible work $\delta Q_R/T$. This implies entropy is an exact derivative and its integral between two points is path independent.

Now consider a process with an irreversible step $A \rightarrow B$ and a reversible step $B \rightarrow A$. This total cycle is irreversible so

$$\begin{aligned} \oint_{A \rightarrow B \rightarrow A} \frac{\delta Q}{T} < 0 &\rightarrow \int_A^B \frac{\delta Q}{T} + \int_B^A \frac{\delta Q_R}{T} < 0 \\ &\rightarrow \Delta S > \int_A^B \frac{\delta Q}{T} \end{aligned}$$

where the fact that the entropy is a state variable was used to let $\Delta S = S_B - S_A$. Considering the limit of a smaller process $\Delta S \rightarrow dS$, leads to the general statement for the entropy change in a process:

$$dS \begin{cases} = \frac{\delta Q}{T}, & \text{if reversible} \\ > \frac{\delta Q}{T}, & \text{if irreversible.} \end{cases}$$

Thermodynamic Potentials

Potentials

Thermodynamic potentials are different forms of potential energy - they represent the amount of work and heat that can be extracted from a system. Different types of potential must be considered when different things are kept constant, these variables are the natural variables. The different potentials represent different Legendre-transformed functions of the internal energy.

- Internal energy U , Natural variables: entropy S and volume V . Internal energy is defined as the sum of KE and energy needed to assemble a system. The first law gives us

$$dU = TdS - PdV$$

- Enthalpy H , Natural variables: entropy S and pressure P . Enthalpy is defined as

$$H = U + PV$$

so $dH = dU + PdV + VdP$ and

$$dH = TdS + VdP$$

Enthalpy (change) can be interpreted as the heat flow in a reversible isobaric process. Note that we can use this to derive an expression for constant pressure heat capacity C_p . Here $dP = 0$, $dH = TdS = \delta Q$

$$C_p = \frac{\delta Q}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

- Gibbs free energy G , Natural variables: temperature T and pressure P . Gibbs free energy is defined as

$$G = H - TS$$

so $dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$

$$dG = VdP - SdT$$

Any process tends to minimise Gibbs free energy, and the starting value is the limit on work that can be extracted.

- Helmholtz free energy F , Natural variables: temperature T and volume V . defined as

$$F = U - TS$$

so $dF = dU - TdS - SdT$

$$dF = -SdT - PdV$$

Helmholtz free energy can be interpreted as the energy available to do work in a isothermal process (maximum amount of work available is the decrease in F)
A mechanical equilibrium is reached when F is minimum.

Maxwell's Relations

These relations are useful tools that relate $T, V, S,$ and P . Each of the 4 are derived from the 4 thermodynamic potentials - a general process to derive them is

1. Write the differential form of the potential using the first law
2. Write the potential P in terms of its natural variables $P = P(A, B)$ and take the total derivative of the potential.
3. Inspect the differentials' coefficients to get definitions for the (non natural) variables in terms of the potentials
4. Recognise that as dP is total derivative and $dP = X dA + Y dB$,

$$\frac{\partial^2 P}{\partial A \partial B} = \left(\frac{\partial X}{\partial B} \right)_A = \left(\frac{\partial Y}{\partial A} \right)_B$$

Example for enthalpy:

$$dH = T dS + V dP$$

let $H = H(S, P)$, so

$$dH = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dP$$

This tells us that $T = \left(\frac{\partial H}{\partial S} \right)_P$ and $V = \left(\frac{\partial H}{\partial P} \right)_S$

We can also see that

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

Repeating for all potentials gives the Maxwell relations

$$\frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$$

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$\frac{\partial^2 F}{\partial T \partial V} = - \left(\frac{\partial S}{\partial V} \right)_T = - \left(\frac{\partial P}{\partial T} \right)_V$$

$$\frac{\partial^2 G}{\partial T \partial P} = - \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

Chemical Potential

Chemical potential is introduced to account for variable particle number - it is the energy associated with adding particles to a system. Change the first law to be:

$$dU = T dS - P dV + \mu dN$$

where chemical potential is defined

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

The chemical potential of each species can be defined, in which case the dU equation gets a term for each $\mu_i dN_i$.

Chemical potential can be seen as the molar Gibbs free energy

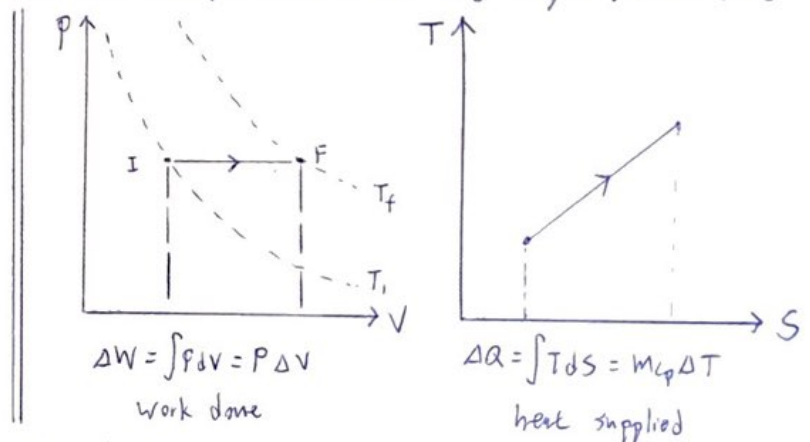
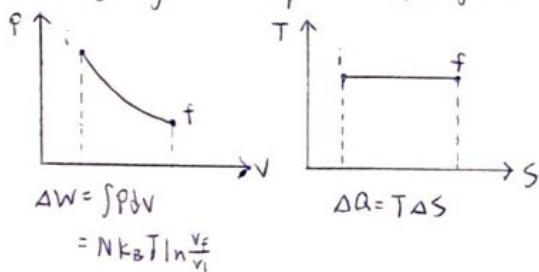
Generalised Variables

Consider a force driving a displacement — the work done $\delta W = \underline{F} \cdot d\underline{x}$. The force is intensive and displacement is extensive, This situation can be generalised to describe sets of thermodynamic variables as conjugate pairs. For example, for a gas expansion $\delta W = -P dV$, pressure is the generalised force and volume is generalised displacement, the pressure drives the volume change. Equally in the exchange of work, $\delta Q = T dS$, the temperature difference causes an entropy change. In the exchange of particles, μdN , the chemical potential drives a change of particle number.

Processes & Cycles

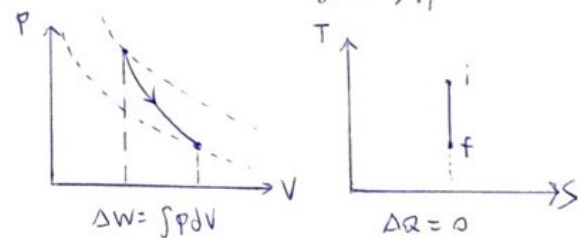
Processes

- Quasistatic: A process where all state variables remain well defined throughout is quasistatic. Processes that are not quasistatic cannot be represented by a line on a P-V or T-S diagram.
- Reversible: Reversible processes ignore effects like friction. For our macroscopic definition of entropy to hold, we need to assume reversibility. Heat transfers between two objects is irreversible. However, an infinitesimal transfer of heat is reversible and purely quasistatic — this implies that an isothermal quasistatic process is reversible. Isentropic processes like adiabatic expansion are also reversible.
- Isobaric expansion: Pressure constant and volume increases, temperature must increase to maintain pressure. The entropy increases because because of the larger volume and the higher temperature. (right)



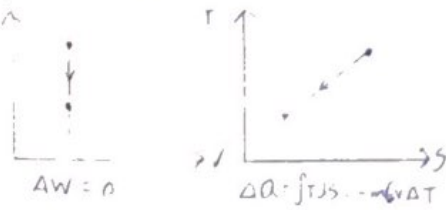
- Isothermal expansion: Temperature constant and volume increases, pressure must decrease on an isotherm. Heat flows in and this energy is all used to do work on the piston. (left) For an ideal gas, the work done is found by integrating $\int P dV$. As the process is isothermal the internal energy must be constant — meaning $\int T dS = \int P dV \rightarrow T \Delta S = Nk_B T \ln \frac{V_f}{V_i}$

- Adiabatic expansion: No heat flow ($\delta Q = 0$) and volume increases, temperature must decrease. As $\delta Q = 0$ we can see that $\delta S = \delta Q / T = 0$ too, adiabatic processes are isentropic. $dU = \frac{n_0}{2} Nk_B dT$ and $dU = -P dV$ under the ideal gas law, so $dU = \frac{n_0}{2} Nk_B dT = -\frac{Nk_B T}{\gamma} dV$



which gives $dT/T = -\frac{\gamma}{\gamma-1} \frac{dV}{V}$ which integrates to $TV^{\gamma-1} = \text{constant}$, $\gamma = 1 + \frac{2}{n_d}$
As $\gamma > 1$, the gradient of adiabats is greater than isotherms

- Isochoric cooling: Temperature decreases and volume constant, internal energy and entropy must decrease. No work is done as $\Delta V = 0$, and $P \propto 1/V$. The heat transferred to the system is $-C_v \Delta T$ meaning heat is expelled.



Heat Capacity

Taking internal energy $U = U(V, T)$, we can write

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Then using the first law $\delta Q = dU + P dV$

$$dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- Constant volume: at constant volume we know $dV = 0$, so

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

- Constant pressure: Define $V = V(P, T)$ so that

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

then as $dP = 0$ at constant pressure

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT \Rightarrow dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial T}\right)_V dT$$

For an ideal gas $V = Nk_B T / P$ and $U = \frac{n_d}{2} Nk_B T$, so $\underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_v}$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \text{ as } U = \frac{n_d}{2} P V$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_P = P \left(\frac{\partial V}{\partial T}\right)_P + C_v$$

$$= Nk_B + \frac{n_d}{2} Nk_B = \gamma C_v$$

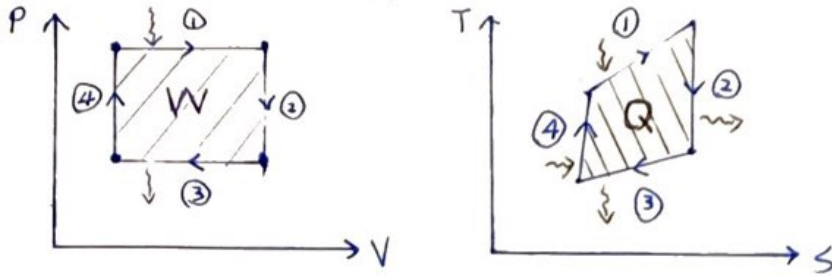
Cycles

Thermodynamic cycles involve several processes which return the system to its initial state, meaning all thermodynamic variables are returned to their initial values. In any cycle $\Delta U = 0$, the work done

$$W = Q_{in} - Q_{out}$$

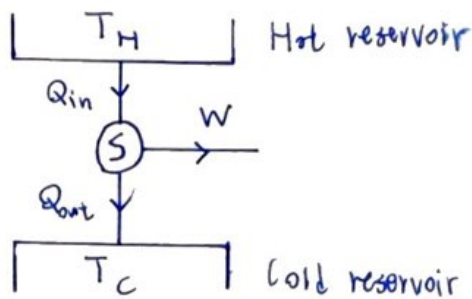
A general cycle involves putting the working substance through temperature variations. An example of a isobar-isochore cycle is shown in the next page. ① is an isobaric expansion, ② is isochoric cooling, ③ is isobaric compression, and ④ is isochoric heating. The heat flows in in steps ④ and ①, and out in ② and ③. In step ① work is done by the gas (expansion), and in step ③ work is done

On the gas (compression). The area of the P-V diagram is the work done by the working substance W , and the area of the T-S diagram is the heat supplied Q .



Heat Engines

General heat engines take heat and use it to do work — they are represented by clockwise cycles on the P-V diagram. A general 2-reservoir heat engine is shown below, it moves Q_{in} from the source reservoir and expels Q_{out}

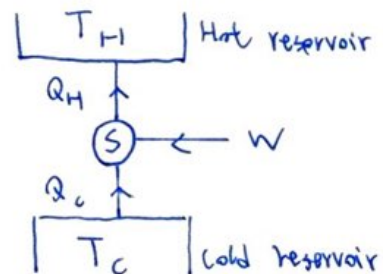
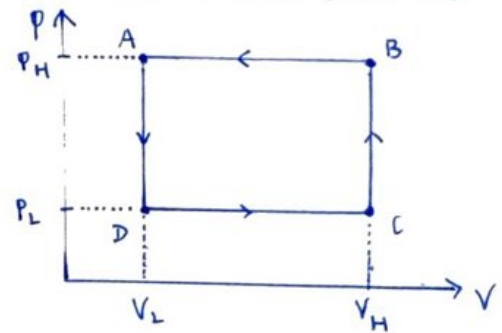


Efficiency: we define the efficiency of a heat engine as the fraction of work put in that is converted to useful work. By the first law this can be written

$$\eta = \frac{W}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

Heat Pumps & Refrigerators

Anticlockwise thermodynamic cycles in general can be used to cool a system — work must be done to move heat from a cold area to a hotter area. It is clear that the area of the P-V diagram is negative so work must be done on the working substance. This system could be used to cool the cold reservoir by cooling the system (isotherm) at D to below T_c , then placing the working substance in thermal contact with the cold reservoir, allowing it to isobarically expand as it warms up to T_c (D→C). Note in step B→A, work is done on the working substance to compress it and force heat out into the hot reservoir.



A heat pump and a refrigerator are the same.

- coefficient of performance: we define the coefficient of performance w to rate the efficiency of these systems. For a heat pump, the useful energy is Q_H , and for a refrigerator the useful energy is Q_c .

$$W_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_c}$$

$$W_R = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_c}$$

Unlike an efficiency, W_R can be > 1 , and W_{HP} has to be > 1 . Higher is better.

- Refrigeration cycle: Refrigeration cycles are most efficient when phase changes are used to transport more heat. An efficient cycle is:
 1. Compress a vapour to a supercritical fluid (SCF)
 2. Isobaric cooling behind fridge releases heat into room; SCF \rightarrow liquid phase
 3. JK free expansion, forms a mixed liquid/vapour phase at low temperature.
 4. Heating by contents of fridge causes evaporation to vapour phase

Carnot Cycle

The Carnot cycle is the idealized heat engine, with maximum possible efficiency. To maximise efficiency, the process has to be frictionless and reversible. For reversible heat flow to occur, the objects have to be at the same temperature. This means heat is transferred to the hot reservoir at a constant temperature T_H , and the cold reservoir at another constant temperature T_C . These isotherms should be connected by adiabats, so that it is reversible and isentropic. Any other process would involve heat transfer, reducing efficiency. The Carnot cycle shown on the right P

is:

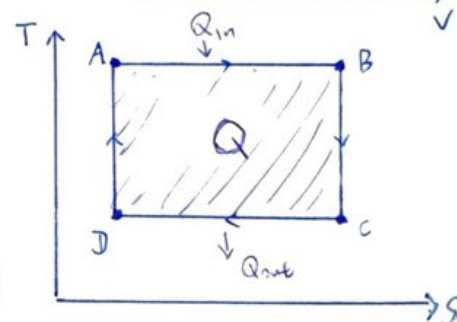
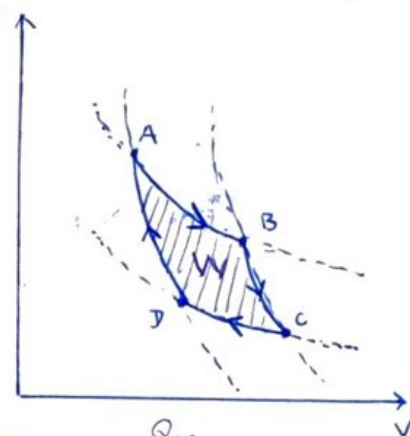
A \rightarrow B System held at heat T_H and isothermally expanded, absorbing heat from the hot reservoir

B \rightarrow C System adiabatically expanded and allowed to cool to temperature T_C

C \rightarrow D System isothermally compressed, expelling heat to the cold reservoir

D \rightarrow A System adiabatically compressed and heated

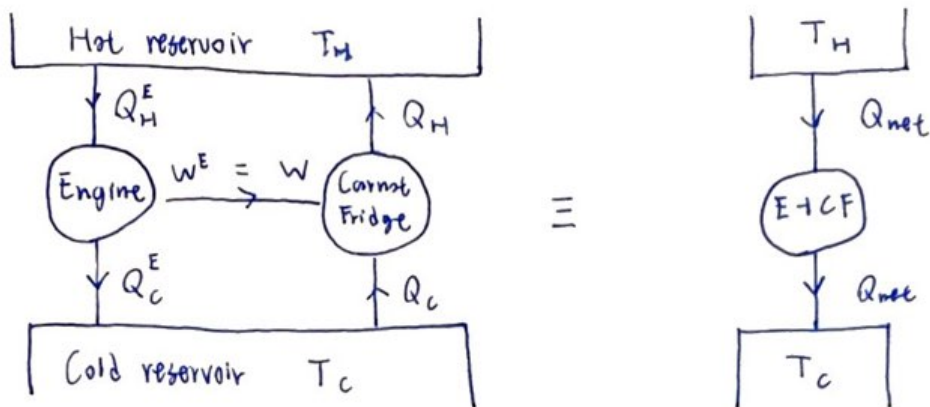
- Efficiency: The general way to derive efficiency η of any Carnot cycle is to look at the T - S diagram. The heat in is the integral of A-B line, and the heat out is the integral of C-D.



$$\eta_{Carnot} = 1 - \frac{\Delta S T_C}{\Delta S T_H} = 1 - \frac{T_C}{T_H}$$

Carnot's Theorem: The Carnot cycle is the most efficient cycle.

-Proof: A Carnot engine is run as a fridge - it takes work W and moves Q_c from the cold reservoir, and places $Q_H = Q_c + W$ in the hot reservoir. This engine has efficiency η_c when run forwards: $W = \eta_c Q_H$. This fridge is run by another engine of arbitrary efficiency η_E . It takes heat Q_H^E from the hot reservoir and uses it to produce work $W^E = \eta_E Q_H^E$ and waste heat Q_c^E . The figures below show this setup. It is clear that this system is equivalent to a combined system of engine plus Carnot fridge which takes Q_{net} from the hot reservoir to the cold. Next, notice $Q_{net} = Q_H^E - Q_H = Q_c^E - Q_c$



Given the definition of efficiency for the engine, $Q_H^E = W^E / \eta_E$. so

$$Q_H^E = \frac{W}{\eta_E} = \frac{\eta_c Q_H}{\eta_E}$$

We can now express the overall heat transfer Q_{net} in terms of the efficiencies of the components:

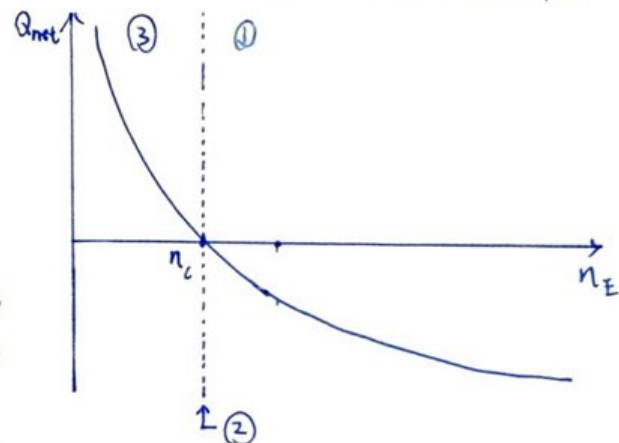
$$Q_{net} = Q_H^E - Q_H = \frac{\eta_c Q_H}{\eta_E} - Q_H = Q_H \left(\frac{\eta_c}{\eta_E} - 1 \right)$$

The figure below shows a plot of the above function. There is an intercept at $\eta_E = \eta_c$. The three regimes are:

1: $\eta_E > \eta_c$ - this is forbidden by the second law, as $Q_{net} < 0$ this represents heat flowing from cold to hot without work done.

2: $\eta_E = \eta_c$ - this is the case of Carnot engine efficiency and is the highest possible.

3: $\eta_E < \eta_c$ - lower efficiency engines are possible, but they are irreversible as heat is moved from hot to cold.



3.7 Adiabatic Expansion

We look at the expansion of real gases in three cases:

- Regular adiabatic expansion
- Free expansion into a vacuum
- Forced expansion into another gas - called throttling

This section will show adiabatic does not always imply isentropic, we will also see temperature changes which don't occur for the ideal gas. The results are summarised

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V \right]$$

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$$

- Adiabatic Expansion: This is the familiar adiabatic expansion we saw earlier - a gas expands against an environment with no heat flow (this is isentropic). We want to see how temperature changes with volume i.e.

$$\left(\frac{\partial T}{\partial V}\right)_S$$

We know $dS=0$ at constant entropy, so let $S = S(V, T)$, then

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT = 0$$

Next use the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$, and $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ to show

$$\left(\frac{\partial P}{\partial T}\right)_V dV = -\frac{C_V}{T} dT \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V$$

This coefficient is always < 0 , so gases always cool under adiabatic expansion

- Free Expansion: Consider a container with a barrier in the middle and one side full of gas. When the barrier is removed the gas expands into the vacuum. This process is irreversible and non-quasistatic, as the gas cannot be re-compressed without doing work, and it's not in equilibrium during the expansion $\rightarrow \Delta S > 0$

How can we work out the temperature change? The internal energy and temperature must be the same as the gas has done no work to expand. Define the Joule coefficient

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U$$

We know $du=0$ at constant internal energy, so let $u = u(V, T)$, then

$$du = \left(\frac{\partial u}{\partial V}\right)_T dV + \left(\frac{\partial u}{\partial T}\right)_V dT = 0$$

Using $c_V = T \left(\frac{\partial u}{\partial T}\right)_V$

$$\left(\frac{\partial u}{\partial V}\right)_T dV = -c_V dT \rightarrow \left(\frac{\partial T}{\partial V}\right)_u = \eta = -\frac{1}{c_V} \left(\frac{\partial u}{\partial V}\right)_T$$

Next, differentiate the first law dU and re-arrange using Maxwell relation

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P$$

giving

$$\eta = -\frac{1}{c_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]$$

This is similar to the adiabatic piston equation but with an extra $+ P/c_V$

- Ideal gas $\eta_{\text{ideal}} = 0$ so there is no cooling
- Van der Waals gas $\eta_{\text{vdw}} = -aN^2/c_V V^2$ so it cools under adiabatic free expansion.

• Throttling Consider a container with a barrier in the middle and gas on both sides - the gas in the left has pressure P_1 and is forced through a hole to the side with pressure $P_2 > P_1$. In this case, the gas does work on the right hand side as it expands into it.

Define the Joule-Thompson coefficient

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

where we have noted that the process to be isenthalpic. Look for dS let $S = S(T, P)$ then

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Next use the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, thermal expansivity $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ and the formula $\frac{c_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P$

$$dS = -\beta V dP + \left(\frac{c_P}{T}\right)_P dT \rightarrow dS = -\beta V dP - \frac{c_P}{T} dT$$

Recognize $dH = T dS + V dP = 0$

$$dH = -T\beta V dP + T \left(\frac{c_P}{T}\right)_P dT + V dP = 0 \rightarrow \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{c_P} (\beta T - 1)$$

As $dP < 0$ when the gas decompresses, we see the gas cools ($dT < 0$) when $\beta T > 1$, and heats when $\beta T < 1$. A gas would heat when highly compressed and allowed to expand - its reduced PE goes to increased temperature. Rarefied gasses have a net attraction so expanding this cools it.

