Fall 2019

Physics 304

Lec #5: Heat engine

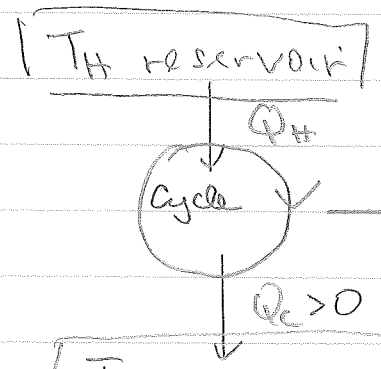
Classical Thermodynamics & entropy

Engine transforms energy into work. Working substance we take to be ideal gas.

Thermodynamic cycle – series of processes returning system to same thermodynamic state: $(U, V, S)_{engine}$.

commercial steam engine invented by Newcomen & Watt, 1712

Idealized cycle of quasi-static processes. Closed loop in P, V diagram



$W_e \equiv$ work done by engine

$\longrightarrow W_e = -W = Q_H - Q_c$

$\Delta U = 0 = Q + W$
$= Q - W_e$
$= Q_H - Q_c - W_e$

$Q_c \equiv$ heat lossed by system

Efficiency $e \equiv \dfrac{W_e}{Q_H} = \dfrac{Q_H - Q_c}{Q_H} = 1 - \dfrac{Q_c}{Q_H}$

What is maximum efficiency? Carnot cycle.

wikipedia: Nicolas Léonard Sadi Carnot (1796 – 1832) was a …often described as the "father of thermodynamics." One book ``Reflections on the Motive Power of Fire" (1824), (@age 27), the first successful theory of the maximum efficiency of heat engines. He laid the foundations of an entirely new discipline, thermodynamics. Carnot's work attracted little attention during his lifetime, but it was later used by Clausius and Kelvin to formalize the second law and define the concept of entropy.

Maximum efficiency is <u>reversible</u> ($\Delta S = 0$) cycle.

$$\Delta S = \Delta S_{engine} + \Delta S_{env.} = 0$$

for cycle, $\Delta S_{engine} = 0$ so $\Delta S = \Delta S_{env}$

(ideal gas) $\Delta S = \frac{Q}{T}$

quasi-static, isothermal expansion

French so don't pronounce 't'

<u>Carnot cycle</u>

		ΔS_{env}
(a)	isothermal expansion	$-Q_H/T_H$
(b)	adiabatic expansion	0
(c)	isothermal compression	$+Q_C/T_C$
(d)	adiabatic compression	0

$$\Delta S_{env} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0$$

equality for reversible

Second law $\Delta S_{env} \geq 0$

$$\frac{Q_C}{T_C} \geq \frac{Q_H}{T_H}$$

$$\boxed{\varepsilon \leq 1 - \frac{T_C}{T_H}}$$

Physics 301: Carnot Cycle September 20, 2020

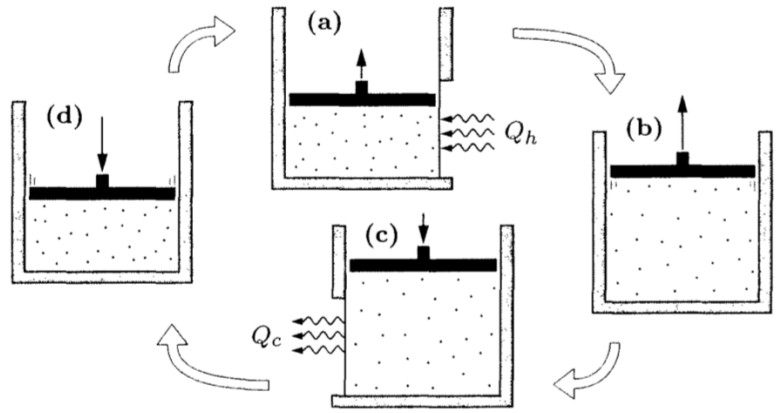


Figure 4.2. The four steps of a Carnot cycle: (a) isothermal expansion at T_h while absorbing heat; (b) adiabatic expansion to T_c; (c) isothermal compression at T_c while expelling heat; and (d) adiabatic compression back to T_h. The system must be put in thermal contact with the hot reservoir during step (a) and with the cold reservoir during step (c).

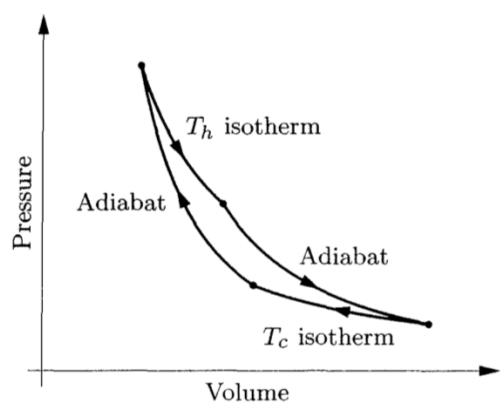


Figure 4.3. *PV* diagram for an ideal monatomic gas undergoing a Carnot cycle.

Figure 1: From Schroeder

- "Reversible" is an idealization in which the working substance (e.g. ideal gas) is cycled so slowly (quasi-statically) that it and the hot and cold reservoirs remain near equilibrium. The idealized Carnot cycle is reversible and there is no change in total entropy $\Delta S = 0$. No real engine can be reversible: all mechanical motions must have some friction.

- An ideal gas taken around a Carnot cycle realizes the maximum possible efficiency $1 - T_c/T_h$.
- Run in reverse, work is used to move heat from the cold reservoir to the hot one, that is it is an ideal, Carnot refrigerator.
- From Schroeder: "Although a Carnot cycle is very efficient, it's also horribly impractical. The heat flows so slowly during the isothermal steps that it takes forever to get a significant amount of work out of the engine. So don't bother installing a Carnot engine in your car; while it would increase your gas mileage, you'd be passed on the highway by pedestrians."

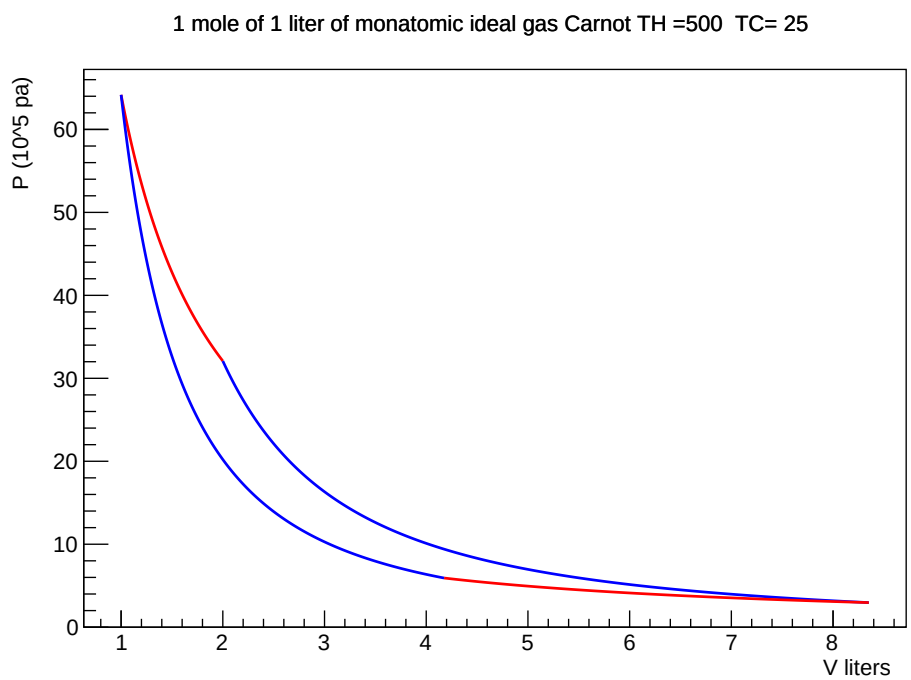
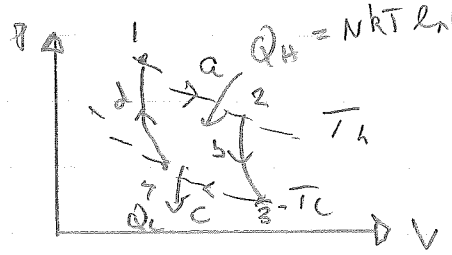


Figure 2: Carnot problem

sketch of Carnot cycle:



W_e = area enclosed

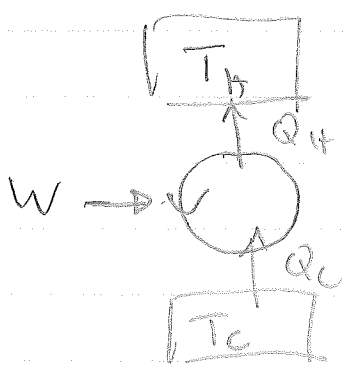
adiabatic $PV^{\gamma} = \text{const.}$ $\gamma = \left(\frac{f+2}{f}\right)$

Entropy balance:

step	engine ΔS_{engine}	hot ΔS_H	cold ΔS_C
a	Q_H/T_H	$-Q_H/T_H$	0
b	0	0	0
c	$-Q_C/T_C$	0	$+Q_C/T_C$
d	0	0	0

$\Delta S_{env} = \Delta S_H + \Delta S_C = 0$

Carnot refrigerator



Coefficient of performance $COP = \frac{Q_C}{W} = \frac{1}{\frac{Q_H}{Q_C} - 1}$

$$COP \leq \frac{1}{\frac{T_H}{T_C} - 1}$$

Physics 301: Carnot Cycle and Absolute Zero September 20, 2020

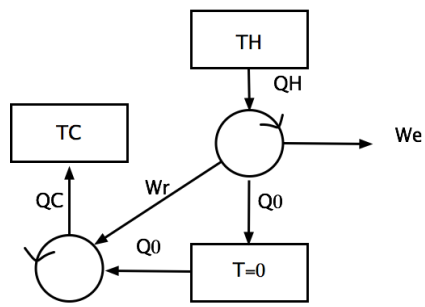


Figure 1: Combined Carnot engine and refrigerator

Resevoir must stay at the same temperature which means that they must be so large that any heat removed or added is negilible compared to the total energy of the resevoir. For a system to remain at absolute zero, any energy added must be removed. Consider the combined cycle of Carnot engine and Carnot refrigerator in the figure. We have from energy conservation

$$W_e = Q_H - Q_0 - W_r$$

$$W_r + Q_0 = Q_C$$

So

$$W_e = Q_H - Q_C$$

and the efficiency of the engine is

$$e = \frac{Q_H}{W_e} = \frac{Q_H}{Q_H - Q_c}$$

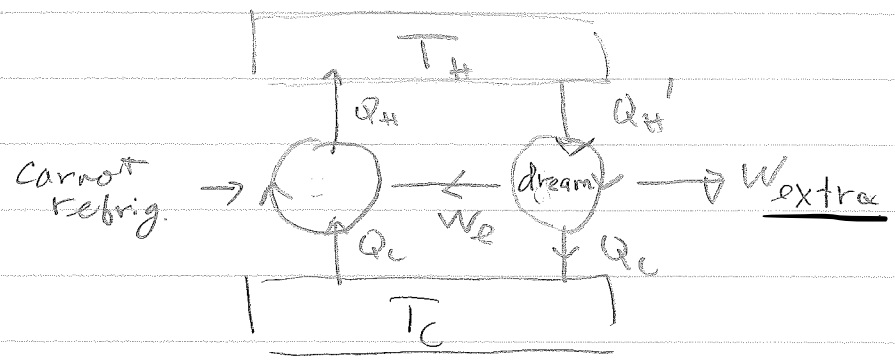
The change in entropy for hot and cold resevoirs must sum to zero giving

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

So the combined Carnot engine plus refrigerator has the Carnot efficiency,

$$W_e = 1 - \frac{T_C}{T_H}$$

Proof that Carnot has maximum efficiency.
Suppose "dream" engine $e_d > e_c$.
Combine with Carnot refrigerator.



"Work from nothing"

$W_d = W_e + W_{extra}$

energy conservation: $Q_H' - Q_H = W_{extra}$

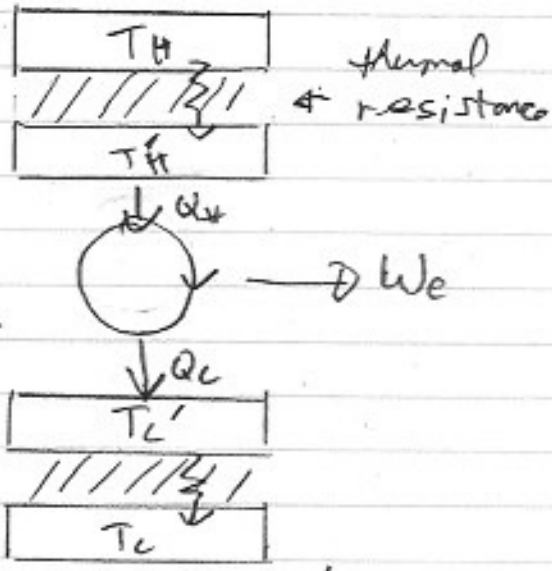
Violates 2nd law:

$$\Delta S = -\frac{Q_H'}{T_H} + \frac{Q_c}{T_c} < -\frac{Q_H}{T_H} + \frac{Q_c}{T_c} = 0$$

$$\boxed{\text{perpetual motion machine of } 2^{ND} \text{ kind violates } 2^{ND} \text{ law.}}$$

First kind violates energy conservation

Example (4.6) Realistic, non-reversible engine model! Working substance at temperature slightly below, above reservoirs



(a) $\frac{Q_H}{\Delta t} = k(T_H - T_H')$ cycle $2\Delta t$

(b) $\frac{Q_c}{\Delta t} = k(T_c' - T_c)$

(a),(b) conduction of heat across resistive layer

dim constant $k = \frac{J}{s}\left(\frac{1}{K}\right)$

energy conservation $W_e = Q_H - Q_c$

engine cycle $\Delta S_{engine} = 0$

from a/b

$$\frac{Q_H}{T_H'} - \frac{Q_c}{T_c'} = 0 \Rightarrow \frac{Q_H}{Q_c} = \frac{T_H'}{T_c'} = \frac{T_H - T_H'}{T_c' - T_c} \quad (c)$$

power of engine

$$P = \frac{W_e}{2\Delta t} = \frac{k}{2}\left(T_H - T_H' + T_c - T_c'\right)$$

write as function of T_H'. Solve T_c' from (c)

$$\frac{T_c'}{T_H'} = \frac{T_c}{2T_H' - T_H}$$

write $P(T_H')$

$$P(T_H') = \frac{k}{2}\left[T_H - T_H' + T_C - \frac{T_C T_H'}{2T_H' - T_H}\right]$$

<u>optimize power</u>

$$\frac{2}{k}\frac{dP}{dT_H'} = -1 - \frac{T_C}{2T_H' - T_H} + \frac{2T_C T_H'}{(2T_H' - T_H)^2} = 0$$

quadratic

$$T_H'^2 - T_H' T_H + \frac{1}{4} T_H (T_H - T_C) = 0$$

$$T_H' = \frac{1}{2}\left(T_H \pm \sqrt{T_C T_H}\right); \quad T_H' > T_C \text{ physical solution +}$$

then $$\frac{T_C'}{T_H'} = \frac{T_C}{2T_H' - T_H} = \frac{T_C}{\sqrt{T_H T_C}} = \sqrt{\frac{T_C}{T_H}}$$

efficiency

$$e_e = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C'}{T_H'} = 1 - \sqrt{\frac{T_C}{T_H}}$$

less than Carnot

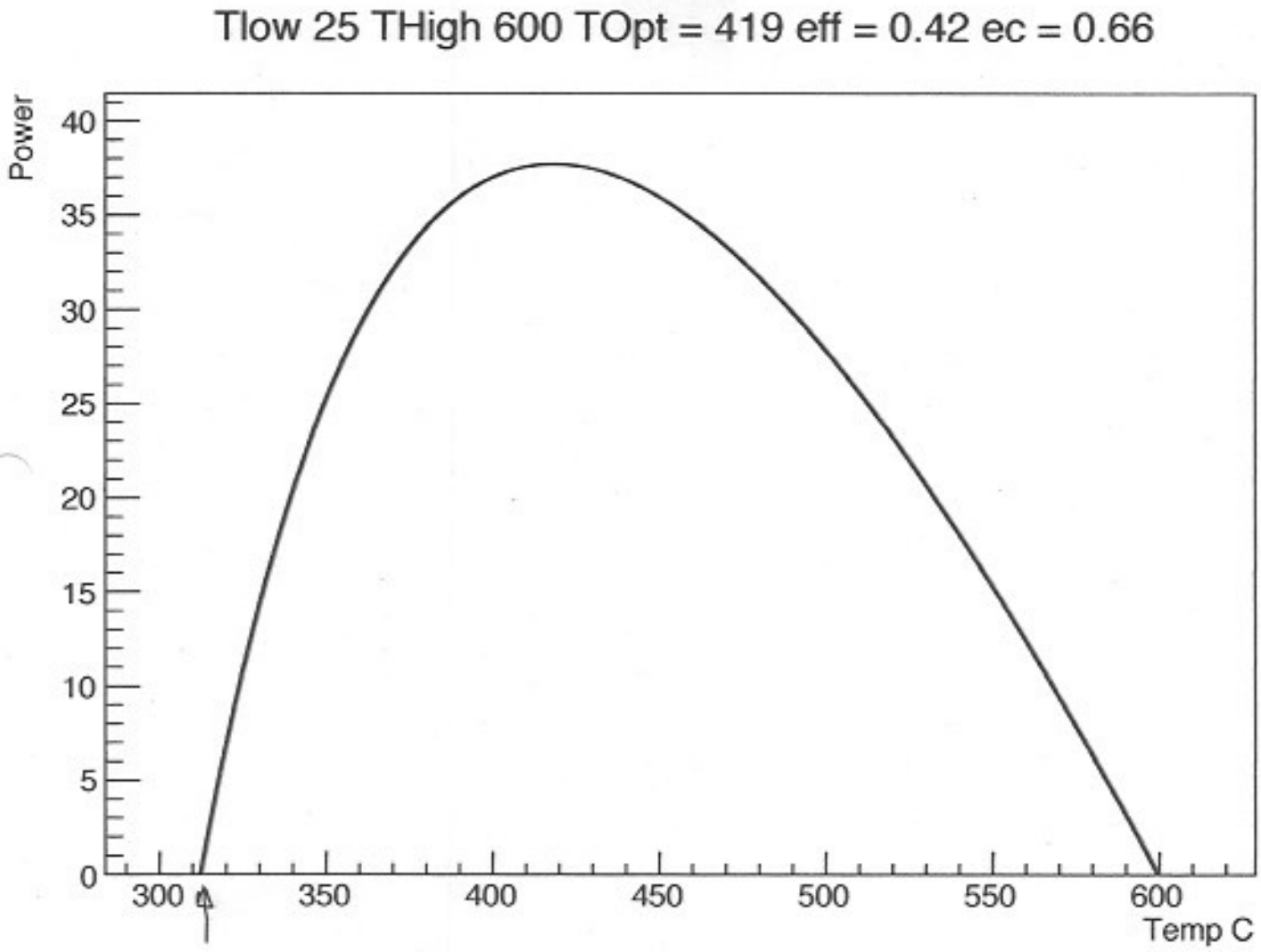
for $T_H = 600°C$ $\quad T_C = 25°C$

$e_e = 44\%$

$e_c = 66\%$

which is close to a real power plant.

5.6a



Power > 0

$T_c' > T_c$

Physics 301: Otto Cycle September 21, 2020

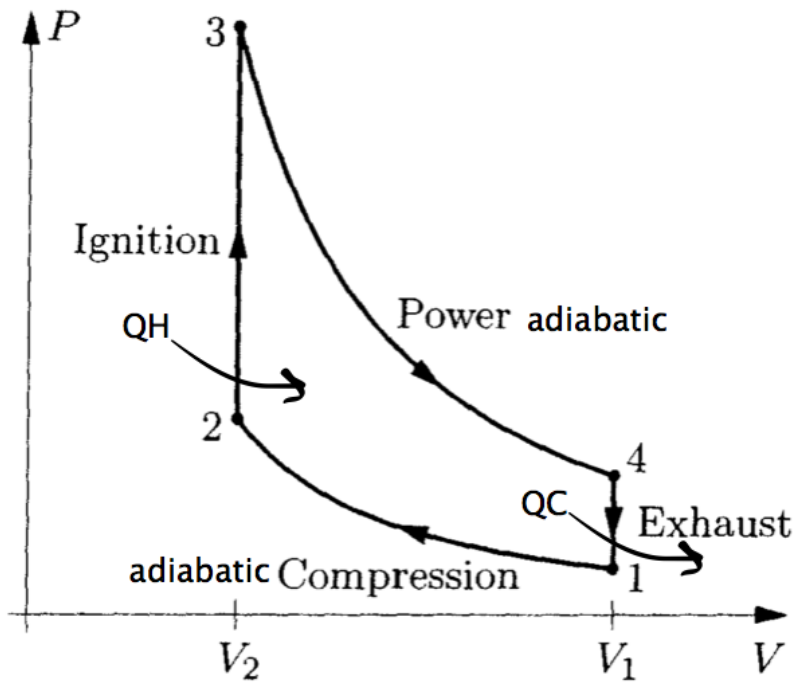


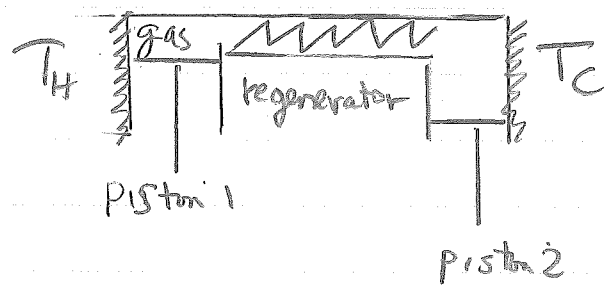
Figure 1: Otto cyle,adapted from Schroeder. Typical gasoline engine compression ratios are $V_1/V_2 = (8 \sim 10)$

On problem 4.18, you will show that the efficiency is

$$e_{Otto} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

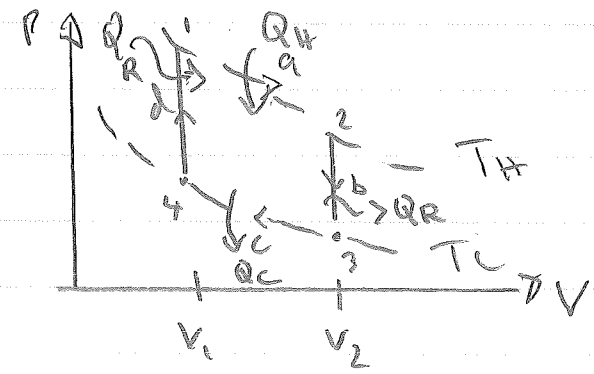
Sterling Engine "hot air engine"

Robert + James Sterling, circa 1843



regenerator – heat exchanger could be metal mesh

Thermodynamic cycle



$$W_1 = \int_1^2 P\,dV = NkT_H \ln\frac{V_2}{V_1} = Q_H$$

$$W_2 = -NkT_C \ln\left(\frac{V_2}{V_1}\right) = -Q_C$$

so

$$\frac{+Q_C}{Q_H} = \frac{T_C}{T_H}$$

$$Q_R = \frac{f}{2}Nk\left(T_H - T_C\right)$$

If Q_R is not reabsorbed

$$e_{not} = \frac{W_1 + W_2}{Q_H + Q_R} = \frac{W_1 + W_2}{W_1 + Q_R} = \frac{(T_H - T_C)\ln\frac{V_2}{V_1}}{T_H \ln\left(\frac{V_2}{V_1}\right) + \frac{f}{2}(T_H - T_C)}$$

if Q_R is perfectly transferred by regenerator,

$$e_{Sterling} = 1 + \frac{W_2}{W_1} = 1 - \frac{T_C}{T_H} = e_{carnot}!$$

Some

<u>Modern applications</u> –

Concentrated solar power CSP-sterling $e \sim 30\%$

Swedish submarines

<u>Sound Energy</u> Netherlands Forbes, 2019
air-conditioning from waste or
solar heat.

Physics 301: Sterling Engine September 13, 2020

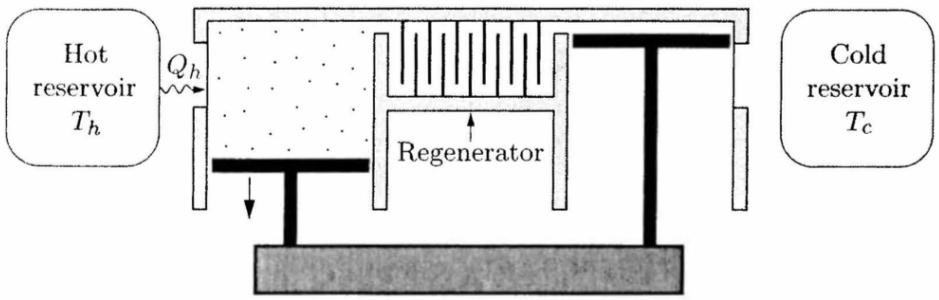


Figure 1: From Schroeder. A Stirling engine, shown during the power stroke when the hot piston is moving outward and the cold piston is at rest. (For simplicity, the linkages between the two pistons are not shown.)

Some Modern Developments:

- "A thermoacoustic Stirling heat engine" S. Backhaus & G. W. Swift, Nature Article
- Commercial Application: Soundenergy

Idealized Steam: Engine Rankine Cycle

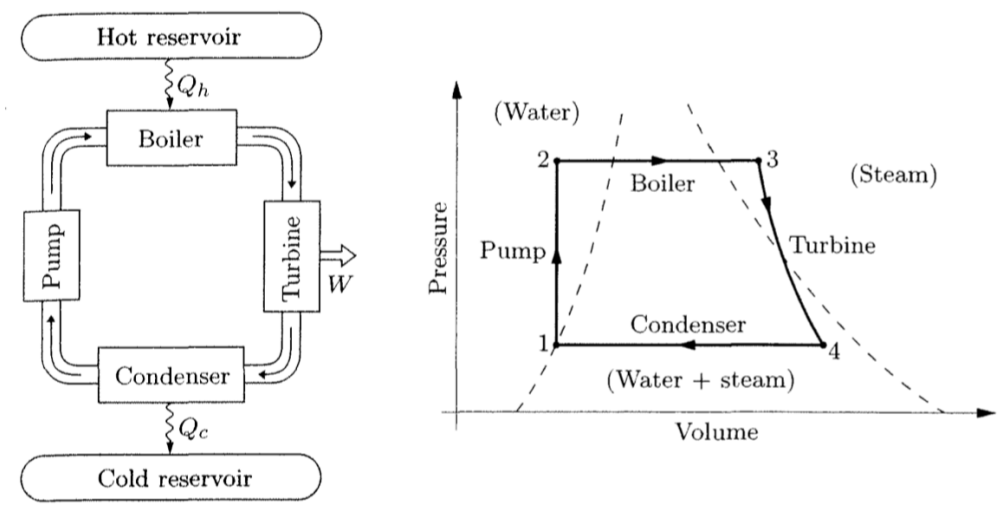
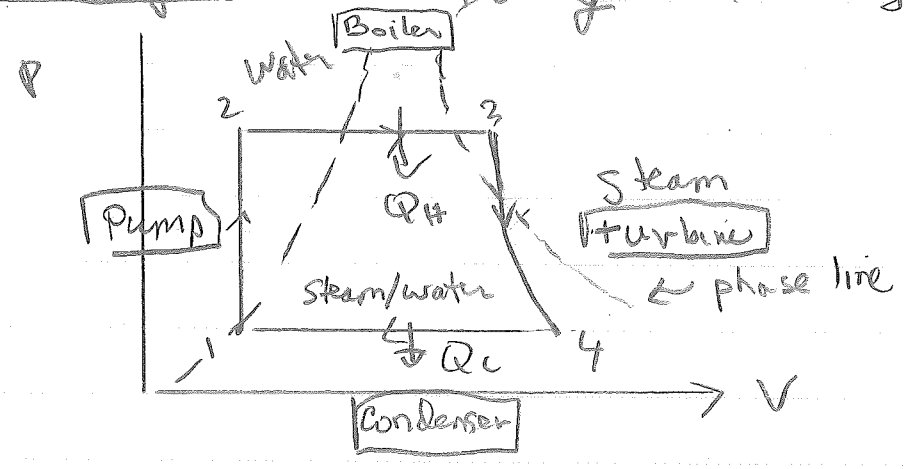


Figure 2: From Schroeder. Schematic diagram of a steam engine and the associated PV cycle (not to scale), called the Rankine cycle. The dashed lines show where the fluid is liquid water, where it is steam, and where it is part water and part steam.

Steam engine idealized by Rankine cycle



$$e = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_c}{Q_H}$$

at constant pressure $H = U + PV$

change in enthalpy $\Delta H = \Delta Q$

$$\frac{Q_c}{Q_H} = \frac{H_4 - H_1}{H_3 - H_2}$$

$H_2 \approx H_1$ ignoring PV of pump

$$\approx \frac{H_4 - H_1}{H_3 - H_1}$$

H for water, steam obtained from tables

typical numbers give $e \sim 50\%$

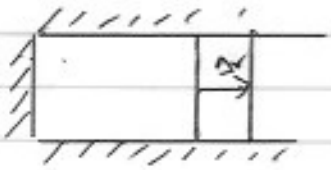
Compare $T_H = 600\,^\circ C$, $T_c = 20\,^\circ C$ $\Big\}$ $e_c = 66\%$

Actual fossil fuel power plants get $e \approx 40\%$

nuclear $e \approx 34\%$

Joule-Thomson, Throttling process

Expansion of gas cylinder insulated



$$\Delta U = -P\Delta V + \underset{0}{\underset{\shortparallel}{Q}}$$

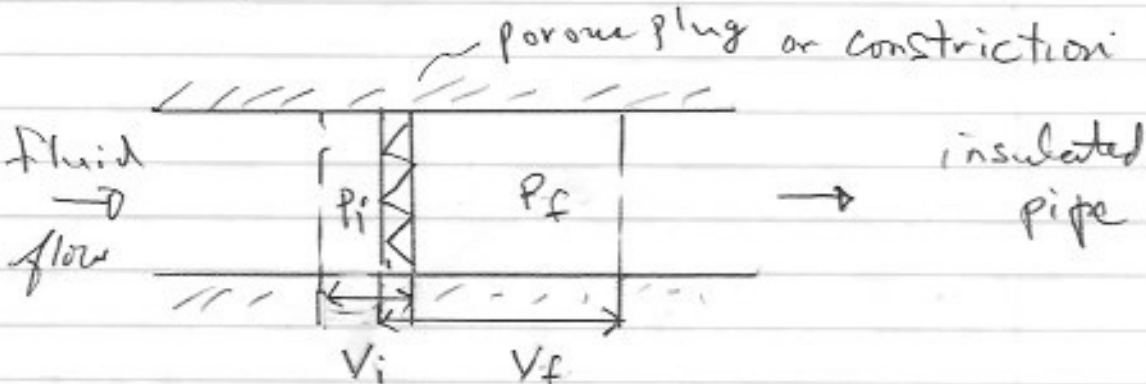
$$Nk(T_f - T_i) = -P\Delta V$$

gas cools by expansion

Accidentally discovered in 1877 by Caillet, throttling process

leak of gas through small hole is cooled.

You can observe this by observing temperature of gas leaking out of bicycle tire with your finger.



$W = -P\Delta V$, $Q = 0$ so

$$U_f - U_i = -P_f V_f - (-P_i V_i) = P_i V_i - P_f V_f$$

$$U_f + P_f V_f = U_i + P_i V_i$$

enthalpy doesn't change $H_f = H_i$

No cooling for <u>ideal gas since</u>

$$H = U + PV$$

$$U = \frac{f}{2} NkT \qquad PV = NkT$$

$$H = \left(\frac{f}{2} + 1\right) NkT = \text{constant}$$

For non-ideal gas, Van der Waal molecular attractions give increase in potential energy, decrease in kinetic as gas expands.

$$dH = \overset{\left(\frac{\partial H}{\partial S}\right)_P}{T}\, dS + V\, dP$$

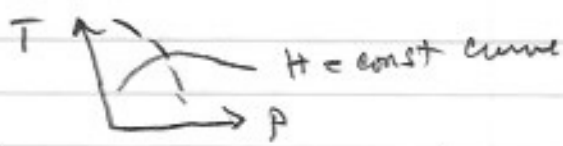
$dS = (dS/dT)_P dT + (dS/dP)_T dP$

recall $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

giving

$$dH = C_P\, dT + \left[T\left(\frac{\partial S}{\partial T}\right)_T + V\right] dP$$

So $H(T, P)$.



slope of constant H curve in T, P plane

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{-T\left(\frac{\partial S}{\partial P}\right)_T + V}{C_P}$$

then

Maxwell relation (Prob 5.12)

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

Coefficient of volume expansion α

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

so

$$dH = C_p\, dT + V(1-\alpha T)\, dp$$

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(T\alpha - 1)$$

for ideal gas $\quad pV = NRT$

$$p\left(\frac{\partial V}{\partial T}\right)_p = NR$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{NR}{p} = \frac{V}{T}$$

so <u>$\alpha T = 1$ for ideal gas</u>

ideal gas $\quad dH = C_p\, dT$

$\Delta H = 0 \Rightarrow \Delta T = 0$ and $\mu = 0$

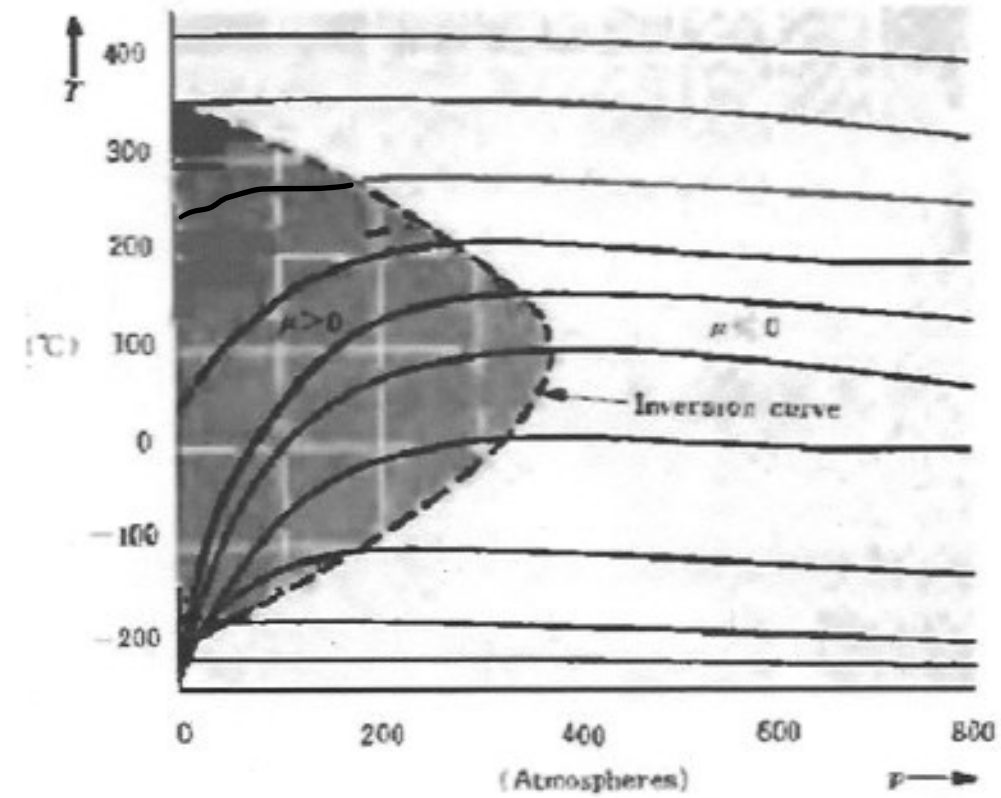
flat curve in T, P plane

<u>Non-ideal gas equation of state, see p. 1.17</u>

constant enthalpy curves

From Reif, Fundamentals of Statistical and Thermal Physics

lines of constant H in T, P plane for N_2 gas



slope $\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\alpha - 1)$ changes sign at inversion curve. Throttling cools gas in $\mu > 0$ (dark) region.

Physics 301: Constant Enthalpy curves September 22, 2020

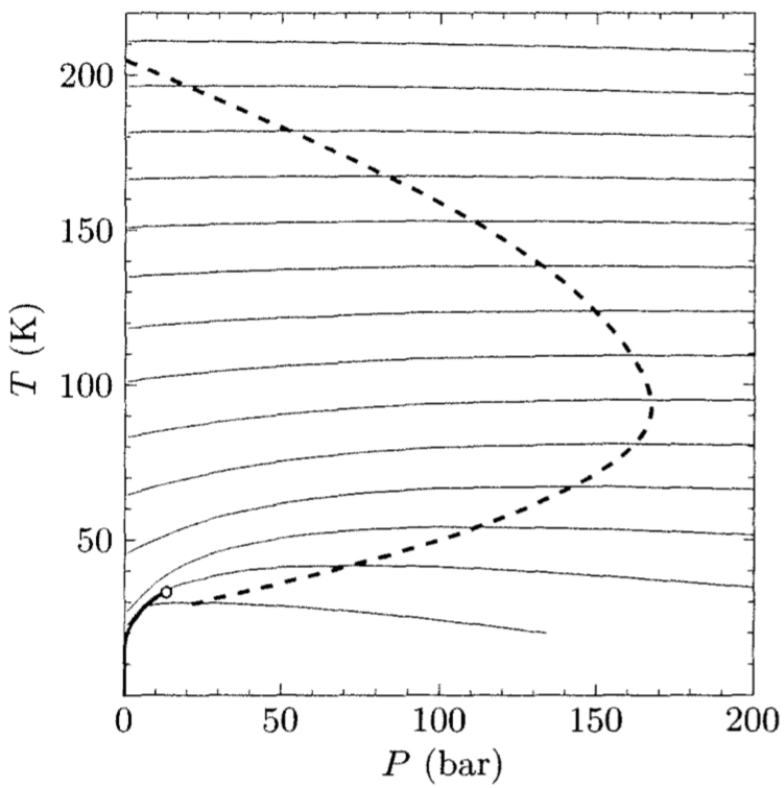


Figure 1: From Schroeder– constant enthalpy curves for Hydrogen.

Physics 301: Joule-Thomson Liquification September 22, 2020

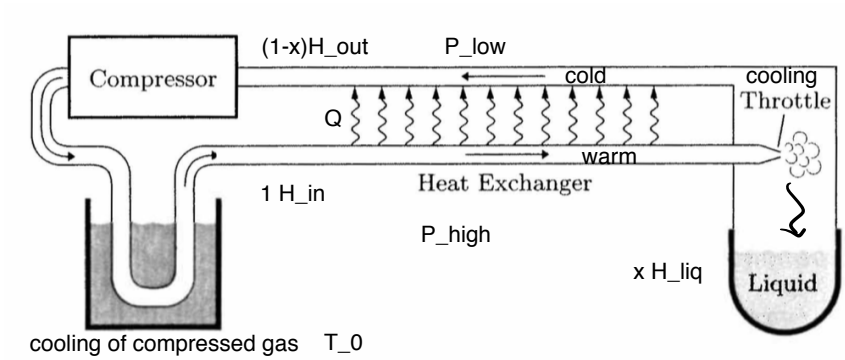


Figure 1: From Schroeder (Fig 4.11) – Hampson-Linde Cycle

Heat Q is exchanged at constant high or low pressure, so enthalpy is conserved in flow. For 1 mole of gas and liquified fraction x

$$1H_{in} = xH_{liq} + (1-x)H_{out}$$

$$x = \frac{H_{out} - H_{in}}{H_{out} - H_{liq}}$$

For further reference, see "Basics of Joule-Thomson Liquefaction and JT Cooling", Waele

Joule-Thomson liquification

Table 4.5 gives enthalpy for Nitrogen

Take $P_{high} = 100$ bar, $P_{low} = 1$ bar

$T_0 = 300K$

$H_{liq} = -3407$ J/mol $\quad T = 77K$

$H_{in} = 8174$ J/mole $\quad T = 300K$, $P = 100$ bar

$H_{out} = 8717$ J/mole $\quad T = 300K$, $P = 1$ bar

gives $x = 0.045$

lower $T_0 = 200K$, $\quad x = 0.15$

helps to pre-cool gas