2. Thermodynamics, 4

lecture 11, September 22, 2017

housekeeping

exam 1 is in about 1.0 weeks

- Friday, 29 September
- Relativity and Thermodynamics…through Monday's content

Some changes:

- Made some changes to ch 19 problems
- I'll tell you tomorrow AM if there are any more for ch 20

Shameless plug:

- ISP220

Honors option

- we're good.

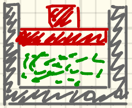
Gripes

REVIEW OF ...STUFF

Specific heats $Q = cm\Delta T$

Latent heats $Q = mL_{F,V}$

Systems of interest

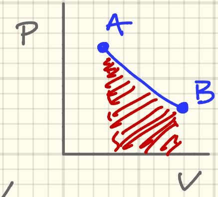


W done by gas

P

V

$$W_{gas} = \int_A^B P\,dV$$



1st Law of Thermodynamics

$$\Delta Q = \Delta U + \Delta W$$

internal energy typically characterized by temperature

State Functions

U, T, P, V

PARTICULAR FOCUS:

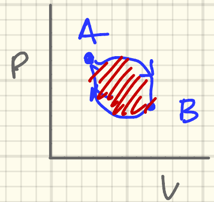
1) isothermal processes $\qquad \Delta T = 0 \Rightarrow \Delta u = 0$

$\Delta Q = \Delta W$

2) adiabatic processes $\qquad \Delta Q = 0$

$\Delta u = -\Delta W$

3) cycles



Ideal Gas

identical, non-interacting, numerous, point-like masses

$$PV = n\frac{2}{3}\langle K \rangle$$

$$\left.\begin{aligned} PV &= nRT \\ PV &= NkT \end{aligned}\right\}$$ relates T to $\langle K \rangle$

work done $\quad \Delta W = \int_A^B \frac{nRT}{V}\, dV = nRT \ln\left(V_B/V_A\right)$

molar specific heats

$$\Delta Q = nC_v \Delta T \Big|_V \qquad \Delta Q = nC_p \Delta T \Big|_P$$

$$= \tfrac{3}{2} nRT \qquad\qquad = \tfrac{5}{2} nRT$$

adiabatic processes

$$PV^{\gamma} = \text{constant} \qquad \gamma = C_p/C_v$$

$$W = \frac{P_B V_B - P_A V_A}{1-\gamma}$$

2nd LAW OF THERMODYNAMICS

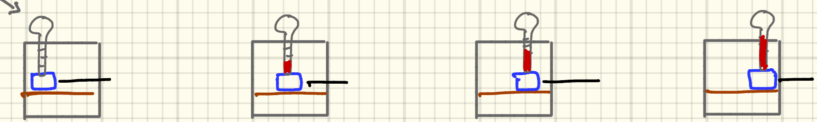
very subtle

no distinct "arrow of time"

$\xrightarrow{t}$ identical to

$\xleftarrow{t}$ in equations

thermometer



$\xrightarrow{t}$ gets hotter

REVERSIBILITY & IRREVERSIBILITY

"leave no change on the environment"

→ always unsatisfying

until a new concept...

stay tuned

feature of any process that generates heat

1st law of thermodynamics doesn't include this "running down" aspect

If you're cold in February → cuddle up to a snow drift

... consistent with 1st law

... not a way to get warm

THERMODYNAMICS ESTABLISHES A DIRECTION FOR TIME

Heat Engines

any device that converts thermal energy → mechanical energy

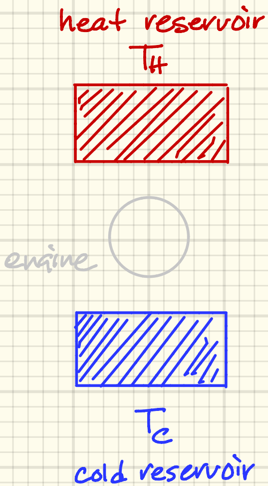
All the same

1. heat is absorbed from a source at high T

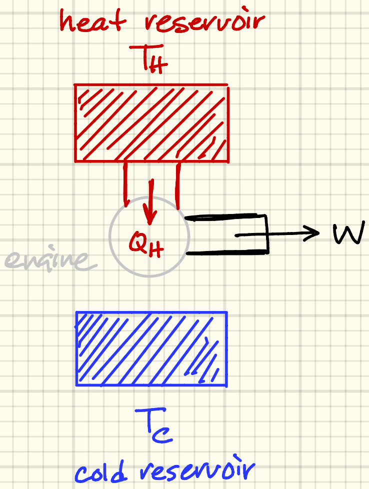
2. work is done

3. waste heat is expelled to a sink at lower T

"Engine" ⇒ over and over .. a cycle



An abstract engine



PERFECT ENGINE

$$\Delta U = \Delta Q - \Delta W$$

since $\Delta T = 0 \Rightarrow \Delta U = 0$

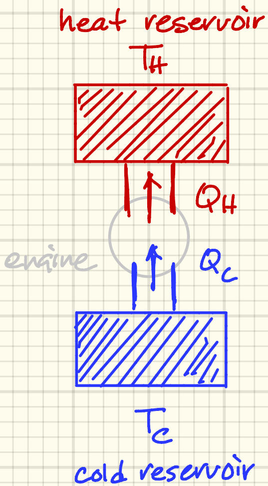
always @ T_H

$$\Delta Q_H = \Delta W$$

It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of thermal energy from a reservoir and the performance of an equal amount of work.

"Kelvin-Planck Statement"

2nd LAW OF THERMODYNAMICS

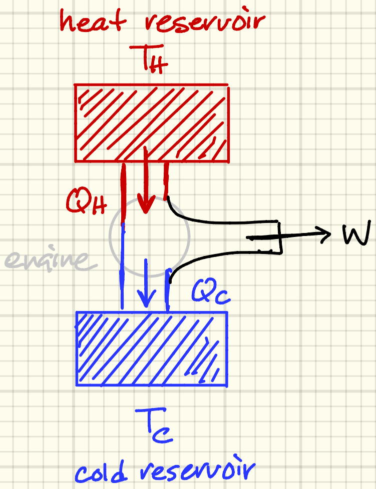


PERFECT REFRIGERATOR

2nd LAW OF THERMODYNAMICS

It is impossible to construct a refrigerator, in a cycle, to produce no other effect than to transfer thermal energy from a cold object to a hot object.

"Clausius Statement"



(actually $Q_c < 0$ ...

$$\epsilon = \frac{Q_H + Q_c}{Q_H} = \frac{Q_H - |Q_c|}{Q_H})$$

REALISTIC ENGINE

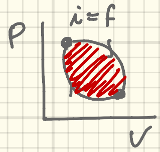
cyclical $\rightarrow$ $i \rightarrow f \rightarrow i$ $\quad T_i = T_f$

$U_i = U_f$

$\Delta U_{net} = 0$

$$\Delta Q = \Delta U + \Delta W$$

$$Q_H - Q_c = W_{net}$$



THERMAL EFFICIENCY

$$\epsilon = \frac{\text{what you get}}{\text{what you paid}}$$

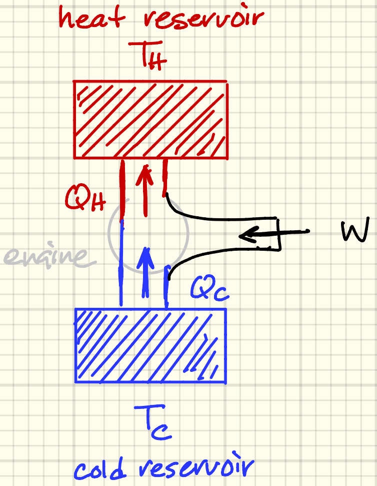
$$\epsilon = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{Q_H}{Q_c}$$

typical: $\epsilon(\text{auto}) \sim 20 - 30\%$

$\epsilon(\text{diesel}) \sim 30 - 40\%$

2^{nd}_{1} STATEMENT

$\Rightarrow$ ϵ cannot be 1.0



REALISTIC REFRIGERATOR

a heat engine in reverse...

Q_c absorbed by engine

W work done on engine

$|Q_h|$ energy rejected by system

$$|Q_h| = Q_c + W$$

$$K \doteq \frac{Q_c}{W} = \frac{Q_c}{Q_H + Q_c} = \text{coefficient of performance}$$

2^{nd}_{1} STATEMENT

$\Rightarrow$ K cannot be ∞

$$2^{nd}_1 \equiv 2^{nd}_2$$

lack of perfect engine $\Rightarrow$ lack of perfect refrigerator

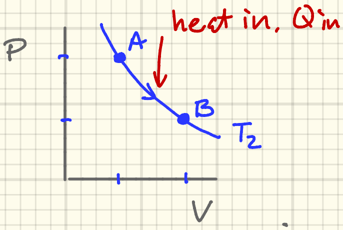
$\Downarrow$

energy cannot flow from cold to hot reservoirs — on its own

There is a best engine

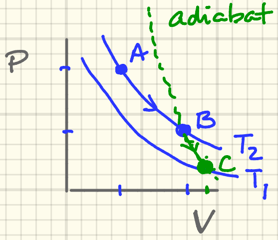
Nicolas Carnot 1824

"Carnot Cycle"



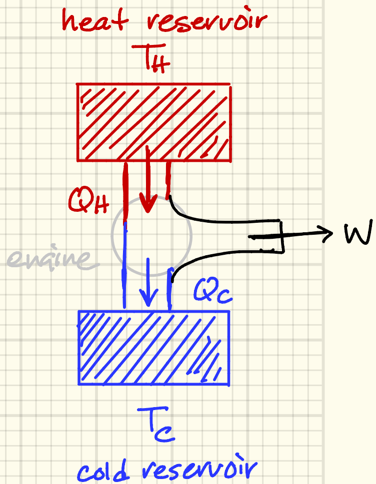
isothermal expansion

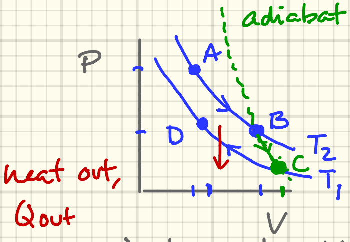
$P_AV_A = P_BV_B$



adiabatic expansion

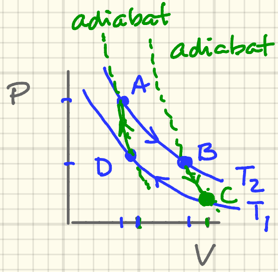
$P_BV_B^\gamma = P_CV_C^\gamma$





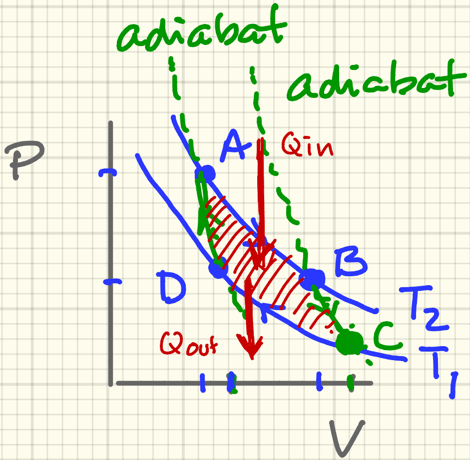
isothermal compression

$P_CV_C = P_DV_D$



adiabatic compression

$P_DV_D^\gamma = P_AV_A^\gamma$

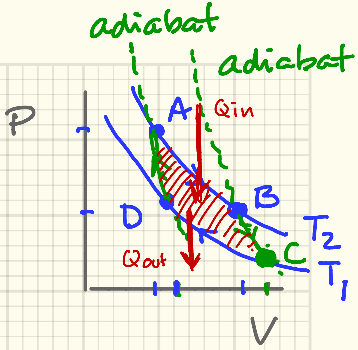


$$\epsilon = \frac{W}{Q_{in}}$$

$$= \frac{Q_{out} - Q_{in}}{Q_{in}}$$

$$\epsilon = 1 - \frac{Q_{out}}{Q_{in}}$$

analyze as ideal gas example



$A \to B$ isothermal expansion

$$\Delta U = \Delta Q - \Delta W = 0$$

$$W_{AB} = Q_{in}$$

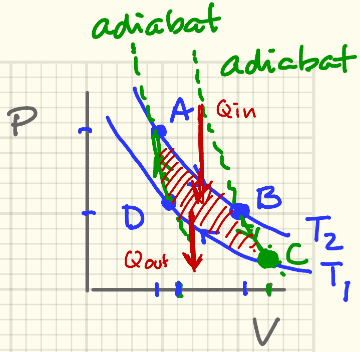
$$W_{AB} = \int_A^B P\,dV = \int_A^B \frac{nRT_2}{V}\,dV = nRT_2 \ln\left(\frac{V_B}{V_A}\right) > 0$$

C-D isothermal compression

$$W_{CD} = |Q_{out}|$$

$$W_{CD} = nRT_1 \ln\left({}^{V_D}/_{V_C}\right) < 0$$

$$Q_{out} = nRT_1 \ln\left({}^{V_C}/_{V_D}\right) = -W_{CD}$$



B – C adiabatic expansion

$$W_{BC} = \frac{nR}{\gamma - 1}(T_2 - T_1)$$

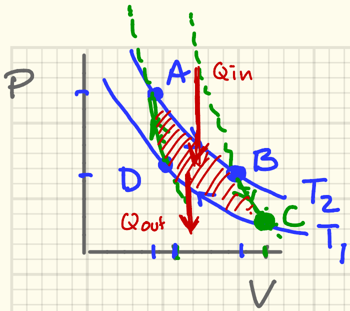
and

$$\Delta U = -n c_v (T_2 - T_1) = n c_v (T_1 - T_2)$$

gets cooler

D – A adiabatic compression

ditto



	W (by gas)	Q (added)	ΔU
A → B	$nRT_2 \ln(V_B/V_A)$	$Q_{in} = nRT_2 \ln(V_B/V_A)$	0
B → C	$\frac{nR}{\gamma-1}(T_2 - T_1)$	0	$nC_v(T_1 - T_2)$
C → D	$nRT_1 \ln(V_D/V_C)$	$Q_{out} = nRT_1 \ln(V_D/V_C)$	0
D → A	$\frac{nR}{\gamma-1}(T_1 - T_2)$	0	$nC_v(T_2 - T_1)$
net change	$nR(T_2-T_1)\ln\left(\frac{V_B}{V_A}\right)$	$nR(T_2-T_1)\ln\left(\frac{V_B}{V_A}\right)$	0

D4 Show This

From $\frac{Q_{out}}{Q_{in}} = \frac{T_1}{T_2} \frac{\ln(V_C/V_D)}{\ln(V_B/V_A)}$ and $\frac{V_B}{V_A} = \frac{V_C}{V_D}$ (needed for D4)

The Carnot Efficiency is:

$$\epsilon_C = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_C}{T_H}$$ $\leftarrow$ depends only on temperatures

--- a series of reversible changes

forward $\updownarrow$ backward

example: a steam engine intakes steam @ 100°C
an exhausts at 0°C → what is the theoretical maximum efficiency of such an engine?

$$\epsilon = 1 - \frac{T_1}{T_2} = 1 - \frac{273K}{373K} = 26.8\%$$

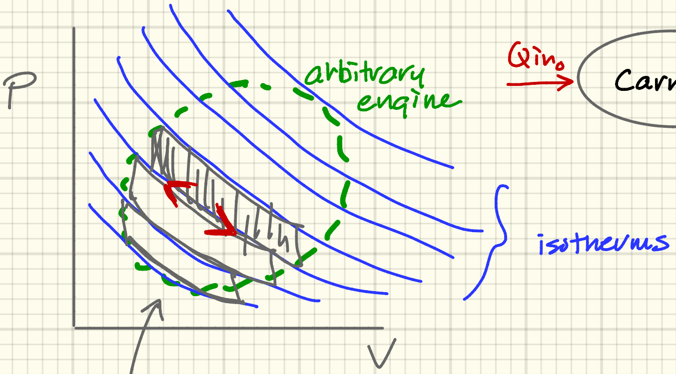
the only ways to improve:

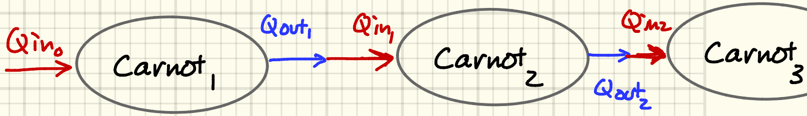
intake temperature hotter

and/or

exaust temperature lower

“proof” that the Carnot engine is ... the theoretically most efficient engine





an ifinitesimal series of Carnot engines

→ limit: a single carnot engine

Absolute temperature

$$\epsilon = 1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2} \quad !$$

so $$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

only heat, nothing to do with physical properties

temperature only related to

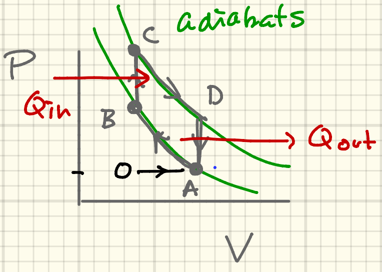
Kelvin scale pins down 1 particular temperature

$T_c(\text{water}) = 0.01°C = -273.16K$

AND there is an absolute minimum of heat $(=0)$

so there is an absolute minimum of temperature $(K=0)$

Real engines

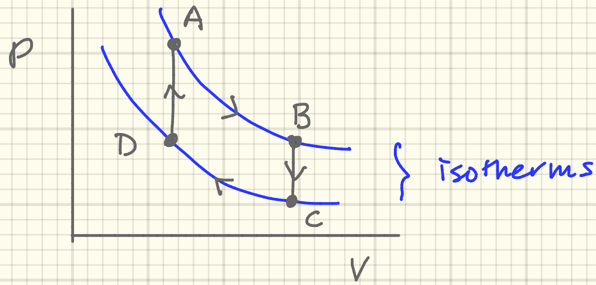


Otto Cycle – internal combustion engine

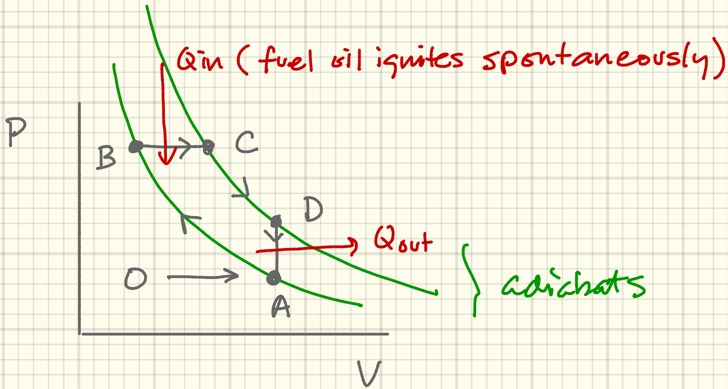
O → A	air in @ 1 atm
A B	adiabatic compression
B C	heat in → spark plug fires
C D	adiabatic expansion – work done ↪ turns crank shaft
D A	cooling
A–O	exhaust

$$\epsilon_{Otto} = 1 - \frac{1}{(V_A/V_B)^{\gamma-1}}$$ ~ 56% theoretically

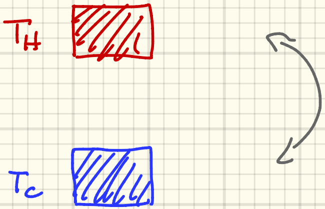
Stirling Engine → near Carnot



Diesel Engine

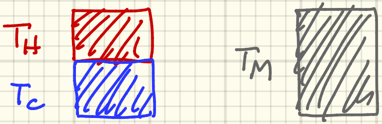


Entropy



Useful.. could get W out between them

Bring them together... adiabatically... equilibriate them



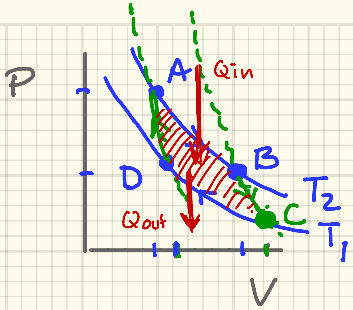
$T_M > T_c$

$T_M < T_H$

right?

Total energy? <u>same</u> — no work done

BUT! LESS USEFUL... LOWER "QUALITY" ENERGY



For Carnot we found:

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2} = \frac{Q_c}{Q_H} = \frac{T_c}{T_H}$$ Rearrange:

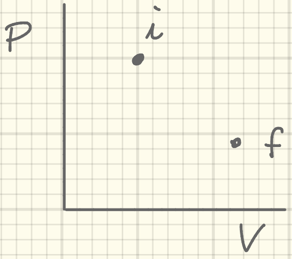
$$\frac{Q_c}{T_c} = \frac{Q_H}{T_H}$$

$$0 = \frac{Q_H}{T_H} - \frac{Q_c}{T_c} = \sum_{\text{cycle}} \frac{Q}{T}$$ for whole cycle

or infinitesimally...

$$\Delta S = \oint \frac{dQ}{T} = 0$$ arbitrary, reversible closed cycle

"Entropy" J/K Clausius, 1865



some arbitrary path for ideal gas $\quad T_i V_i \to T_f V_f$

1st Law: $\quad dQ = dU + dW$

$dW = P\,dV$

$dU = nC_v\,dT$

$P = \dfrac{nRT}{V}$

so $\quad dQ = nC_v\,dT + nRT\dfrac{dV}{V}$

$$\frac{dQ}{T} = nC_v\frac{dT}{T} + nR\frac{dV}{dV}$$

$$\int_{Q_i}^{Q_f}\frac{dQ}{T} = nC_v\int_{T_i}^{T_f}\frac{dT}{T} + nR\int_{V_i}^{V_f}\frac{dV}{V}$$

$$\Delta S = nC_v \ln\left(T_f/T_i\right) + nR\ln\left(V_f/V_i\right)$$

NOTHING ABOUT THE PATH... only i and f states

$\Rightarrow$ S is a State Function like P, V

Since S is a state function ...

Consider any finite process 1 – 2 (not cycle)

S doesn't depend on path:

$$\Delta S = S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{dQ}{T}$$