HEAT and WORK

Previously we introduced the differential form of the First Law of Thermodynamics :-

$$dU = \tau d\sigma - pdV + \mu dN$$

Now we will introduce two ideas - heat and work. We say heat transfer $\Leftrightarrow$ entropy transfer!

$$đQ = \tau d\sigma = TdS$$

↑ why do we put a - on the d here?

▶ The reason is actually quite deep - and important - namely, đQ is not a true differential... alternatively, It is not d of something!

In particular, $d(TS) = dT \cdot S + T \cdot dS$

so that Q is not TS.

Work and heat are path-dependent!!

[With a more sophisticated analysis, one can show this at the level of a proof. For those who're met differential forms: $d^2X \equiv 0 \quad \forall X$

but $d(đQ) = d(TdS) = dT \wedge dS + T\underbrace{d^2S}_{=0} = dT \wedge dS \neq 0.$

Another way to express what's going on is that the temperature provides an integrating factor for heat

$$\int dS = \Delta S = \int \frac{đQ}{T}.$$

(THIS IS NOT ON THE FINAL EXAM!]

We also identify the work as

$$đW = pdV - \mu dN$$

which is the work done BY the system

(the book calls it $-đW$ which is obviously the work done ON the system).

Then $$dU = TdS - pdV + \mu dN$$

$$= đQ - đW$$

Both heat and work can occur reversibly or irreversibly. (Recall: reversible = a process in which thermodynamic equilibrium is maintained throughout. In practice, this means doing things slowly enough.)

★ Generally, irreversibility comes from 2 possible sources-

(a) we do things too quickly
(e.g. sudden expansion into vacuum)

(b) we dissipate energy - lose it from our system usually via friction.

About (b): what dissipating into friction (e.g. energy) really means is that in our coarse-grained thermodynamic description we lost track of degrees of freedom on the micro-level. eg. "Heat went into friction".

How, then, would we expect irreversible & reversible work & heat to compare to their reversible counterparts?

▶ $đQ$ is the heat added to the system

So if, during the heat-adding process we lose some to "the environment" then we'd expect to have less in the system later. Text also gives additional reasoning ⇒

$$đQ_{irrev.} < đQ_{rev.}$$

▶ $(-đW)$ is work done on system.

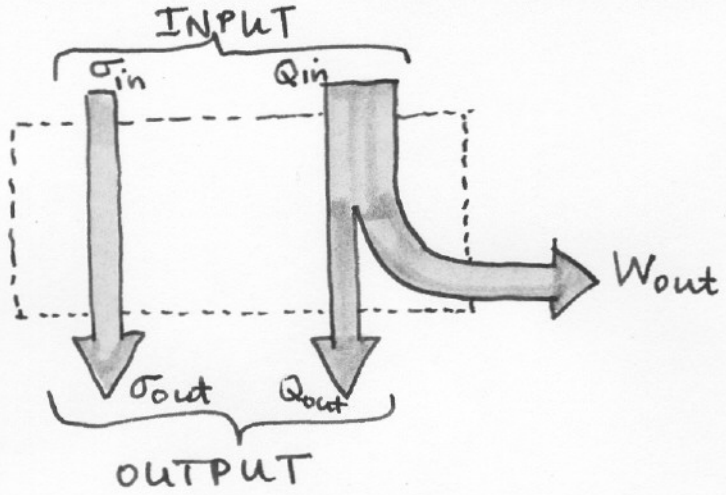
Again, if somehow we lose some to friction then $(-đW)_{irrev.} > (-đW)_{rev.}$

because we had to do more work to achieve the desired dU. Text also gives additional reasoning

Notes: - all types of work are interconvertible, (when &) because there is no attendant transfer of entropy or heat.

- while work can be completely converted into heat the reverse is not possible (!)

Consider a **HEAT ENGINE**:-



Idea is to take input heat Q_{in}
(also commonly called Q_h)

and produce $Q_{out} < Q_{in}$ plus work, W.

"Take heat, produce work".

▶ To prevent buildup in the engine, $\sigma_{out} = \sigma_{in}$
(if we ran the above cycle a million times we wouldn't want ridiculous entropy buildup!)

• It is a common setup to put the upper edge of the idealized heat engine (**CARNOT ENGINE**) @ temperature T_h and the lower edge @ T_c. Then

$$Q_h = \sigma_h T_h \quad \text{and} \quad Q_c = \sigma_c T_c \quad ;$$

since $\sigma_h = \sigma_c$, $\quad Q_h > Q_c$.

Note that our argument CLEARLY shows why Q_c is not zero - $Q_c = \sigma_c T_c$ and $T_c > 0$ (can't get to absolute zero). So

$$Q_{in} \rightarrow Q_c + W$$

(Q_c: waste heat; W: desired work.)

Second Law:- Can't completely convert heat into work. Always waste some

NO PERPETUAL MOTION MACHINE

[▶ Sorry, but the conventions are to represent all these guys by positive quantities - Q_c, Q_h, W all ≥ 0. This is inconsistent with previous conventions, but don't worry.]

How efficient is our engine? We say

efficiency $e = \dfrac{W}{Q_{in}} = \dfrac{Q_h - Q_c}{Q_h} = 1 - \dfrac{Q_c}{Q_h}$

[The book calls this "η".] $\Rightarrow$ $\boxed{e_{Carnot} = 1 - \dfrac{T_c}{T_h}}$

This is the efficiency attained by the Carnot engine. It can be shown that no engine can do better! [See Text...]

Essentially - other engines waste more - less work done by engine and more heat ejected as waste.

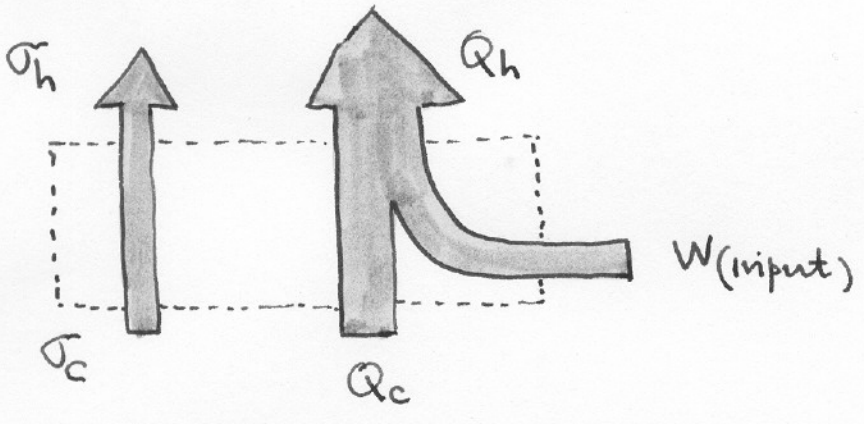
100% efficiency could theoretically be attained by taking $\frac{T_c}{T_h} \to 0$. Either $T_c = 0$ or $T_h = \infty$ is impractical.

★ Engines in cars & trucks, in REAL LIFE, do a lot worse than a Carnot engine.

(Unmaintained engines especially ☺)

FRIDGES

Fridges, or heat pumps, are essentially heat engines run backwards.



Again, to prevent ridiculous entropy buildup,

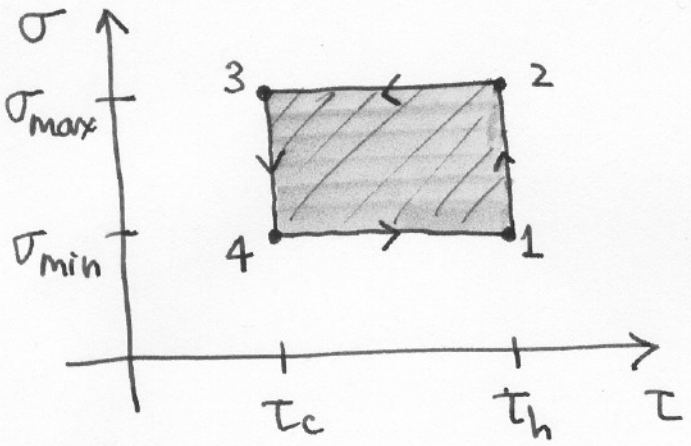
$$\sigma_c = \sigma_h .$$

Conservation of energy $\Rightarrow$ $Q_c + W_{in} = Q_h$.

Coefficient of performance $c = \frac{Q_c}{W_{in}} = \left(\frac{Q_h - Q_c}{Q_c}\right)^{-1} \neq$

For a Carnot fridge, $c = \frac{T_c}{(T_h - T_c)} > 1$ (this is fine.)

CARNOT CYCLE



Imagine running the engine via

← 2 isotherms & 2 adiabats

σ_{max}, σ_{min} are the max. & min. entropy of our "working substance" - the stuff in the engine.

$1 \to 2$ and $3 \to 4$ are isothermal

$2 \to 3$ and $4 \to 1$ are adiabatic

We have in general

$đW = ??$ We don't know $pdV - \mu dN$!

Well, we know that $dU = đQ - đW$.

★ In one complete cycle, $\Delta U = 0$ because the system was -reversibly- returned to its previous state

$\Rightarrow \quad \Delta Q = \Delta W$ for the whole cycle.

$\Rightarrow \quad \Delta W_{cycle} = \oint đQ = \oint T\,d\sigma =$ area of rectangle

$\Rightarrow \quad \Delta W_{cycle} = (T_h - T_c)(\sigma_{max} - \sigma_{min})$

What is Q_h? Heat input.

During the isothermal process 1→2, heat is adde

$$Q_h = \tau_h(\sigma_{max} - \sigma_{min})$$

So... $$e = \frac{W_{out}}{Q_h} = \frac{(\tau_h - \tau_c)(\sigma_{max} - \sigma_{min})}{\tau_h(\sigma_{max} - \sigma_{min})}$$

$$= \frac{\tau_h - \tau_c}{\tau_h} = 1 - \frac{\tau_c}{\tau_h}$$ as promised

Ideal Gas as working substance

During (1→2) isothermal process, $\Delta U = 0$ because $U = \frac{f}{2}N\tau$, and τ doesn't change. We also have

$$\Delta Q_{12} = \Delta W_{12} = \int p\,dV = N\tau_h \int \frac{dV}{V} = N\tau_h \log\left(\frac{V_2}{V_1}\right)$$

$(pV = N\tau)$

= heat added to gas

$\Rightarrow (V_2 > V_1)$

For (2→3) we know $\Delta Q = 0$ because it's isentropic (adiabatic).

So... $\Delta U_{23} = \frac{f}{2}N(\tau_c - \tau_h)$, and since

$\Delta U_{23} = \Delta Q_{23} - \Delta W_{23}$, $\Rightarrow \Delta W_{23} = \frac{f}{2}N(\tau_h - \tau_c) > 0$

How are volumes related? - What's V_3?

Know for adiabatic process $TV^{\gamma-1} = $ constant

$\Rightarrow \tau_2 V_2^{\gamma-1} = \tau_3 V_3^{\gamma-1}$; $\tau_2 = \tau_h$ & $\tau_3 = \tau_c$.

$\Rightarrow V_3^{\gamma-1} = V_2^{\gamma-1}\frac{\tau_h}{\tau_c}$ gas expanded (√did work)

Now, to (3→4). This is an isotherm.

So $\Delta U_{34} = 0 = \Delta Q_{34} - \Delta W_{34}$. So heat ejected is

$$\Delta Q_{34} \equiv Q_C = \int_3^4 p\,dV = N\tau_c \int_3^4 \frac{dV}{V} = N\tau_c \log\left(\frac{V_4}{V_3}\right)$$
$$(= \Delta W_{34})$$

During this isothermal compression,

obviously, $\Delta W_{34} = +\Delta Q_{34} = N\tau_c \log\left(\frac{V_4}{V_3}\right)$.

How is V_4 related to V_1, V_2, V_3?

Well, we know (4→1) is an adiabat. So

$$T_1 V_1^{\gamma-1} = T_4 V_4^{\gamma-1} \quad \text{so}$$

$$V_4^{\gamma-1} = V_1^{\gamma-1} \frac{\tau_1}{\tau_4} = \frac{\tau_h}{\tau_c} V_1^{\gamma-1}$$

But $\frac{\tau_h}{\tau_c} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$ so

$$\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \text{i.e.} \quad \boxed{\frac{V_4}{V_1} = \frac{V_3}{V_2}}$$

Since $\frac{V_2}{V_1} > 0$, $\frac{V_3}{V_4} > 0$ $\Rightarrow$ $\Delta W_{34} < 0$. Gas had work done on it.

Lastly, let's find W_{41}. We know $\Delta Q_{41} = 0$

so $\Delta W_{41} = -\Delta U_{41} = -\left(\frac{f}{2}N\tau_h - \frac{f}{2}N\tau_c\right) = \frac{f}{2}N(\tau_c - \tau_h) < 0$

Total work $\Delta W_{cycle} = \Delta W_{12} + \Delta W_{23} + \Delta W_{34} + \Delta W_{41}$

$$= N\tau_h \log\left(\frac{V_2}{V_1}\right) + \frac{f}{2}N(\tau_h - \tau_c) + N\tau_c \log\left(\frac{V_4}{V_3}\right) + \frac{f}{2}N(\tau_c - \tau_h)$$

i.e. overall

$$\Delta W_{cycle} = N\tau_h \log\left(\frac{V_2}{V_1}\right) + N\tau_c \log\left(\frac{V_4}{V_3}\right)$$

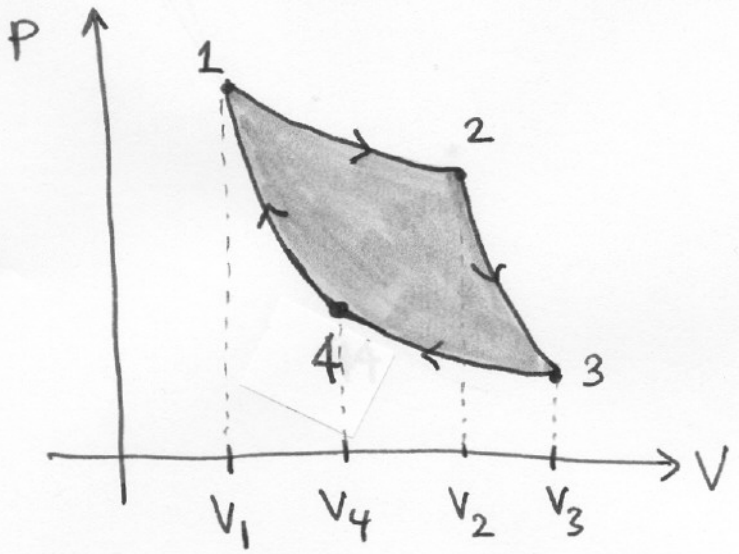
but $\frac{V_4}{V_3} = \frac{V_1}{V_2}$ so

$$\boxed{\Delta W_{cycle} = N(\tau_h - \tau_c) \log\left(\frac{V_2}{V_1}\right)}$$

We also know $\boxed{\Delta Q_{input} = N\tau_h \log\left(\frac{V_2}{V_1}\right)}$

so, as promised, $e = \frac{\Delta W_{cycle}}{\Delta Q_{input}} = 1 - \frac{\tau_c}{\tau_h}$ ☺

What does this cycle look like on a p-V plot?



isotherm : $pV = \text{const}$ i.e. $p \propto \frac{1}{V}$

adiabat : $pV^\gamma = \text{const.}$ i.e. $p \propto \frac{1}{V^\gamma}$ where $\gamma = \frac{C_p}{C_V} > 1$

$\Rightarrow$ steeper than isotherm