Work & Heat

$$dU = đQ + đW \qquad \text{energy cons.}$$

Work:

$$đW = -P\,dV$$

Heat:

$$dS\Big|_{\substack{V,N \\ \text{const}}} = S(U + đQ, V, N) - S(U, V, N)$$

$$= \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} đQ \Rightarrow dS = \frac{đQ}{T}\Big|_{\substack{V,N \\ \text{const.}}}$$

$$\Rightarrow \quad đQ = T\,dS$$

So energy conservation is

$$dU = T\,dS - P\,dV \qquad (N \text{ const})$$

On the other hand from $S(U,V,N)$ we can derive its (exact) differential

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N}}_{\frac{1}{T}} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

Multiply by T and solve for dU gives

$$dU = T dS - \underbrace{T\left(\frac{\partial S}{\partial V}\right)_{U,N}}_{+P} dV - \underbrace{T\left(\frac{\partial S}{\partial N}\right)_{U,V}}_{-\mu \text{ (def.)}} dN$$

or

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

So that

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

The differential form of the fundamental relation in the energy representation.

$U = U(S,V,N)$

The differential form of the fundamental relation in the entropy representation is

$$\boxed{dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN}$$

TD Processes

$dS \geq 0$ in an isolated system.

$dS = 0$ only when the system is already in equilibrium.

Processes where $dS > 0$ are called irreversible

Quasistatic process: Infinitesimal changes of an equilibrium system $dS = 0$
(Not a real process. Idealization, but useful. compare to the ideal gas (also an idealization))

Heat engines

Produce work from heat (steam engine)

arrows marks positive directions of the quantities

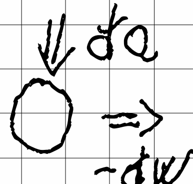
Engines are cyclic: $dU = 0$, $dS = 0$ $dV = 0$

Energy conservation in one cycle

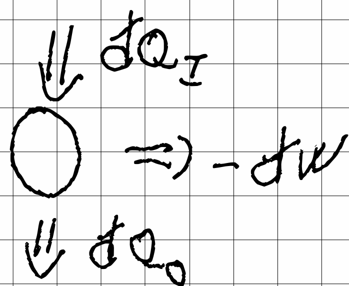
$$\text{đ}Q + \text{đ}W = 0$$

$$\underbrace{-\text{đ}W}_{\text{work done by the engine}} = \text{đ}Q$$

net heat input



Want to also account for heat produced by the engine and dumped to the surroundings.



Energy conservation

$$đQ_I - đQ_0 + đW = 0$$

$$-đW = đQ_I - đQ_0 \leq đQ_I$$

(for $đQ_0 > 0$)

when heat is transfferred to the engine the entropy of the engine increases

$$dS = \frac{đQ_I}{T}$$

for a cyclic engine $dS = 0$
To avoid that the outgoing heat be the same as the incoming (no work) The heat exchange must happen at different temperatures T_I, T_0

$$0 = dS = \frac{đQ_I}{T_I} - \frac{đQ_0}{T_0}$$

$$\boxed{\begin{aligned} -đW &= đQ_I - đQ_0 \\ 0 &= \frac{đQ_I}{T_I} - \frac{đQ_0}{T_0} \end{aligned}}$$

We can solve the 2. eq. for $đQ_0$

$$đQ_0 = \frac{T_0}{T_I} đQ_I$$

Plugging back into energy cons.

$$-đW = đQ_I - \frac{T_0}{T_I} đQ_I$$

$$-đW = đQ_I \left(1 - \frac{T_0}{T_I}\right)$$

efficiency:

$$\eta = \frac{-đW}{đQ_I} = 1 - \frac{T_0}{T_I} = \frac{T_I - T_0}{T_I}$$

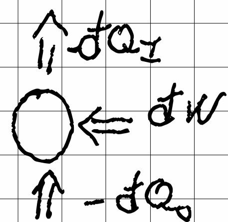
You will only get an efficiency of $\eta = 1$ when $T_0 = 0$.

Refridgerators & Air conditioners (heat pumps)

"Heat engines run in reverse"

~~excess he back~~ outside (back) of fridge.

Fridge:



inside fridge

Now the the performance is judged by the $COP_{cooling}$

$$COP_{cooling} = \frac{-\text{đ}Q_0}{\text{đ}W} = \frac{T_0}{T_I - T_0}$$

solve ~~to~~ 2. eq. for $\text{đ}Q_I = \frac{T_I}{T_0}\,\text{đ}Q_0$

Typically $T_0 = 277\,K$ ($4^\circ C$)

$T_I = 293\,K$ ($20^\circ C$)

$$\Rightarrow COP_{cooling} = \frac{277}{293-277} \approx 17$$ very efficient.

Heat pumps

Same as retridgerators, but inside of fridge is outside of house.

$$COP_{heating} = \frac{-đQ_I}{đW} = \frac{T_I}{T_I - T_O}$$

for a house you typically want

$$T_I = 323\,K \quad (50°c)$$
$$T_O = 273\,K \quad (0°c)$$

$$\Rightarrow COP_{heating} = \frac{323}{50} = 6.5$$

Typically a real heat pump has $COP_H \sim 2\text{-}5$

for Higher T_I the COP_{heat} is reduced.

<u>Carnot cycle</u>: A specific model for a reversible heat engine.

TD Potentials

Fundamental relation: $S = S(U,V,N)$

or

$U = U(S,V,N)$

These contain all TD info.

How can we extract TD if system is at const T, P ... etc?

Legendre transform

We have a function $Y = Y(x)$ of one var. x.

We want another funct. $\tilde{Y}$ with $P \equiv \frac{\partial Y}{\partial x}$ as a variable $\tilde{Y}(P)$ that contains the same info.

Legendre transform: $\tilde{Y} = Y - Px$

where it is understood that $P = \frac{\partial Y}{\partial x}$, $P = P(x)$ is inverted $x = x(P)$, and x is replaced by $x(P)$

Example: $y = x^2$

$$p = \frac{dy}{dx} = 2x \Rightarrow x = \frac{p}{2}$$

(p is assumed monotenons so that it can be inverted)

$$\tilde{y} = y - px = x^2 - px = \left(\frac{p}{2}\right)^2 - p\left(\frac{p}{2}\right)$$

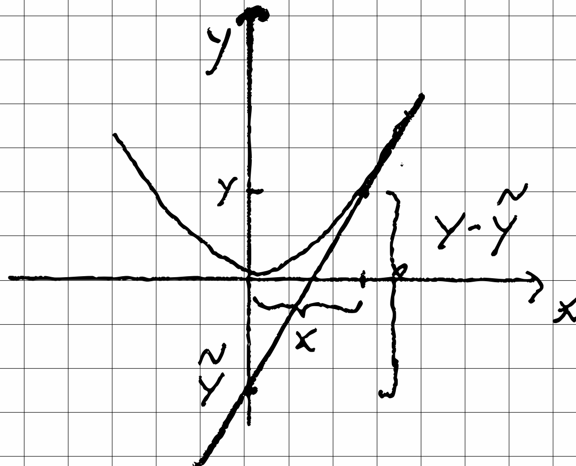
$$= -\frac{p^2}{4}$$

The inverse transform is

$y(x) = \tilde{y} + px$, where p is replaced by $p = p(x)$

For the example:

$$y = -\frac{p^2}{4} + px = -\frac{(2x)^2}{4} + 2x \cdot x = \underline{x^2}$$



slope $p = \dfrac{y-\tilde{y}}{x} \Rightarrow \tilde{y} = y - px$

So $\tilde{y}$ can be read off as the y-axis intercept for a given slope p.

Helmoltz free energy

Relevant for systems at const. T.

$$U = U(S, V, N)$$

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

We want to replace S with T

Legendre transform

$$F = U - TS$$ (Eliminate S in favor of T)

$$F = F(T, V, N)$$