Other useful relationships

x, y, z, w four state variables, still two degrees of freedom

(i) $\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$

(ii) $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

(iii) $\left(\frac{\partial x}{\partial w}\right)_z = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial w}\right)_z$

(iv) $\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial y}\right)_w + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z$

proof:

$x = x(y,z)$: $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

$y = y(x,z)$: $dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$

combine $\rightarrow \underbrace{\left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z - 1\right]}_{=0 \Rightarrow (i)} dx + \underbrace{\left[\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y\right]}_{=0 \Rightarrow (ii)} dz = 0$

9/30 ↓

10/2 ↓

$x = x(w,y)$: $dx = \left(\frac{\partial x}{\partial w}\right)_y dw + \left(\frac{\partial x}{\partial y}\right)_w dy$

$x = x(y,z)$: $dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$

$w = w(y,z)$: $dw = \left(\frac{\partial w}{\partial y}\right)_z dy + \left(\frac{\partial w}{\partial z}\right)_y dz$ ← insert into

$$\left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz = \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y dz + \left(\frac{\partial x}{\partial y}\right)_w dy$$

$$\underbrace{\left[\left(\frac{\partial x}{\partial y}\right)_z - \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial y}\right)_z - \left(\frac{\partial x}{\partial y}\right)_w\right]}_{=0 \Rightarrow (iv)} dy + \underbrace{\left[\left(\frac{\partial x}{\partial z}\right)_y - \left(\frac{\partial x}{\partial w}\right)_y \left(\frac{\partial w}{\partial z}\right)_y\right]}_{=0 \Rightarrow (iii)} dz = 0$$

Dependence via equation of state

Ideal gas:

$$PV = nRT \qquad R = 8.314 \ \frac{J}{mol\,K}$$

Virial Expansion:

$$P = \frac{nRT}{V}\left[1 + \frac{n}{V}B_2(T) + \left(\frac{n}{V}\right)^2 B_3(T) + \cdots\right]$$

van der Waals gas:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

a, b phenomenological parameters

Solids:

$$V = V_0\,(1 + \alpha_p T - \kappa_T P)$$

Curie's law

$$\vec{M} = \frac{nD}{T}\,\vec{H}$$

Electric Polarization

$$\vec{P} = \left(a + \frac{b}{T}\right)\vec{E}$$

I.2

The laws of thermodynamics

Zeroth Law

Two bodies, each in thermodynamic equilibrium with a third system, are in thermodynamic equilibrium with each other.

→ "we can build a thermometer"

First Law

Energy is conserved

dU = external changes in energy

change in work

$$đW = P\,dV - \underset{\text{tension}}{J}\,d\overset{\text{length}}{L} - \underset{\text{surface tension}}{\sigma}\,d\overset{\text{area}}{A} - \vec{E}\,d\vec{P} - \vec{H}\,d\vec{M} - \underset{\text{electrical potential}}{\Phi}\,d\overset{\text{charge}}{e} - \sum_j \mu_j\,dN_j$$

$đW$ is not exact !

→ need "something else"

$đQ$ change in heat

$$\boxed{dU = đQ - đW}$$

notation:

generalized mechanical force $Y \in \{-P, J, \sigma, \vec{E}, \vec{H}, \Phi\}$

generalized displacement $X \in \{V, L, A, \vec{P}, \vec{M}, e\}$

$$dU = \overbrace{đQ}^{\text{heat}} + \overbrace{Y\,dX}^{\text{mechanics}} + \overbrace{\sum_j \mu_j N_j}^{\text{chemistry}}$$

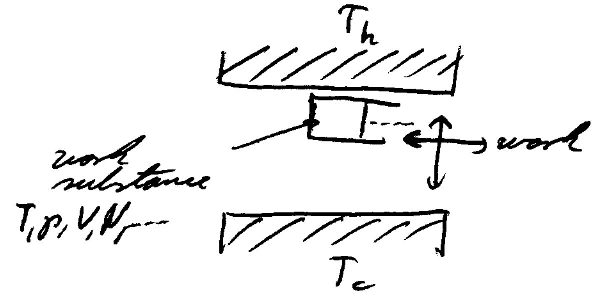
Second Law

Heat flows spontaneously from high temperature to low temperature

Application: heat engines

heat engine: a machine that allows heat to flow continuously from a high temperature reservoir to a low temperature reservoir and extracts mechanical work

examples: steam engine, Otto engine, power plant, refrigerator, air conditioner



move work substance back and forth in cyclic fashion $\Rightarrow \Delta U = 0 \Rightarrow \Delta Q_{tot} = \Delta W_{tot}$

$$\Delta Q_{tot} = \underbrace{\Delta Q_h}_{\text{heat taken from hot reservoir}} - \underbrace{\Delta Q_c}_{\text{heat given to cold reservoir}}$$

efficiency: $\eta = \dfrac{\Delta W_{tot}}{\Delta Q_h} = \dfrac{\Delta Q_h - \Delta Q_c}{\Delta Q_h} = 1 - \dfrac{\Delta Q_c}{\Delta Q_h}$

"energy gained" / "energy taken"

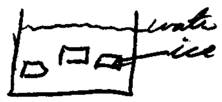
how to build an efficient engine?

<u>reversible change</u>: system stays in thermodynamic equilibrium at all times

- can be reversed without anything in the universe changing state
- state variables well-defined throughout the process
- gradual

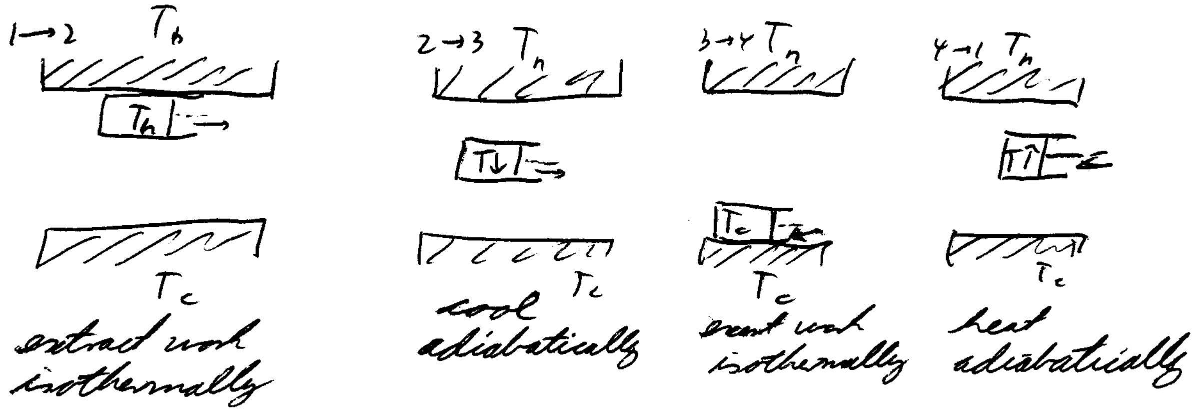
<u>irreversible change</u>:

- intermediate non-equilibrium states
- fast
- state variables not defined at intermediate times



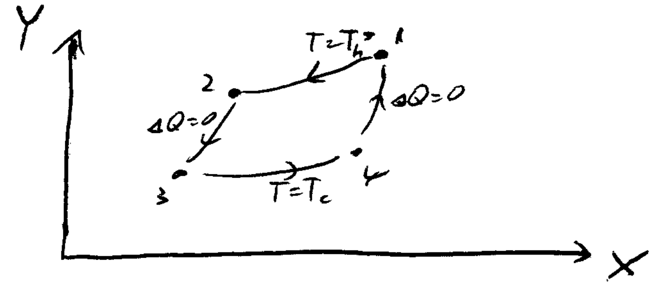
idea: something gets lost in irreversible changes, thus construct engine only using reversible changes.

⇒ work substance must be at $\begin{Bmatrix} T_h \\ T_c \end{Bmatrix}$ when brought into contact with $\begin{Bmatrix} \text{hot} \\ \text{cold} \end{Bmatrix}$ reservoir



Carnot process:

Y-X-diagram



$\Delta Q_h = \Delta Q_{12}$
$\Delta Q_c = \Delta Q_{43}$

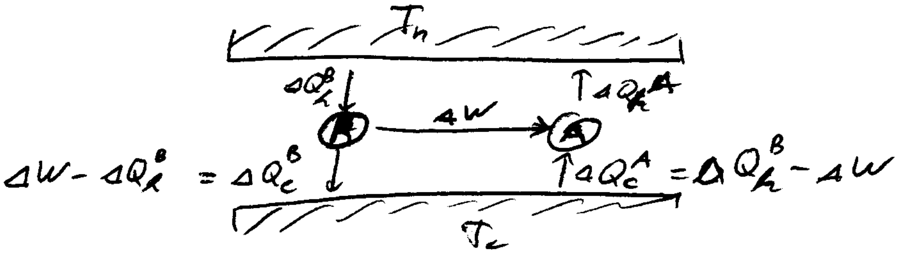
Is this a good engine?

Let A be a Carnot engine with $\Delta W_{tot}^A, \Delta Q_h^A, \Delta Q_c^A, \eta^A$

Let B be any other engine working between the same reservoirs with $\Delta W_{tot}^B, \Delta Q_h^B, \Delta Q_c^B, \eta^B$

assume: $\eta^B > \eta^A$

- scale engines such that $\Delta W_{tot}^A = \Delta W_{tot}^B$
- run Carnot engine backwards (reversible!)



$$\eta^B > \eta^A \Rightarrow \frac{\Delta W}{\Delta Q_h^A} < \frac{\Delta W}{\Delta Q_h^B} \rightarrow \Delta Q_h^B < \Delta Q_h^A$$

total heat from hot reservoir: $\Delta Q_h^B - \Delta Q_h^A < 0$!

$\Rightarrow$ heat is flowing from cold reservoir to hot reservoir in contradiction to second law