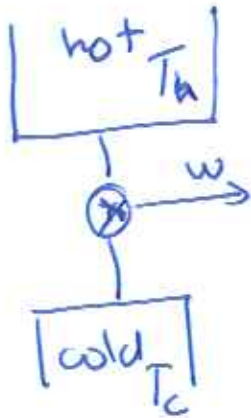


Maximum work and Heat Engines

①

heat engine: X - device which operates between two heat reservoirs in a cyclic manner

- two heat reservoirs \Rightarrow one hot (T_h) one cold (T_c)



- work done in process

1.) X - draws heat from hot source at temperature T_h

- source (reservoir) is very big compared to engine X \Rightarrow no change in temperature of heat source

($Q_h \rightarrow$ heat drawn \Rightarrow infinitesimal compared to heat source)

- entropy change of heat source: $-\frac{Q_h}{T_h}$

- the drawing of heat thermally isolated



diathermic while heat is supplied

- during heat supply \Rightarrow X goes from one equilibrium state to another while doing work

$$W = -\Delta E + Q_h$$

entropy change of heat source + engine

②

$$\Delta S_{\text{tot}} = \Delta S - \frac{Q_n}{T_n} \geq 0$$

$$T_n \Delta S \geq Q_n$$

$$\boxed{W \leq T_h \Delta S - \Delta E}$$

theorem of maximum work \Rightarrow maximum occurs when process is reversible, i.e. $\Delta S_{\text{TOT}} = 0$

$$\Rightarrow W = T_h \Delta S - \Delta E$$

- device functions in a cycle
 - draws heat from hot source Q_n
 - does work
 - dumps heat to cold source Q_c
- total entropy change of total system: heat source, engine, cold source

$$\Delta S_{\text{tot}} = -\frac{Q_n}{T_n} + 0 + \frac{Q_c}{T_c}$$

0 because engine makes a cycle

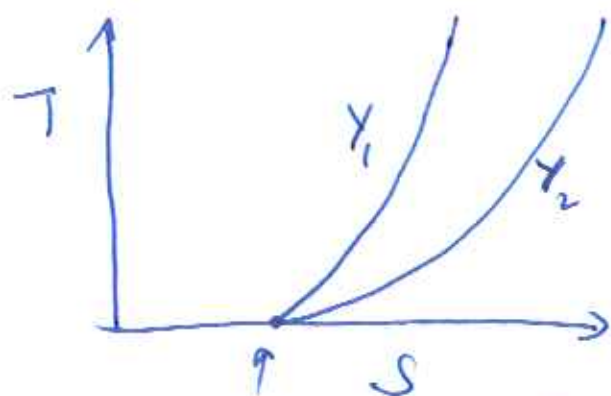
$$\text{if reversible} \Rightarrow \Delta S_{\text{tot}} = 0 \Rightarrow \frac{Q_n}{T_n} = \frac{Q_c}{T_c}$$

$$\text{efficiency: } \eta = \frac{W}{Q_n} = \frac{Q_n - Q_c}{Q_n} = 1 - \frac{Q_c}{Q_n} = 1 - \frac{T_c}{T_n}$$

3rd law of thermodynamics

(3)

- One can not reach absolute zero temperature in a ~~not~~ finite number of reversible steps
- demonstrate by plot on S-T plane



$\gamma_1, \gamma_2 \Rightarrow$ two different values of generalized force

S is the same (one quantum state at $T=0$)

- identity: consider $Z = Z(x, y)$

$$dZ = \left. \frac{\partial Z}{\partial x} \right|_y dx + \left. \frac{\partial Z}{\partial y} \right|_x dy$$

if Z is assumed constant $\Rightarrow Z(x, y) = A$
 $dZ = 0$

$$\left. \frac{\partial Z}{\partial x} \right|_y = - \left. \frac{\partial Z}{\partial y} \right|_x \frac{\partial y}{\partial x} \Big|_Z$$

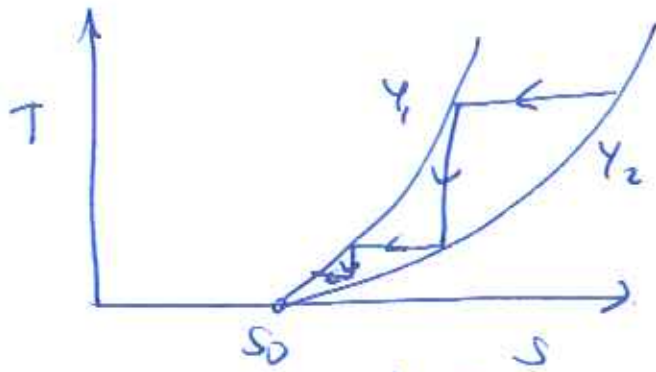
$$\left. \frac{\partial T}{\partial Y} \right|_S = - \left. \frac{\partial T}{\partial S} \right|_Y \left. \frac{\partial S}{\partial Y} \right|_T \quad (\text{fixed } N)$$

later we will show that $C_Y = T \left. \frac{\partial S}{\partial T} \right|_Y \geq 0$
(specific heat at constant Y)

\Rightarrow it follows that if T decreases as Y increases adiabatically then S must,

decrease as Y decreases isothermally

(4)



if $Y_2 > Y_1$

- since curves at $T=0$ must approach each other \Rightarrow one can not reach this pt. by reversible steps

- also \Rightarrow certain derivatives tend to zero as

$$T \rightarrow 0 \quad \text{if } dN=0 \Rightarrow dS = \left. \frac{\partial S}{\partial Y} \right|_{T=0, N} dY = 0$$

$$\left. \frac{\partial S}{\partial Y} \right|_{T=0, N} = 0$$

$$\text{or } \left. \frac{\partial S}{\partial X} \right|_{T=0, N} = 0$$

where X is a generalized displacement

Fundamental equation of thermodynamics (5)

entropy: $S = S(E, V, N)$

all variables are extensive, hence it must hold that

$$\lambda S = S(\lambda E, \lambda V, \lambda N)$$

differentiate with respect to λ and set $\lambda = 1$

$$\Rightarrow S = \frac{\partial S}{\partial(\lambda E)} E + \frac{\partial S}{\partial(\lambda V)} V + \frac{\partial S}{\partial(\lambda N)} N$$

$$S = \frac{\partial S}{\partial E} E + \frac{\partial S}{\partial V} V + \frac{\partial S}{\partial N} N$$

$$S = \frac{E}{T} + \frac{PV}{T} - \frac{\mu N}{T}$$

$$TS = E + PV - \mu N$$

or

$$E = TS - PV + \mu N$$

- can also derive an equation in which the intensive variables are the independent variables \Rightarrow

$$dE = Tds + SdT - pdv - vdp + \mu dn + nd\mu$$

but for an equilibrium process

$$dE = Tds - pdv + \mu dn$$

$$\Rightarrow \boxed{SdT - vdp + \mu dn = 0}$$

Gibbs-Puham
relation

for an isothermal process

(6)

$$-v dp + \mu dN = 0$$

$$\Rightarrow \left. \frac{\partial \mu}{\partial p} \right|_T = \frac{N}{V} = \rho \text{ (density)}$$

Thermodynamic potentials

- conservative mechanical systems:

- potential energy corresponds to work stored

- can do work by compressing spring,
or raising an object against gravity,
work can be recovered by releasing
spring or lowering object

- in thermodynamics \Rightarrow thermodynamic potentials play the same role

- there are many thermodynamic potentials, since one can apply many constraints on the system

examples: isothermal $\overset{\text{vs.}}{\longleftrightarrow}$ adiabatic

isobaric $\overset{\text{vs.}}{\longleftrightarrow}$ isochoric

constant chemical potential $\overset{\text{vs.}}{\longleftrightarrow}$ constant particle number

- for each set of constraints there exists one (7)
- thermodynamic potential
- its value gives the maximum work which can be extracted from a system under the corresponding constraints (maximum work obtained under reversible conditions)
- examples: internal energy, Helmholtz free energy, Gibbs free energy, grand potential
- but there are as many as there are combinations of constraints

Internal energy

combined 1st and 2nd laws (for P-V system)

$$dE \leq TdS - PdV + \mu dN$$

equality holds for reversible changes

inequality holds for spontaneous changes

- for an isolated system ($dS = dN = 0$), if a process is reversible

$$dE = -PdV \Rightarrow \text{maximum work}$$

one can extract from

such a system by changing volume ~~at~~ infinitesimally

- if no work done, no matter exchanged, no change in entropy

(8)

$$(dE)_{S, V, N} \leq 0$$

it follows that for a spontaneous process the internal energy must decrease

and it also follows that for an equilibrium state the internal energy is a minimum if S, V, N are fixed

Enthalpy

- Legendre transform of internal energy
 - changes independent variables
 - also changes concavity to convexity and vice versa
- definition of enthalpy

$$H = E + PV$$

(for a generalized force-displacement pair $\Rightarrow H = E - XY$)

$$dH = dE + PdV + VdP + \cancel{PdV}$$

$$\leq TdS + VdP + \mu dN$$

constant variables $S, P, N \Rightarrow$

- enthalpy $H = H(S, P, N)$ $V = V(S, P, N)$ (9)

$T = T(S, P, N)$

$\mu = \mu(S, P, N)$

- if a process is adiabatic ($dS=0$) and there is no change in particle number ($dN=0$)

$$(dH)_{S,N} \leq VdP$$

- enthalpy corresponds to maximum work which can be gained from a system by varying pressure reversibly

- for $dS=dP=dN=0$

$$(dH)_{S,P,N} \leq 0$$

- for a system at constant pressure, constant entropy, and constant particle number the change in enthalpy must be negative for a spontaneous process

- enthalpy is minimum for equilibrium state when S, P, N are held constant

Helmholtz free energy

(10)

$$F = E - ST$$

$$dF = dE - SdT - TdS$$

$$\leq -SdT - pdV + \mu dN$$

max work if T and N are fixed

$$(dF)_{T,N} \leq -pdV$$

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

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

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

$$\mu = \mu(T, V, N)$$

if a process is isothermal, isochoric, and takes place at constant particle number, then

$$(dF)_{T,V,N} \leq 0$$

in other words the Helmholtz free energy decreases if the process is spontaneous and is minimized for equilibrium states

Gibbs Free energy

(11)

$$G = E - TS + PV$$

$$dG \leq -SdT + vdp + \mu dN$$

similar conclusions follow (T, P, N -independent variables, G, S, v, μ are dependent)

Grand Potential

$$\Omega = E - TS - \mu N$$

$$d\Omega \leq -SdT - PdV - Nd\mu$$

- similar conclusions with different set of independent variables)