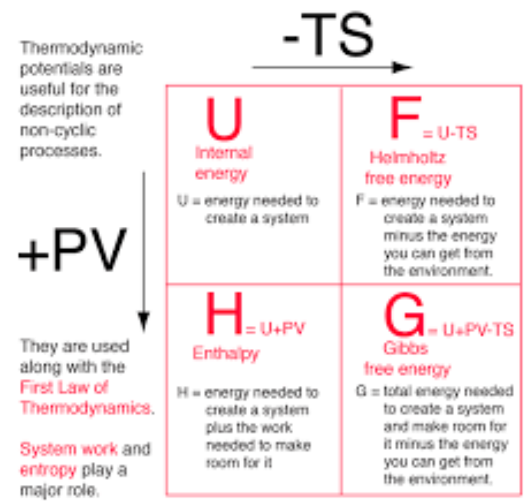
General Physics II: Thermodynamics

Prof. M. Hirschmann

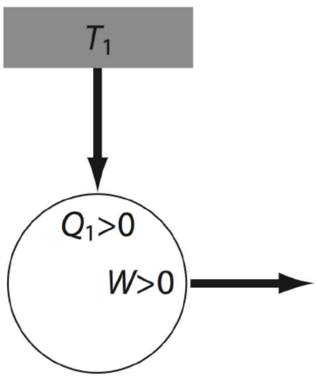


Spring semester 2024

Recap Chapter 9… — Thermal machines

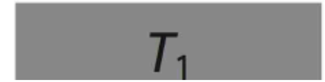
- What is a thermal machine?

- What is an equivalent formulation of 2nd law of TD?



Recap Chapter 9 — Thermal machines

- What is the set up and efficiency of a thermal machine?



Recap Chapter 9— Carnot cycle

- How does the Carnot cycle work? Plot the PV and TS diagrams of the Carnot cycle. What is the summed work/heat? What is the efficiency?

A B C

Recap — Refrigerators, heat pumps, perpetual motion machines

Recap Chapter 9 — Which other thermal engines do you know?

Content of this course — today's lecture

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

Lecture 6: —Chapter 7. First law of thermodynamics and thermal processes

Lecture 7: — Mock exam I *with Dr. Tress*

Lecture 8: —Chapter 8. Entropy and the second and third law of thermodynamics

Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

Lecture 14: —Final review and open questions

10. Thermodynamic potentials and equilibria

- 10.1 Basic relations of TD
    - Chemical potential
    - Gibbs (fundamental) relation
    - Euler equation
    - Gibbs-Duhem relation
- 10.2 Thermodynamic potentials and exact differentials
- 10.3 Enthalpy H
- 10.4 Free Energy F
- 10.5 Gibbs Free Enthalpy G
- 10.6 Equilibrium of subsystems coupled to a reservoir

10.1 Basic relations of TD

1. law: $\boxed{dE_{int} = dQ - dW}$ — always valid

$\boxed{dE_{int} \stackrel{!}{=} TdS - PdV}$ — equality only for reversible processes

$E_{int}(S, V)$

$$dE_{int} = \underbrace{\frac{\partial E_{int}}{\partial S}}_{=T} dS + \underbrace{\frac{\partial E_{int}}{\partial V}}_{=-P} dV$$

$\Rightarrow$ valid for a closed system!

Open system: matter exchange with environment

Chapter 7: $dE_{int} = dQ - dW + dC$

C: total/net chemical potential

Matter transport & chemical potential:

$$\boxed{dG = \sum_{i=1}^{N} \mu_i \, dn_i}$$

# of moles of substance i

sum over N types of substances involved

chemical potential of substance i per mol [J/mol]

μ_i : energy to add / remove dn_i moles of a substance i to / from the system ($dW = 0$, $dQ = 0$)

$$\mu_i = \frac{\partial E_{int}}{\partial n_i}$$

Every chemical reaction can be described by removing initial substances & adding final ones.

E.g.: $2H_2 + O_2 \longrightarrow 2H_2O$; $2\mu_1 + 1\mu_2 \longrightarrow 2\mu_3$

$$\sum_{i=1}^{k} \mu_i n_i \longrightarrow \sum_{j=k+1}^{p} \mu_j n_j$$

* T diff. ⟶ heat flow
* P diff. ⟶ work flow
* diff in chemical potential ⟶ matter flow
(naturally always moving from a higher to a lower chemical potential)

Examples:

① Diffusion: Particles move from regions of higher concentr. (= higher μ) to regions of lower concentration (= lower μ)

(2) Phase transitions

Mass moves from a phase of higher μ to that with a lower μ; e.g. water evaporating at $T > 100°C$ & atmospheric pressure.

mass flow stops, once μ of diff. phases equalise or when one phase is fully converted into another

(3) Chemical reactions

Reactants convert into products because μ of products is lower than than that of reactants

stops once μ of products is equal to that of reactants.

Put dC into 1 law:

$$\boxed{dE_{int} = TdS - PdV + \underbrace{\sum_i \mu_i \, dn_i}_{dC}}$$

Gibbs' fundamental relation

$$E_{int} = E_{int}(S, V, n)$$

Another basic relation: Euler equation (algebraic rel.)

$$\boxed{E_{int} = TS - PV + \sum_i \mu_i n_i}$$

Derivation of Euler equation:

Consider a system consisting of λ identical subsystems each with its S, V, n

$\longrightarrow$ total entropy : λS

total volume : λV

total # of moles : λn

} since S, V, n are extensive

$$E_{int}(\lambda S, \lambda V, \lambda n) = \lambda E_{int}(S, V, n)$$

Derivative to λ, $\frac{d}{d\lambda}$:

$$\frac{\partial E_{int}}{\partial(\lambda S)} \cdot \frac{d(\lambda S)}{d\lambda} + \frac{\partial E_{int}}{\partial(\lambda V)} \cdot \frac{d(\lambda V)}{d\lambda} + \frac{\partial E_{int}}{\partial \lambda n} \frac{d(\lambda n)}{d\lambda} =$$

$$= \frac{\partial(\lambda E_{in})}{\partial \lambda}$$

Since S, V, n are independent of λ, we obtain

$$\frac{\partial E_{int}}{\partial(\lambda S)} S + \frac{\partial E_{int}}{\partial(\lambda V)} V + \underbrace{\frac{\partial E_{int}}{\partial(\lambda n)} n}_{\sum_i \frac{\partial E_{int}}{\partial(\lambda n_i)} n_i} = E_{int}$$

Trick: has to be fulfilled for all λ $\longrightarrow$ choose $\lambda = 1$

$$\Longrightarrow \quad E_{int} = \underbrace{\frac{\partial E_{int}}{\partial S}}_{=T} S + \underbrace{\frac{\partial E_{int}}{\partial V}}_{=-p} V + \sum_i \underbrace{\frac{\partial E_{int}}{\partial n_i}}_{=\mu_i} n_i$$

$$E_{int} = TS - PV + \sum_i \mu_i n_i \qquad \square$$

Third basic relation:

Differentiate the Euler equation:

$$\underline{dE_{int}} = \underline{TdS} + \underline{SdT} - \underline{PdV} - \underline{VdP} + \underline{\sum_i \mu_i dn_i} + \underline{\sum_i n_i d\mu_i}$$

Gibbs fundamental relation

to fulfil $\longrightarrow$

$$\boxed{SdT - VdP + \sum_i n_i \, d\mu_i = 0}$$

Gibbs-Duhem relation

Summary 10.1 — Basic relations of TD

- Chemical potential:

$$dC = \sum_{i=1}^{N} \mu_i dn_i$$

- Gibbs fundamental relation: first law open syst

$$dE_{int} = TdS - PdV + \sum_i \mu_i dn_i$$

- Euler relation:

$$E_{int} = TS - PV + \sum_i \mu_i n_i$$

- Gibbs-Duhem relation:

$$SdT - VdP + \sum n_i d\mu_i = 0$$

10.2 Thermodynamic Potentials and Exact Differentials

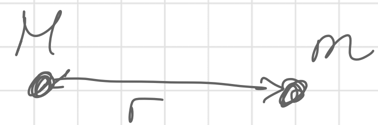
Physical meaning motivation of TD potentials:

- analogic role as potentials in classical mechanics

  Force derived from gradient of a potential U:

$$\underline{F} = \underline{\nabla} U$$

$\Rightarrow$ gravitational potential: $U = -\frac{GMm}{r}$



$$F_{grav} = \frac{\partial U}{\partial r} = \frac{GMm}{r^2}$$

Forces lead to movements of particles

TD potentials:

Gradients / derivatives of TD potentials result in state variables (T, P...) whose change induce TD processes (expansion, heating...)

↳ until system is in equilibrium via reaching minimum of a TD potential

Example: E_{int} is a TD potential

$$dE_{int} = \underbrace{\frac{\partial E_{int}}{\partial S}}_{= T} dS + \underbrace{\frac{\partial E_{int}}{\partial V}}_{= -P} dV$$

Mathematical concept of thermodynamic potentials

follows mathematical definition an exact differential:

Key of an exact differential:

* describes a quantity/fct. that can be integrated along any path between two points with the same result.
* $df = P\,dx + Q\,dy$ with $P = \left(\frac{\partial f}{\partial x}\right)_y$; $Q = \left(\frac{\partial f}{\partial y}\right)_x$

  is an exact differential, if there exists a well-defined scalar fct $f(x,y)$ fulfilling $\left(\frac{\partial P}{\partial y}\right)_x = \left(\frac{\partial Q}{\partial x}\right)_y$

this means:

$$\boxed{\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}} \; ; \quad \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)$$

Schwartz theorem

Example

$$f(x,y) = 3xy$$

then $P = \left(\frac{\partial f}{\partial x}\right)_y = 3y$; $Q = \left(\frac{\partial f}{\partial y}\right)_x = 3x$

$$\left(\frac{\partial P}{\partial y}\right)_x = 3 = \left(\frac{\partial Q}{\partial x}\right)_y = 3$$

$df(x,y)$ is an exact differential

Counterexample for an inexact differential:

$$dD = y\,dx - x\,dy \; ; \; \underbrace{\left(\frac{\partial D}{\partial x}\right)_y}_{P} = y \; ; \; \underbrace{\left(\frac{\partial D}{\partial y}\right)_x}_{Q} = -x$$

$$\frac{\partial^2 D}{\partial x\,\partial y} = 1 \quad \neq \quad \frac{\partial^2 D}{\partial y\,\partial x} = -1$$

unequal!

D is an inexact differential!

Exact differential $\bar{E}_{int}$:

$$dE_{int} = \underbrace{\left(\frac{\partial E_{int}}{\partial S}\right)_{V,n}}_{=T} dS + \underbrace{\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n}}_{=-p} dV + \sum_i \underbrace{\left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}}_{=\mu_i} dn_i$$

$$T = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n} \; ; \quad P = -\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n} \; ; \quad \mu_i = \left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}$$

Let's apply the Schwartz theorem to E_{int}:

$$\frac{\partial^2 E_{int}}{\partial S \, \partial V} = \frac{\partial^2 E_{int}}{\partial V \, \partial S} \longrightarrow \left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}$$

$$\frac{\partial^2 E_{int}}{\partial S \, \partial n_i} = \frac{\partial^2 E_{int}}{\partial n_i \, \partial S} \longrightarrow \left(\frac{\partial T}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial S}\right)_{T,n}$$

$$\frac{\partial^2 E_{int}}{\partial V \, \partial n_i} = \frac{\partial^2 E_{int}}{\partial n_i \, \partial V} \longrightarrow -\left(\frac{\partial P}{\partial n_i}\right)_{V,S} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{S,n}$$

Maxwell equations

Natural variables of a TD potential:

TD potential fully determined, if natural variables are specified (S, V, n for E_{int}), & if dependent variables (E_{int}: T, P, μ) be derived from derivatives of the TD potential to the natural variables

for E_{int}: S, V, n

Counter example: $E_{int}(T, V, n)$

$$dE_{int} = \underbrace{\frac{\partial E_{int}}{\partial T}}_{= C_V} dT + \frac{\partial E_{int}}{\partial V} dV + \sum_i \frac{\partial E_{int}}{\partial n_i} dn_i$$

↯ T cannot be a natural variable as S would not be obtained.

Introduce other TD potentials, in addition to E_{int}:

Disadvantage of $E_{int}(S, V, n)$: entropy hard to measure or fix, E_{int} in equilibrium is minimised when S & V are const. (internal equilibrium in an isolated system)

$$dE_{int} = T\,dS - P\,dV = 0 \text{ as } dS = 0 \text{ \& } dV = 0$$

↳ new Energy fcts / TD potential to describe other experiments (e.g. at const T or/and P)

↳ with other sets of natural variables which are easier to measure & control (e.g. T / P)

↳ Use these TD potentials to make estimates on related equilibrium states (when & how)

Mathematically to get other thermodynamic potentials: via Legendre transformation →

Imagine we have a state function $f(x)$ (e.g. E_{int}) with $y(x) = \frac{df(x)}{dx}$

Then the Legendre transform $g(y)$ is defined as follows:

$$\boxed{g(y) = f(x) - yx}$$

a diff. TD potential with new variable ?

E_{int} with variable x

Math. operation to transform one fct into another with the same information, but expressed via diff. natural variables.

Summary 10.2 — Thermodynamic Potentials & Exact Differentials

- TD potentials play the analogue role as that in classical mechanics: Gradients of TD potentials result in state variables (V, P, T, S, …) whose change introduce a TD process (e.g., expansion)

    ➡️TD process continues until TD system is in equilibrium, via reaching minima of TD potentials under given conditions.

- Thermodynamic potentials are mathematically exact differentials fulfilling the Schwartz theorem $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$, describing a fct. f that can be integrated along any path between two points with the same result.

- Natural variables of a TD system allow for
    - a complete description of the potential
    - a direct derivation of remaining state variables from the derivatives of the potential with respect to the natural variables.

Summary 10.2 — Thermodynamic Potentials & Exact Differentials

- Applying the concept of exact differentials, the Schwartz theorem, to TD potentials results in the Maxwell equations.
- Example for TD potential: internal energy E_{int} with natural variables S, V, n:

$$dE_{int} = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n} dS + \left(\frac{\partial E_{int}}{\partial V}\right)_{S,n} dV + \left(\sum \frac{\partial E_{int}}{\partial n_i}\right)_{S,V} dn_i$$

with $T = \left(\frac{\partial E_{int}}{\partial S}\right)_{V,n}$; $P = -\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n}$ and $\mu_i = \left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}$

- Maxwell relations for E_{int}:

$$\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n}$$

$$\left(\frac{\partial T}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial S}\right)_{V,n}$$

$$-\left(\frac{\partial P}{\partial n_i}\right)_{V,S} = \left(\frac{\partial \mu_i}{\partial V}\right)_{S,n}$$

10.3 Enthalpy H

defined as a Legendre transform of E_{int} w.r.t. V:

$V \to P$: $\quad H = E_{int} + PV$

$H = g(y)$, $\quad E_{int} = f(x)$, $\quad P = y = \frac{\partial E_{int}}{\partial V}$, $\quad V = x$

With Euler equation: $H = TS - \cancel{PV} + \sum_i \mu_i n_i + \cancel{PV}$

$= TS + \sum_i \mu_i n_i$

differential of H: $dH = \underline{dE_{int}} + PdV + VdP$

$\hookrightarrow dH = \underbrace{TdS - \cancel{PdV} + \sum_i \mu_i dn_i}_{dE_{int}} + \cancel{PdV} + VdP$

$$dH = T\,dS + V\,dP + \sum_i \mu_i\,dn_i$$

Natural variables of H: S, P, n

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S,P} dn_i$$

Dependent variables:

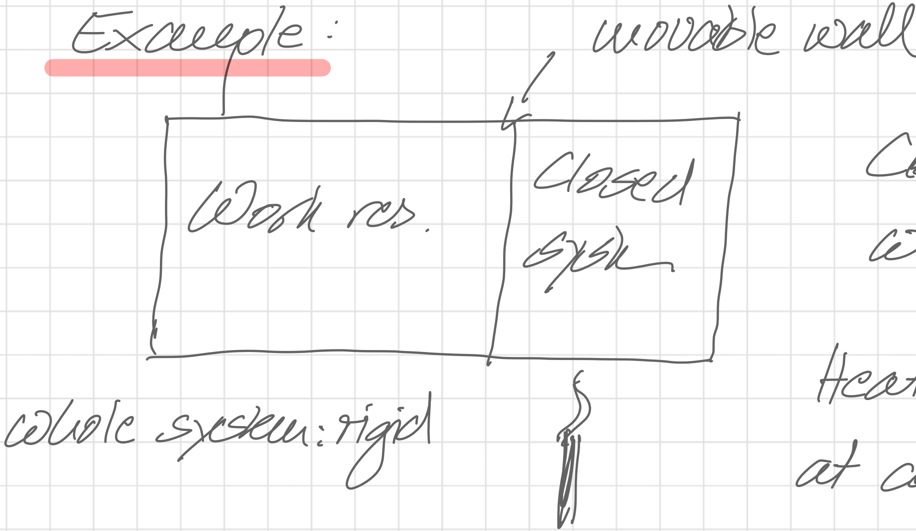
$$T = \left(\frac{\partial H}{\partial S}\right)_{P,n} \; ; \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,n} \; ; \quad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P}$$

Maxwell relations for H:

$$\frac{\partial^2 H}{\partial S\,\partial P} = \frac{\partial^2 H}{\partial P\,\partial S} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{P,n}$$

$\longrightarrow$ remaining Maxwell equation as home exercise

Example:



Closed system in equ. with work res. at all times!

Heat added to system, occurs at const P $\rightarrow$ isobaric process

$$dE_{int} = dQ - dW$$

$$dQ = dE_{int} + dW = dE_{int} + PdV \underset{dP=0}{=} d(\underbrace{E_{int} + PV}_{=H}) = dH$$

$$\hookrightarrow \boxed{Q = \Delta H}$$

Heat added at const P = increase in H

$$\Delta H_{if} = \int_{H_i}^{H_f} dH = H_f - H_i$$

The heat provided to a system, kept a const P, is equal to the difference in H.

(Re-call: for E_{int}: $dE_{int} = dQ$ for isochoric process, i.e. $dV = 0$)

10.4 Free Energy F

Helmholtz

defined as Legendre transform of E_{int} w.r.t. S:

$S \rightarrow T$: $\quad F = E_{int} - \underbrace{T}_{y = \frac{\partial E_{int}}{\partial S}} \underbrace{S}_{x}$

differentials of F:

$$dF = dE_{int} - TdS - SdT$$

$$= \cancel{TdS} - PdV + \sum_i \mu_i dn_i - \cancel{TdS} - SdT$$

$$= -SdT - PdV + \sum_i \mu_i dn_i$$

Natural variables of F: T, V, n

$$dF = \underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,n}}_{= -S} dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_{T,n}}_{= -P} dV + \sum \underbrace{\left(\frac{\partial F}{\partial n_i}\right)_{T,V}}_{= \mu_i} dn_i$$

Maxwell relations

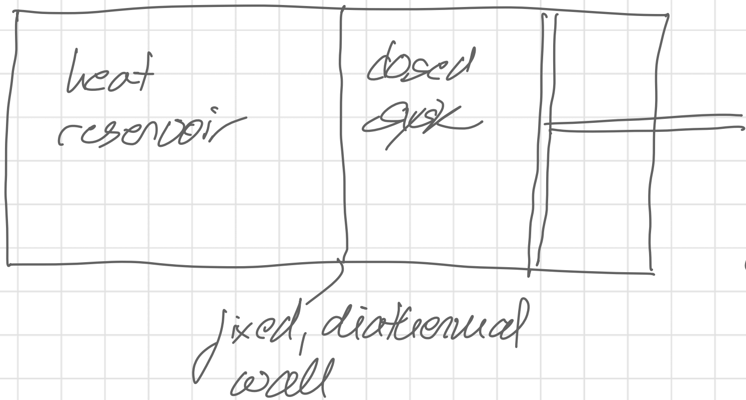
$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \Rightarrow -\left(\frac{\partial S}{\partial V}\right)_{T,n} = -\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

do remaining Maxwell relations as home work!

Example:

Work exerted on a closed system, in equilibrium with a thermal reservoir

→ isothermal process



$$dE_{int} = dQ - dW$$

$$\hookrightarrow -dW = dE_{int} - dQ$$

$$= dE_{int} - TdS =$$

$$= d\underbrace{(E_{int} - TS)}_{=F} = dF$$

$$\boxed{\Delta F = -W} \rightarrow \Delta F_f = \int_{F_i}^{F_f} dF = F_f - F_i$$

Work performed on a system, kept at const T, is equal to the increase in F

(Recall: E_{int}: $dE_{int} = -dW$ for adiabatic processes)

10.5 ~~Gibbs~~ Free Enthalpy G   or Gibbs free energy

Legendre transform of E_{int} w.r.t. S & V
or H w.r.t. S

$S \to T$; $V \to P$ $G = \underbrace{E_{int} + PV}_{H} - TS = H - TS$

Differentiation of G:

$$dG = dH - TdS - SdT$$

$$= \cancel{TdS} + VdP + \sum_i \mu_i dn_i - \cancel{TdS} - SdT$$

$$= -SdT + VdP + \sum_i \mu_i dn_i$$

Natural variables of G: T, P, n

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{P,T} dn_i$$

Compute dependent variables via partial derivatives of G to its natural variables:

$$\Longrightarrow \quad -S = \left(\frac{\partial G}{\partial T}\right)_{P,n} ; \quad V = \left(\frac{\partial G}{\partial P}\right)_{T,n} ; \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

Maxwell relation for G (applying Schwarz theorem to G):

$$\frac{\partial^2 G}{\partial T \, \partial P} = \frac{\partial^2 G}{\partial P \, \partial T} \Longrightarrow -\left(\frac{\partial S}{\partial P}\right)_{T,n} = \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

$$\frac{\partial^2 G}{\partial T \, \partial n_i} = \frac{\partial^2 G}{\partial n_i \, \partial T} \Longrightarrow -\left(\frac{\partial S}{\partial n_i}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n}$$

$$\frac{\partial^2 G}{\partial P \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial P} \Rightarrow \left(\frac{\partial V}{\partial n_i}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n}$$

Relevance of Gibbs' potential:

very important for chemistry (reactions happen o/k at const P & T)

$$G = H - TS = E_{int} + PV - TS$$

$$= \cancel{TS} - \cancel{PV} + \sum_i \mu_i n_i + \cancel{PV} - \cancel{TS}$$

Entered for E_{int}

$$\boxed{G = \sum_i \mu_i n_i}$$

denoted formally as C

↳ Gibbs' potential = total chemical pot.

Summary 10.3-5 — Enthalpy, Free Energy, Gibbs Free Enthalpy

- Enthalpy H = E_{int} + PV: natural variables are S, P, n

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{V,n_i} dP + \sum \left(\frac{\partial H}{\partial n_i}\right)_{S,P} d\mu_i$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} ;\ V = \left(\frac{\partial H}{\partial P}\right)_{V,n_i} ;\ \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P}$$

- Free Energy F = E_{int} - TS: natural variables are T, V, n

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,n} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n} dV + \sum \left(\frac{\partial F}{\partial n_i}\right)_{T,V} dn_i$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,n_i} ;\ V = \left(\frac{\partial F}{\partial V}\right)_{T,n_i} ;\ \mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{T,V}$$

- Gibbs/Free Enthalpy G = E_{int} - TS + PV: T, P, n

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P} dn_i$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,n} ;\ V = \left(\frac{\partial G}{\partial P}\right)_{T,n} ;\ \mu_i = \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

10.6 Equilibria of subsystems coupled to a reservoir

Characterising the approach to equilibrium of a system composed of two simple subsyst. 1+2 coupled to a reservoir (in equilibrium with reservoir)

$$S = S_1 + S_2 \,; \quad U = U_1 + U_2 \,; \quad n = n_1 + n_2$$

TD potentials:

$$E_{int} = E_{int,1} + E_{int,2}$$

$$F = F_1 + F_2$$

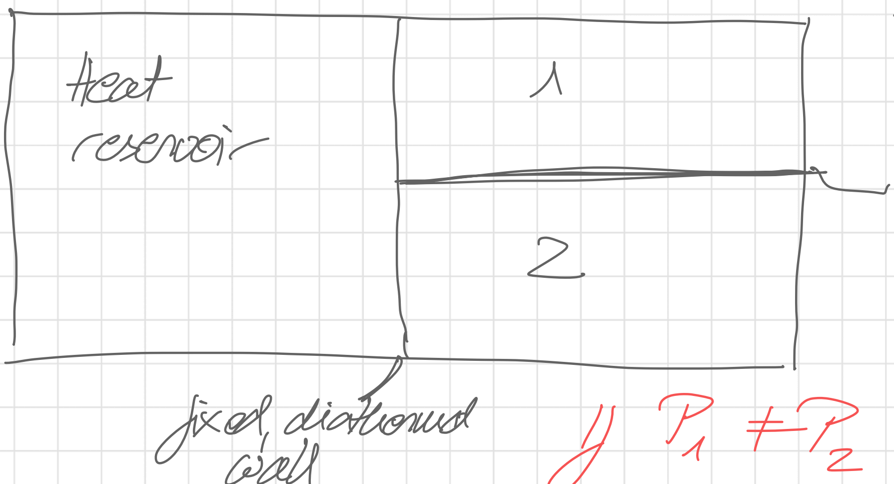
$$H = H_1 + H_2$$

$$G = G_1 + G_2$$

also exten. quantities.

1. Minimum of free energy

Two subsystems are kept in thermal equilibrium with a heat reservoir at const T



$T_{res} = T_1 = T_2 = T$

movable wall

$V = V_1 + V_2 = \text{const}$ (system is rigid)

If $P_1 \neq P_2 \longrightarrow$ approach to mech. equilibrium at const T & const V

Change of total free energy:

$$dF = dE_{int} - TdS$$

Because $V = \text{const} \Rightarrow$ any total mechanical work is vanishing $dW = 0$

$$\hookrightarrow dF = dQ - T\underbrace{dS}_{= dS_{Prod} + \frac{dQ}{T}} = \cancel{dQ} - TdS_{Prod} - \cancel{dQ}$$

$$= -\underbrace{TdS_{Prod}}_{\geq 0} \leq 0$$

$\Rightarrow dF \leq 0$ at const V & T

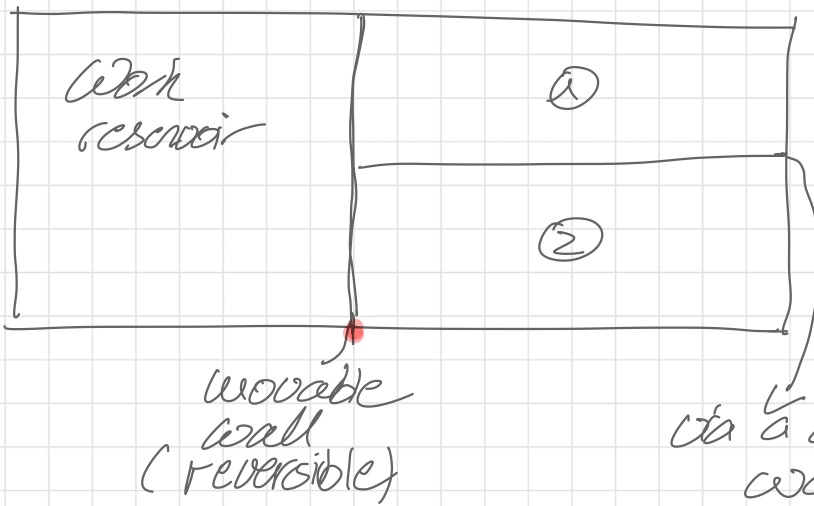
Inequality describes the decrease of free energy when approaching mechanical equ. at const T & V

Final equilibrium states is characterised by a const F, $dF = 0$ & F being a minimum

If a rigid system is kept at const T, the mechanical equ. state (between 1 & 2) is minimising F of the system.

2. Minimum of enthalpy

Two subsystems in mechanical equilibrium with a work reservoir $P_{res} = P_1 = P_2 = P$



action of reservoir on system is assumed to be reversible such that total entropy $S = S_1 + S_2 = \text{const}$

If $T_1 \neq T_2$ → approach to thermal equilibrium at const P & S

Change of total enthalpy when moving to equil. at const P & S

$$dH = dE_{int} + PdV = dQ - \underbrace{dW}_{\cancel{PdV}} + \cancel{PdV} = dQ$$

How to constrain dQ?

$$dS = 0 \longrightarrow \frac{dQ}{T} + dS_{prod} = 0 \quad \text{(entropy balance equ.)}$$

$$\longrightarrow \frac{dQ}{T} = -\underbrace{dS_{prod}}_{\geq 0} \leq 0$$

$\longrightarrow dQ \leq 0$ Since $dH = dQ \longrightarrow \boxed{dH \leq 0}$ at const P & S

Inequality describes the decrease in H while approaching thermal equilibrium at const P & S

Final equilibrium state : H = const, $dH = 0$

H being minimal. ...

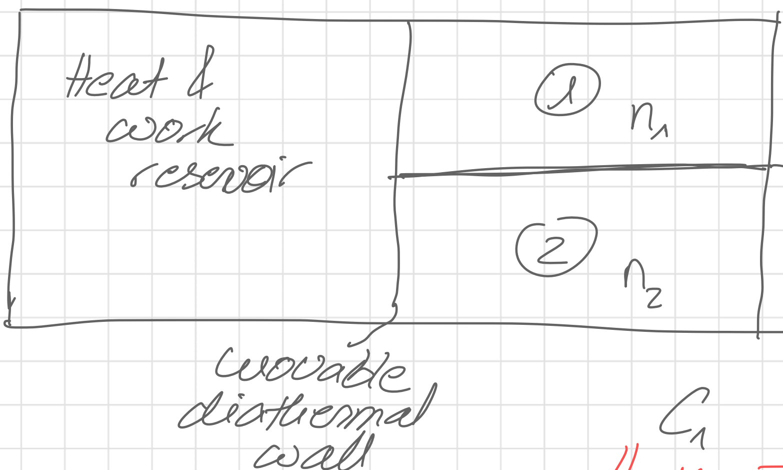
If a system is kept at const P & at const S, then the thermal equi. between 1 & 2 minimises H of the system.

3. Minimum of Gibbs enthalpy

Closed system, composed of two subsystems, which both in thermal & mechanical equi. with a heat & work reservoir

$T_{res} = T_1 = T_2 = T$

$P_{res} = P_1 = P_2 = P$



fixed, non-diathermal, permeable wall

→ matter flow

$n = n_1 + n_2 = const$

$c_1 \quad c_2$

If $\mu_1 \neq \mu_2$ → approach to chemical equilibrium at const T & P

Change of total Gibbs enthalpy G :

$$dG = dE_{int} - TdS + PdV$$

$$= dQ - \underbrace{dW}_{\substack{\| \\ \cancel{PdV}}} - TdS + \cancel{PdV} = \cancel{dQ} - \underbrace{TdS}_{\substack{\| \\ T\left(\cancel{\frac{dQ}{T}} + dS_{prod}\right)}}$$

$$= dQ - dQ - TdS_{prod}$$

$$\Longrightarrow \boxed{dG = -TdS_{prod} \leq 0}$$

The inequality describes the decrease in G when approaching chemical equi. via an irreversible matter transfer between 1 & 2 while kept at const P & T

Final equilibrium: $dG = 0$, G is minimal $(d^2G > 0)$

If a closed system is kept at const P, T, then chemical equ. is reached by minimising the Gibbs potential G.

Typical thermodynamic potentials

Potential	Definition	Natural variables	Minimized when...
Internal energy U E_{int}	E_{int} $U(S, V)$	Entropy, volume	System is isolated const U & S
Helmholtz free energy F	$F = U - TS$	Temperature, volume	Constant T, V
Enthalpy H	$H = U + PV$	Entropy, pressure	Constant S, P
Gibbs free energy G	$G = U + PV - TS = H - TS$	Temperature, pressure	Constant T, P

- Think of thermodynamic potentials as the **“right form” of energy** to track when certain variables are held fixed.
- Systems **spontaneously evolve to minimize the relevant potential** under the given constraints.
- **Analogy**: Just like a ball rolls down a hill to minimize gravitational potential energy, a system ‘rolls down’ its thermodynamic potential to equilibrium.

Summary 10.6 — Equilibria of (sub)systems coupled to a reservoir

Minimization principles are a fundamental concept in thermodynamics and underlies the behavior of thermodynamic systems approaching equilibria states.

- At constant S and P, the thermal equilibrium state of a system corresponds to a minimum in the enthalpy H, i.e. the system naturally evolves towards a state where H is as low as possible.
- At constant T and V, the mechanical equilibrium state of a system corresponds to a minimum in the free energy F, i.e. the system naturally evolves towards a state where F is as low as possible.
- At constant T and P, the chemical equilibrium state of a system corresponds to a minimum in the Gibbs/free enthalpy G, i.e. the system naturally evolves towards a state where G is as low as possible.

(For the internal energy, this is true at constant S and V)

Up next:

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

Lecture 6: —Chapter 7. First law of thermodynamics and thermal processes

Lecture 7: — Mock exam I *with Dr. Tress*

Lecture 8: —Chapter 8. Entropy and the second and third law of thermodynamics

Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

Lecture 14: —Final review and open questions