Lecture 2
16.01.2019

Thermodynamic potentials, response functions and Maxwell's relations, thermodynamic stability

Summary lecture 1

- Thermodynamic laws are encapulated in the thermodynamic inequality

$$\boldsymbol{dU \leq TdS - PdV}$$

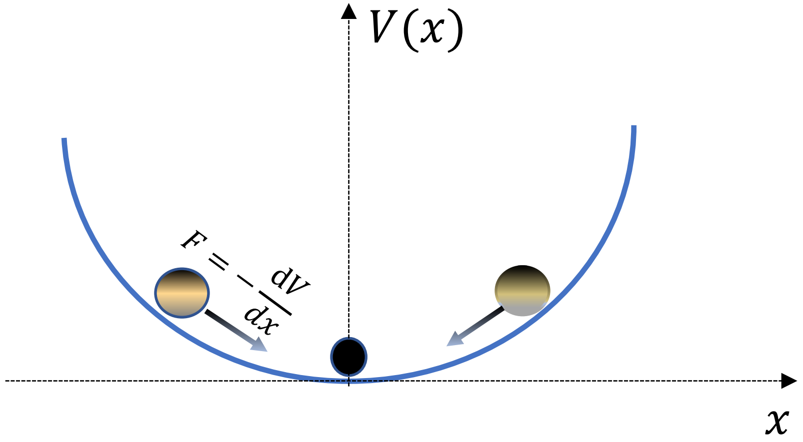
- Entropy cannot be calculated solely from thermodynamics because the expression is determined up the entropy constant and not extensive

$$\boldsymbol{S(U,V,N) = N\,k\left[\frac{3}{2}ln\left(\frac{U}{N}\right) + ln\,V + \sigma_0\right]}$$

A consequence of an non-extensive entropy is the Gibbs paradox: the gas entropy changes even when there is no change in the thermodynamic state of a gas

Classical mechanics versus thermodynamics

- ☐ *In classical mechanics, the stable equilibrium of a mechanical system is related to the minimum of its potential energy*



Potential energy in classical mechanics	Variables	Driving force to equilibrium
V(x,y,z)	x, y, z	$\boldsymbol{F} = -\nabla \mathbf{V}$

What is the analogue of this for a thermodynamic system?

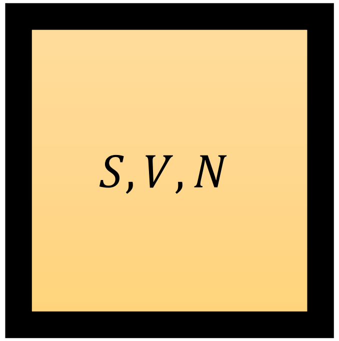
Free energies as thermodynamic potentials

- ☐ Describe the thermodynamic state of a system depending on how the system *interacts with its environment*
- ☐ When a system is **isolated**, the thermodynamic potential that is **minimized at equilibrium** is its internal energy $\boldsymbol{U}$
- ☐ But, when a system is at equilibrium with a thermal bath at fixed T, which *energy* is then minimized?
- ☐ When a system is at equilibrium with a reservoir at fixed $T$and P, which *energy* is then minimized?

Thermodynamic Potentials	**Thermodynamic (natural) Variables**
U (S,V,N)	**S, V, N**
H (S,P,N)	**S, P, N**
F (T,V,N)	**V, T, N**
G (T,P,N)	**P, T, N**

Potential energy in classical mechanics	Variables
V(x,y,z)	x, y, z

Isolated systems and internal energy $U(S,V,N)$



- Sum of all the kinetic and potential energies of all the particles in the system
- An infinitesimal dU is due to infinitesimal and independent changes in S, V, or N

$$\mathrm{dU} = \left(\frac{\partial U}{\partial S}\right)_{V,N} \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_{S,N} \mathrm{d}V + \left(\frac{\partial U}{\partial N}\right)_{S,V} \mathrm{d}N$$

- Identify it with the **thermodynamic identity** **for** energy change in a **reversible** process

$$\mathbf{d}\boldsymbol{U} = \boldsymbol{T}\mathbf{d}\boldsymbol{S} - \boldsymbol{P}\mathbf{d}\boldsymbol{V} + \boldsymbol{\mu}\mathbf{d}\boldsymbol{N}$$

we can define T, P and μ from changes in U with respect to their conjugate variables

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

«ability to exchange energy», «ability to exchange volume», «ability to exchange particles»

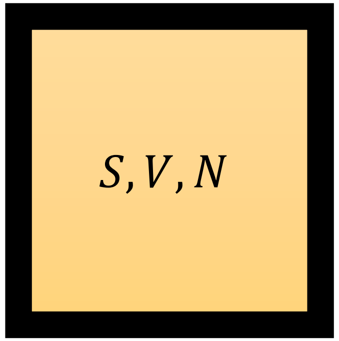
Isolated systems and internal energy $U(S,V,N)$

☐ From the 2nd law of thermodynamics, the entropy change satisfies this inequality

$$TdS \geq \mathrm{dU} + PdV - \mu \mathrm{d}N$$

Hence the change in the internal energy satisfies this **thermodynamic inequality**

$$\boldsymbol{dU \leq \mathbf{TdS} - PdV + \mu dN}$$



Then any change in the internal energy when $S, V,$ and N are fixed is $\boldsymbol{dU|_{S,N,V} \leq 0}$

Which is to *lower* the internal energy to its **miminum value at equilibrium**

☐ Reversible process in an **isolated** system at fixed $S, V,$ and N means that $\boldsymbol{U}$ **is conserved**:

$$dU = 0, hence\ \delta Q = -\delta W$$

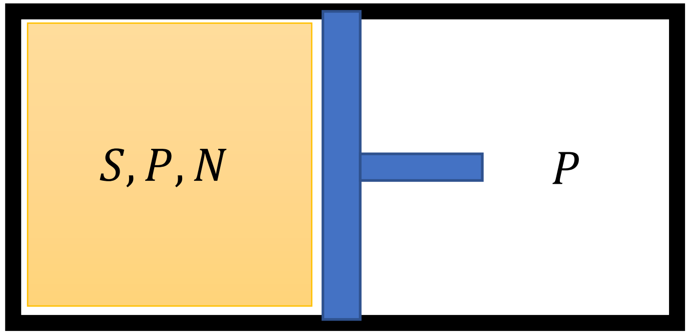
Systems at constant P and Enthaly $H(S,P,N)$

D. Schroeder

- ***The enthalpy H*** is the thermodynamic potential given by the internal energy of a system plus the work needed to keep the system at a given P

$$H = U + PV$$

- It is the energy to create something (*system*) out of nothing and make room for it somewhere (*environment*)



- An infinitesimal change in H is due independent, infinitesimal changes in S, P, N

$$\mathrm{d}H = \left(\frac{\partial H}{\partial S}\right)_{P,N} \mathrm{d}S + \left(\frac{\partial H}{\partial P}\right)_{S,N} \mathrm{d}P + \left(\frac{\partial H}{\partial N}\right)_{S,P} \mathrm{d}N$$

By defining $T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$, $V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$ and $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$

- **Thermodynamic identity** for an infinitesimal **reversible** process

$$\boldsymbol{dH = TdS + VdP + \mu dN}$$

Systems at constant P and Enthaly $H(S,P,N)$

D. Schroeder

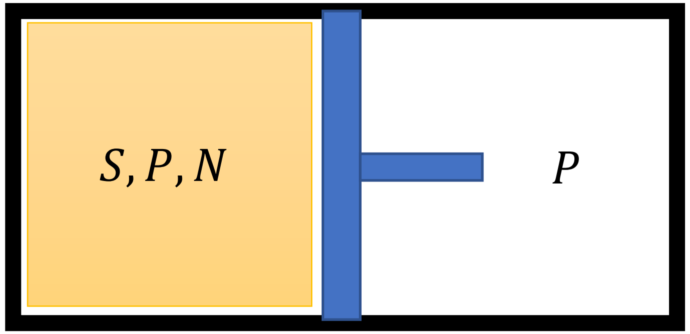
- ☐ Thermodynamic identity for an infinitesimal reversible process

$$\mathrm{d}H = dU + d(PV)$$

Combing this with the 2nd law of thermodynamics,

$$dU \leq TdS - P\mathrm{d}V + \mu \mathrm{d}N$$

- ☐ **Thermodynamic inequality** for any infinitesimal process (reversible «=», irreversible «>»)



$$dU + d(PV) \leq TdS + V\mathrm{d}P + \mu \mathrm{d}N$$

$$\boldsymbol{dH \leq TdS + V\mathrm{d}P + \mu dN}$$

- ➢ Any change in enthalpy H when S, P, and N are fixed is $\boldsymbol{dH|_{S,P,N} \leq 0}$. This is to *lower* ***H*** to its **miminum value at equilibrium**
- ➢ Reversible process at fixed S, $\boldsymbol{P}$, and N means that ***H* is conserved**: $dH|_{S,P,N} = 0$
- ➢ Reversible process at fixed $\boldsymbol{P}$, and N means that : $dH|_{P,N} = TdS = \delta Q_{rev}$

Systems at constant P and Enthaly $H(S,P,N)$

D. Schroeder

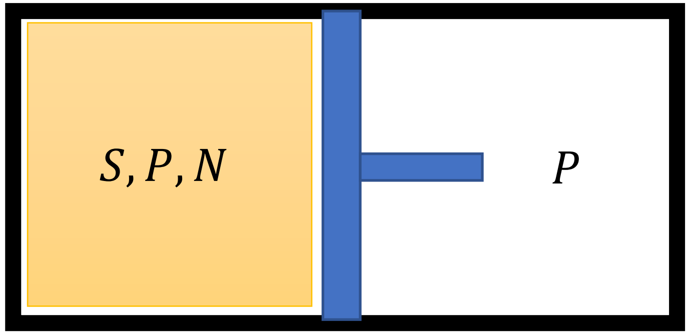
- System + surrounding at constant pressure = isolated system

- System can exchange work with the surrounding, thus from the conservation of energy

$$\mathrm{d}(U+U_{surr})=0\rightarrow dU=-dU_{surr}\rightarrow -\delta W=\delta W_{surr}$$

- **Principle of maximum work**

$$\delta W\leq PdV\rightarrow dU\leq -PdV$$



- *Pressure is constant, thus this spontaneous process will minimize enthalpy at equilibrium*

$$d(U+PV)\leq 0\rightarrow dH\leq 0$$

- *Working with enthalpy , we can describe the system in contact with its surrounding at constant P without actually keeping track of the transformations in the surroundings*

Joule-Thomson expansion: constant enthalpy

$$Q = 0 \rightarrow \Delta U = -W$$

Work done on the gas at P_1=const:

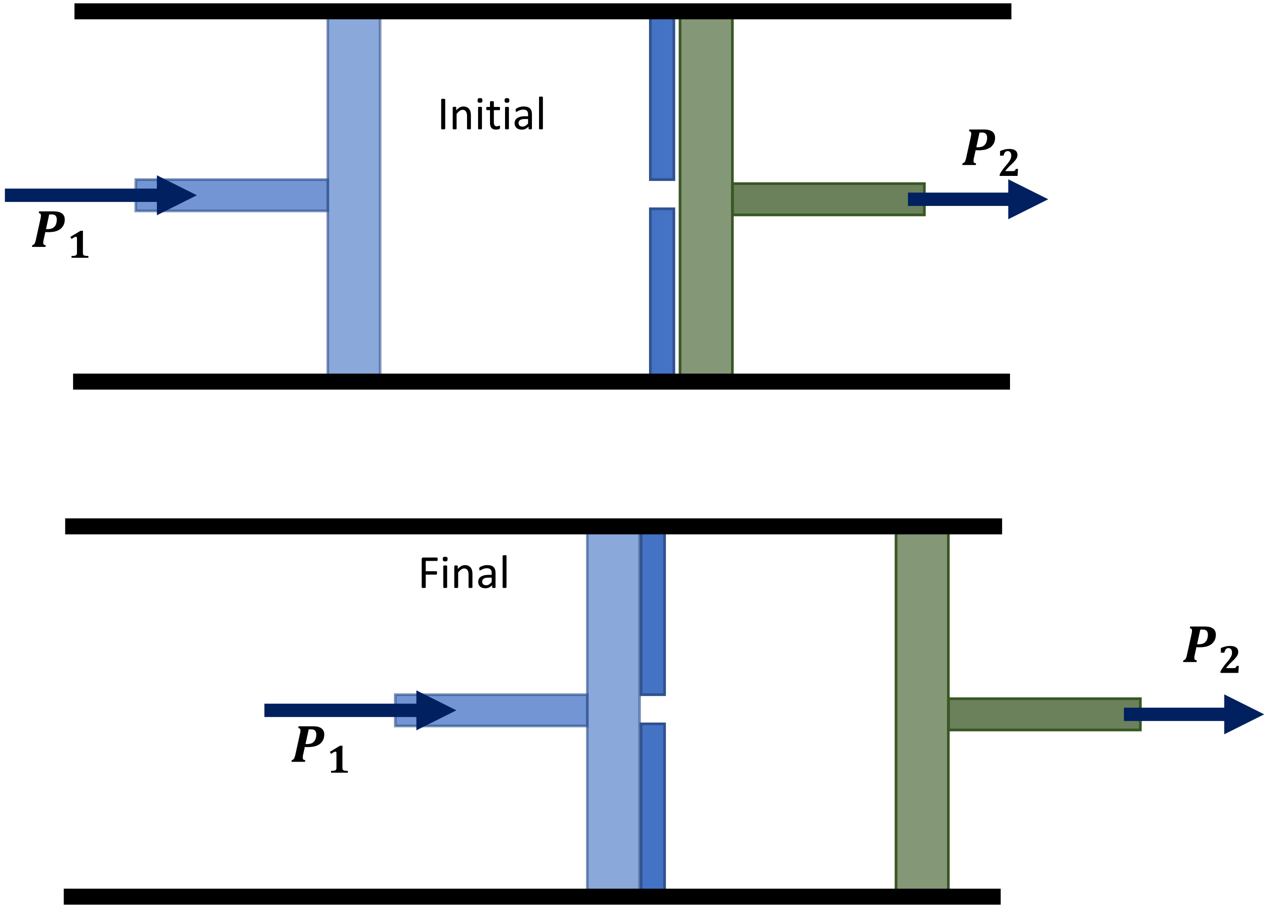
$$W_1 = \int_{V_1}^{0} P_1\, dV = -P_1 V_1$$

Work done by the gas at $P_2 = const:$

$$W_2 = \int_{0}^{V_2} P_2\, dV = P_2 V_2$$

Total work to move the gas from one chamber to the other

$$-W = -W_1 - W_2 = P_1 V_1 - P_2 V_2$$

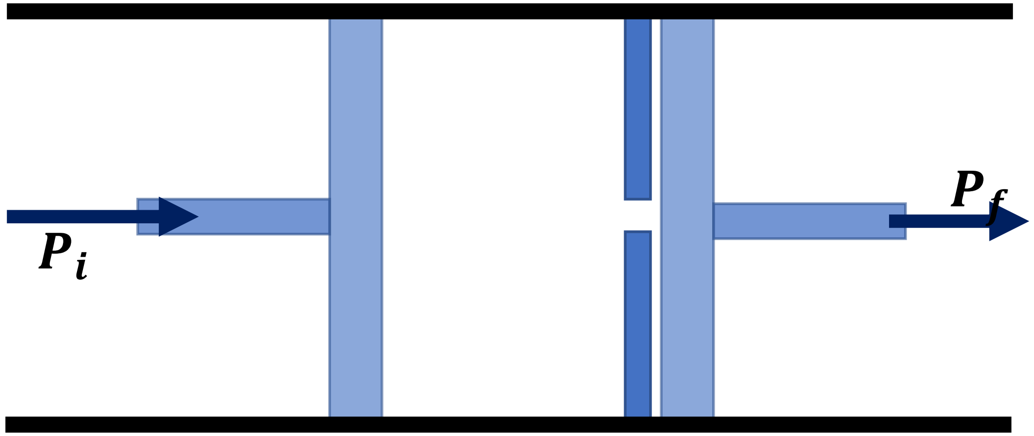


Joule-Thomson expansion

$$\Delta U = -W \rightarrow$$

$$U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

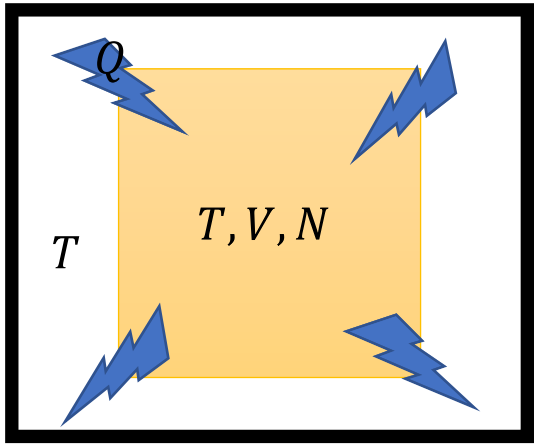


This expansion is at constant enthalpy

$$\Delta H = \Delta(U + PV) = 0$$

Systems at constant T and Helmholtz free energy $F(T,V,N)$

- ☐ ***The Hemholtz free energy F*** is the thermodynamic potential given by the internal energy of a system minus the available heat exchange with the thermal bath fixed T



$$F = U - TS$$

- ☐ It is the energy to create something (system) out of nothing when there is “free” heat supply from the environment
- ☐ An infinitesimal change in F is due to independent, infinitesimal changes in T, V, N

$$\mathrm{d}F = \left(\frac{\partial F}{\partial T}\right)_{V,N} \mathrm{dT} + \left(\frac{\partial F}{\partial V}\right)_{T,N} \mathrm{d}V + \left(\frac{\partial F}{\partial N}\right)_{T,V} \mathrm{d}N$$

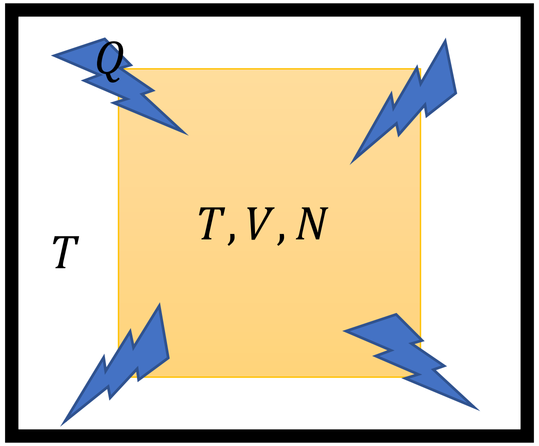
By defining $\mathrm{S} = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$, $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$ and $\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$

- ☐ **Thermodynamic identity** for an infinitesimal **reversible** process

$$\mathbf{d}\boldsymbol{F} = -\boldsymbol{S}\mathbf{d}\boldsymbol{T} - \boldsymbol{P}\mathbf{d}\boldsymbol{V} + \boldsymbol{\mu}\mathbf{dN}$$

- ☐ The system + its thermal bath = isolated system. Hence total internal energy is conserved

$$d(U + U_{bath}) = 0 \rightarrow dU = -dU_{bath}$$



- ☐ System can exchange heat with its thermal bath, while both maintained the same temperature T. Using the conservation of energy and Clausius inequality

$$\delta Q_{bath} = -\delta Q = -dU \rightarrow \frac{\delta Q_{bath}}{T} = -\frac{dU}{T} \leq dS_{bath}$$

- ☐ Hence, the change in the total entropy, $\mathrm{S_t} = S + S_{bath}$, is

$$dS + dS_{bath} \geq dS - \frac{dU}{T} \geq 0 \rightarrow \frac{TdS - dU}{T} \geq 0$$

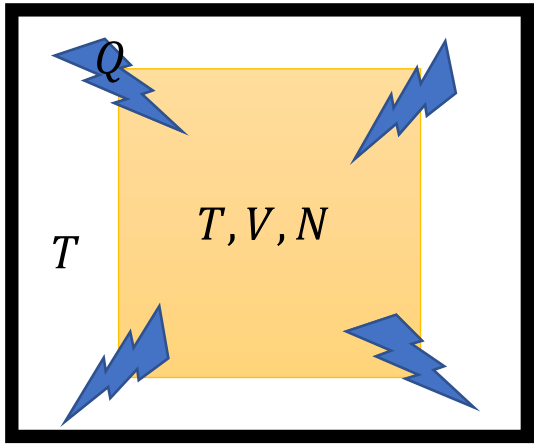
- ☐ *Minimizing the Helmholtz free energy is equivalent to maximizing the total entropy*

$$\boldsymbol{dS_t \geq 0 \rightarrow d(U - TS) \leq 0 \rightarrow dF \leq 0}$$

- **Describing the system by its Helmholtz free energy, we capture the evolution of both the system and its thermal bath in accord to the thermodynamic principles**

Systems at constant T and Helmholtz free energy $F(T,V,N)$

- ❑ Thermodynamic identity for an infinitesimal reversible process



$$\mathrm{d}F = -SdT - PdV + \mu\mathrm{d}N$$

Combing this with the 2nd law of thermodynamics,

$$dU \leq TdS - \mathrm{P}dV + \mu\mathrm{d}N$$

- ❑ **Thermodynamic inequality** for any infinitesimal process (reversible «=», irreversible «>»)

$$dU - d(TS) \leq -TdS - PdV + \mu\mathrm{d}N$$

$$\boldsymbol{dF \leq -SdT - \mathrm{P}dV + \mu dN}$$

- Any change in F when $\mathrm{T}, \mathrm{V},$ and N are fixed must be $\boldsymbol{dF|_{T,V,N} \leq 0}$. This is to *lower* $\boldsymbol{F}$ to its **miminum value at equilibrium**
- Reversible process at fixed $\boldsymbol{T}$, V, and N means that F **is conserved**: $dF|_{T,V,N} = 0$
- Reversible process at fixed $\boldsymbol{T}$, and N means that : $dF|_{T,N} = -PdV$
- Changes in F at a fixed T equals to the ***available work*** that a system can do.

Systems at constant T and P and Gibbs free energy $\mathrm{G}(T, P, N)$

- ***The Gibbs free energy F*** is the thermodynamic potential given by the internal energy of a system minus the available heat exchange plus the work done on the reservoir

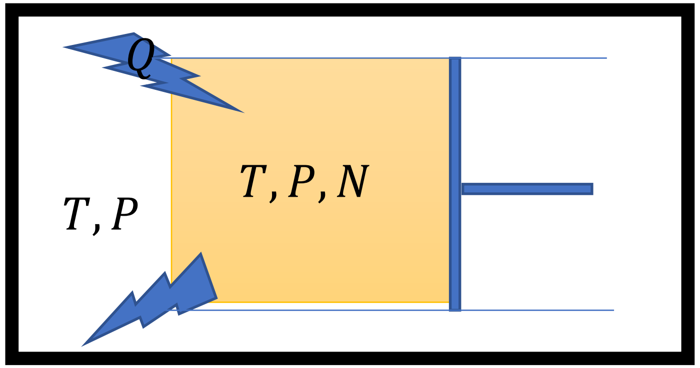
$$G = U - TS + PV$$

D. Schroeder

- It is the energy to create something (system) out of nothing and put into an environment when there is “free” heat
- An infinitesimal change in G is due to independent, infinitesimal changes in T, P, N

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{P,N} \mathrm{dT} + \left(\frac{\partial G}{\partial P}\right)_{T,N} \mathrm{d}P + \left(\frac{\partial G}{\partial N}\right)_{T,P} \mathrm{d}N$$

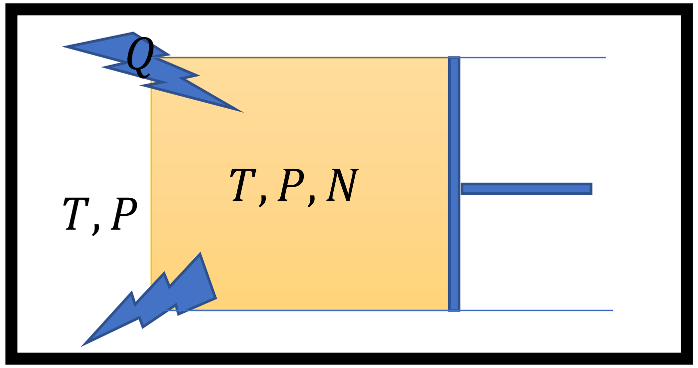
By defining $\mathrm{S} = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$, $V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ and $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$



- **Thermodynamic identity** for an infinitesimal reversible process

$$\boldsymbol{\mathrm{d}G = -SdT + VdP + \mu\mathrm{dN}}$$

Systems at constant $T\ and\ P$ and Gibbs free energy $\mathrm{G}(T, P, N)$



- Thermodynamic identity for an infinitesimal reversible process

$$\mathrm{d}G = -SdT + VdP + \mu\mathrm{d}N$$

Combing this with the 2nd law of thermodynamics,

$$dU \leq TdS - PdV + \mu\mathrm{d}N$$

- **Thermodynamic inequality** for any infinitesimal process (reversible «=», irreversible «>»)

$$dU - d(TS) + d(PV) \leq -TdS + VdP + \mu\mathrm{d}N$$

$$\boldsymbol{dG \leq -SdT + VdP + \mu dN}$$

- Any change in the Gibbs free energy G when $\mathrm{T}, \mathrm{P},$ and N are fixed must be $\boldsymbol{dG|_{T,P,N} \leq 0}$
  Which is **to minimize *G* at equilibrium**
- Reversible process at fixed $\boldsymbol{T}$, $\boldsymbol{P},$ and N means that G **is conserved**: $dG|_{T,P,N} = 0$
- Reversible process at fixed $\boldsymbol{T},$ and P means that : $dG|_{T,P} = \mu dN$
- Changes in G at a fixed T and P equals to the ***available chemical work*** to increase or decrease the number of particles, or any **other work which is not mechanical**

Thermodynamic potentials are related by Legendre transforms

- The extensive variables (S, V, N) and intensive variables (T, P, μ) are conjugate variables

  When one is an independent (control) variable fixed by the surroundings, its conjugate variable is a derivative:

$$\text{When S is } a\ control\ variable\ then\ T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$$

- Variables like S are hand to control experimentally, hence it is better to transform the internal energy U into another thermodynamic potential that has instead T as a natural variable

- Legendre transform does precisely this: it is a transformation from one thermodynamic potential to another by changing between conjugate variables

Example: the transformation from internal energy $U(S, V, N)$ to entalphy $H(S, P, N)$

$$U(S, V, N) \to H(S, P, N)$$

$$H(S, P, N) = U(S, V, N) + PV, where\ P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

Example in mechanics:

$$\boldsymbol{L(q, \dot{q}) = K(\dot{q}) - U(q), \qquad p = \frac{\partial L}{\partial \dot{q}}}$$

$$\boldsymbol{-H(p, q) = L(q, \dot{q}) - p\,\dot{q} \to H(p, q) = K(p) + U(q), \qquad K = m\frac{\dot{q}^2}{2} = \frac{p^2}{2m}}$$

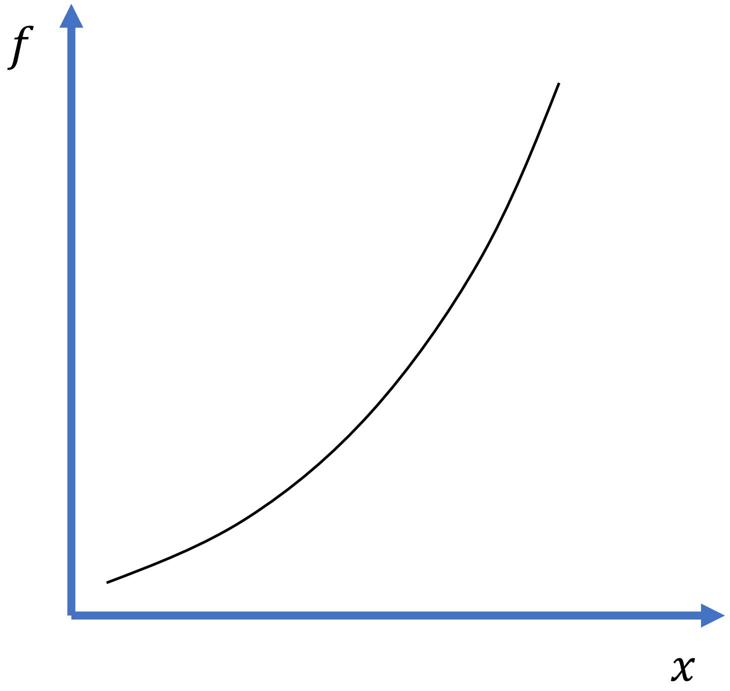
Legendre transform: graphic intepretation

Given a function of x with the slope u

$$\boldsymbol{f(x), \qquad with\ \ u = \frac{df}{dx}}$$

The Legendre transform is

$$\boldsymbol{g\,(u) = \ f(x) - ux,}$$



Legendre transform

Suppose we have a function $\mathrm{F}(x,y)$ where $\mathrm{z}=\left(\frac{\partial F}{\partial x}\right)_y$ then the function $G(z,y)$ is related to $\mathrm{F}(x,y)$ by the Legendre transform

$$\boldsymbol{G(z,y)=F(x,y)-zx}$$

Proof:

$$d(F-\mathrm{zx})=\left(\frac{\partial F}{\partial x}\right)_y dx+\left(\frac{\partial F}{\partial y}\right)_x dy-zdx-xdz$$

$$d(F-\mathrm{zx})=\left(\frac{\partial F}{\partial y}\right)_x dy-xdz, \qquad using\ that\ \mathrm{z}=\left(\frac{\partial F}{\partial x}\right)_y$$

The y-dependence is not changed thus $\left(\frac{\partial F}{\partial y}\right)_x=\left(\frac{\partial G}{\partial y}\right)_z$. Also $G=F(x,y)-zx\rightarrow x=-\left(\frac{\partial G}{\partial z}\right)_y$

$$d(F-\mathrm{zx})=\left(\frac{\partial F}{\partial y}\right)_x dy-xdz=\left(\frac{\partial G}{\partial y}\right)_z dy+\left(\frac{\partial G}{\partial z}\right)_y dz=dG$$

Legendre transforms:

$$\mathrm{U}(S,V,N)$$

$$\mathrm{H}(S,P,N) = U(S,V,N) + PV, P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$$

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

$$\mathrm{G}(T,P,N) = U(S,V,N) - TS + PV$$

Thermodynamic identities

$$\mathrm{dU} = TdS - PdV + \mu dN$$

$$\mathrm{dF} = -SdT - PdV + \mu dN$$

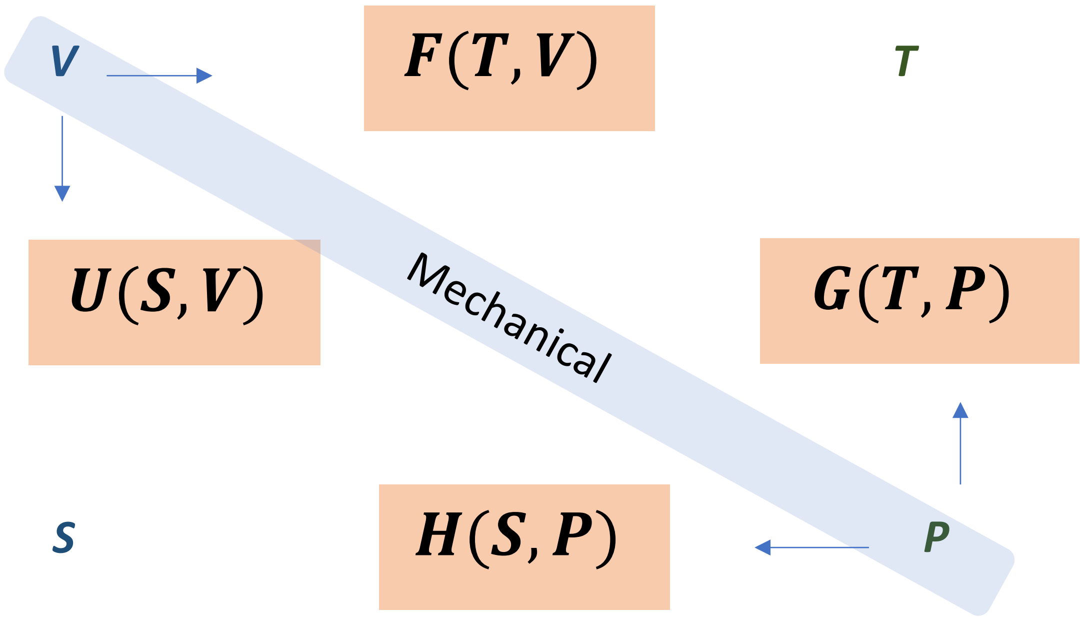
$$\mathrm{d}H = TdS + VdP + \mu dN$$

$$\mathrm{d}G = -SdT + VdP + \mu dN$$

Thermodynamic square

Extensive variables

Intensive variables



V $\quad$ $F(T,V)$ $\quad$ T

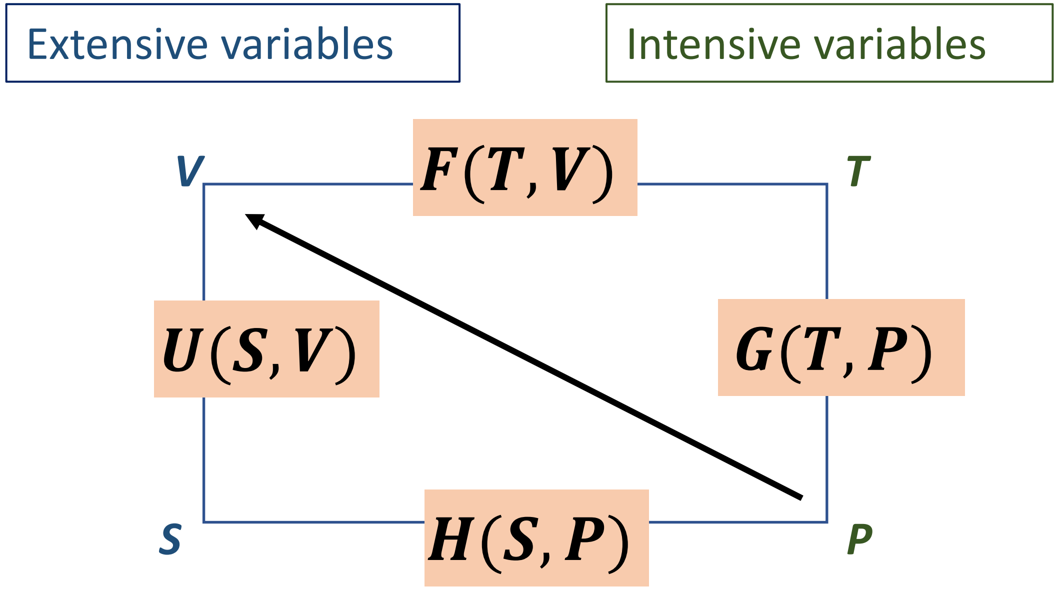
$U(S,V)$ $\quad$ Mechanical $\quad$ $G(T,P)$

S $\quad$ $H(S,P)$ $\quad$ P

$$H(S,P) = U(S,V) + PV$$

$$G(T,P) = F(T,V) + PV$$

Thermodynamic square

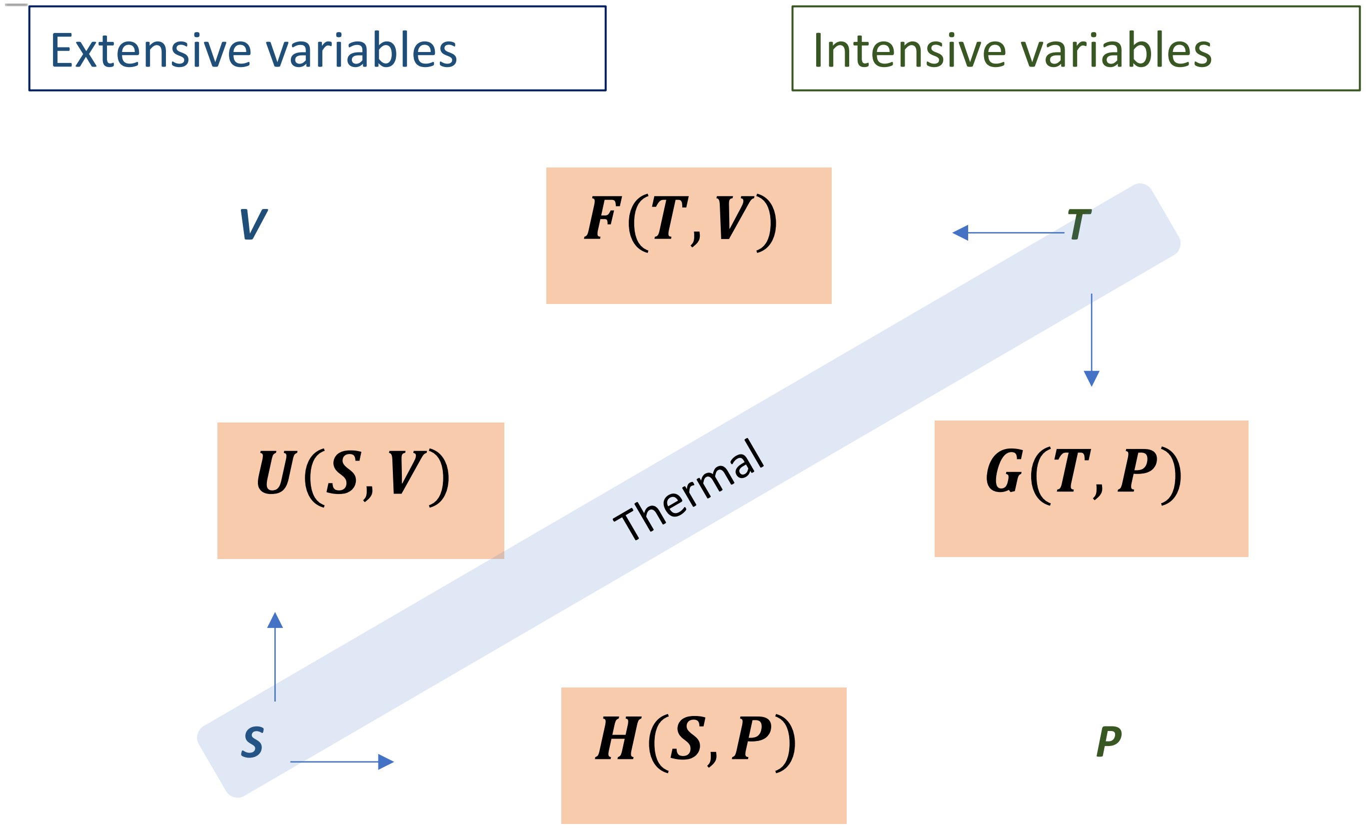


- ☐ Derivative of the thermodynamic potential with respect to one of its arguments while keeping the other constant is determined by going along a diagonal line either with(+) or against(-) the direction of the arrow

$$P = -\left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S$$

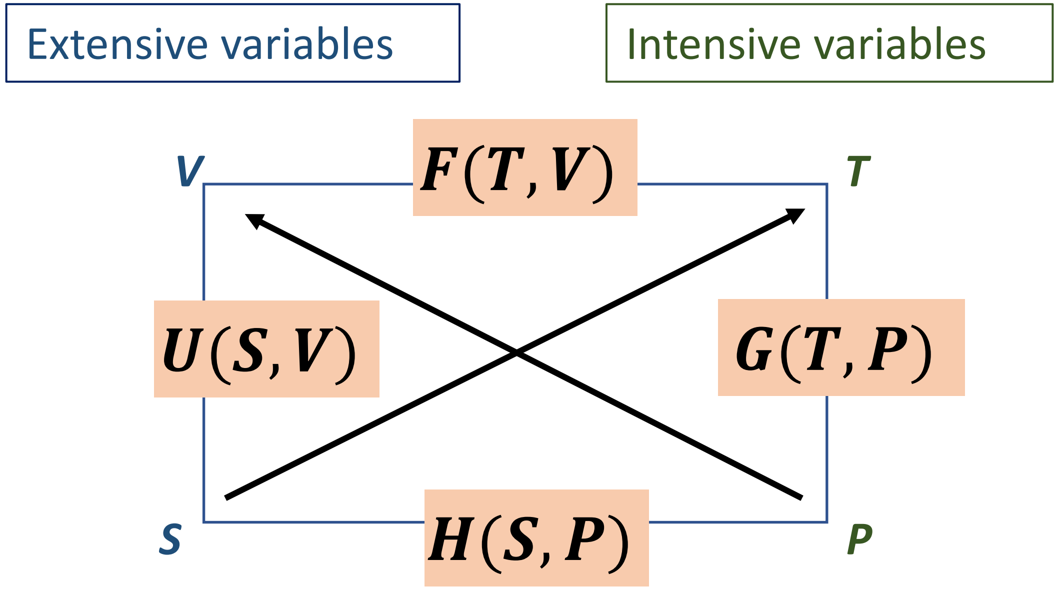
Thermodynamic square



$$G(T,P) = H(S,P) - TS$$

$$F(T,V) = U(S,V) - TS$$

Thermodynamic square



- ☐ Derivative of the thermodynamic potential with respect to one of its arguments while keeping the other constant is determined by going along a diagonal line either with (+) or against (-) the direction of the arrow

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$$

Maxwell's relations

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

- Thermodynamic potential U is a state variable, which implies that $\frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S}$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

- Other Maxwell relaxations follow from the other thermodynamic potentials

- Used to compute relations between response functions: heat capacities, thermal expansion coefficients

Maxwell's relations

$$dF = -SdT - PdV$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

☐ Find the Maxwell's relation corresponding to $F(T, V)$

Extensive thermodynamic potentials:

Thermodynamic potentials are extensive functions: invariant under dilation

- $\mathrm{U}(\mathrm{S},\mathrm{V},\mathrm{N}) = \mathrm{N}\,\widetilde{\mathrm{U}}(\tilde{\mathrm{S}},\widetilde{\mathrm{V}}),\ \tilde{\mathrm{S}} = \mathrm{S}/\mathrm{N}$ and $\widetilde{\mathrm{V}} = \mathrm{V}/\mathrm{N}$
- $\mathrm{H}(\mathrm{S},\mathrm{P},\mathrm{N}) = \mathrm{N}\,\widetilde{\mathrm{H}}(\tilde{\mathrm{S}},\mathrm{P}),\ \tilde{\mathrm{S}} = \mathrm{S}/\mathrm{N}$
- $\mathrm{F}(\mathrm{T},\mathrm{V},\mathrm{N}) = \mathrm{N}\,\tilde{\mathrm{F}}(\mathrm{T},\widetilde{\mathrm{V}}),\ \ \widetilde{\mathrm{V}} = \mathrm{V}/\mathrm{N}$
- $\mathrm{G}(\mathrm{T},\mathrm{P},\mathrm{N}) = \mathrm{N}\,\widetilde{\mathrm{G}}(\mathrm{T},\mathrm{P})$

Gibbs free energy $G(T, P, N)$ and chemical potential μ

- Gibbs free energy $G(T, P, N)$ is an extensive thermodynamic potential. Since, T *and* P are intensive variable, the only extensive variable that it depends on is N, therefore

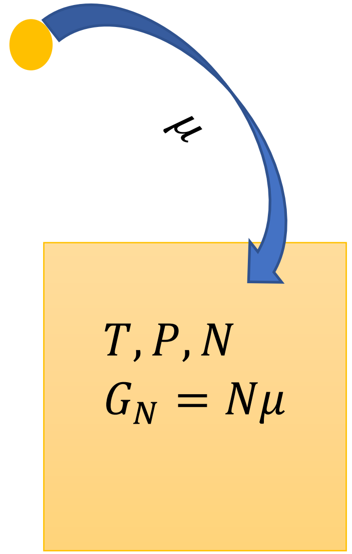
$$G(T, P, N) = NG(T, P, 1)$$

Combining this with the definition of the chemical potential

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = G(T, P, 1) = \frac{G(T,P,N)}{N}$$

- $$\mu(T, P) = \frac{G(T,P,N)}{N}, \qquad G(T, P, N) = N\mu(T, P)$$

Chemical potential is the Gibbs free energy per unit particle at fixed pressure P and temperature T



T, P, N

$G_N = N\mu$

- This means that when we add a particle to the system, its Gibbs enery increases by one unit equal to μ
- By adding more particles we dont change the value of μ: *each particles comes with the same amount of energy indepent of the density of particles in the system when we keep the pressure and temperature constant!*
- In all the other thermodynamics conditions described by U, H and F, μ can vary with N

Gibbs-Duham relation:

Gibbs free energy: $G = U - TS + PV = N\mu$

Euler equation: $U = ST - PV + \mu N$

$$dG = -SdT + VdP + \mu dN = Nd\mu + \mu dN \rightarrow$$

Gibb-Duham relation $\boldsymbol{SdT - VdP + Nd\mu = 0}$

For a multi-component system at constant T and P,

$$\sum_i N_i d\mu_i = 0$$

Thermodynamic equilibrium condition for the chemical potentials in multi-component systems

Heat Capacity at constant volume C_V

How much heat is needed to raise the T of an object by a small amount $\mathrm{d}T$ by keeping the ***volume*** *constant?*

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V, \qquad [C_V] = 1\ \mathrm{J\,K^{-1}}$$

Reversible process: $\boldsymbol{\delta Q = TdS} \rightarrow C_V = \left(T\frac{\partial S}{\partial T}\right)_V$

$$TdS = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \rightarrow \boldsymbol{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

So, if we know the heat capacity of a system, we can immediately estimate the change in its internal energy and entropy upon a *reversible* change in T at fixed V

$$\boldsymbol{dU = C_V dT}, \qquad \boldsymbol{dS = C_V \frac{dT}{T}}$$

Heat Capacity at constant pressure C_P

How much heat is needed to raise the T of a system by a small amount $\mathrm{d}T$ when keeping the ***pressure*** *constant?*

$$C_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P, \qquad [C_P] = 1\ \mathrm{J\,K^{-1}}$$

Reversible process: $\boldsymbol{\delta Q = TdS} \rightarrow C_P = \left(T\frac{\partial S}{\partial T}\right)_P$

$$TdS = dU + PdV = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP + PdV \rightarrow \boldsymbol{C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P} \rightarrow \boldsymbol{C_P = \left(\frac{\partial (U+PV)}{\partial T}\right)_P}$$

$$\boldsymbol{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

So, if we know the heat capacity of a system, we can immediately estimate the change in its enthalpy and entropy upon a *reversible* change in T at fixed P

$$\boldsymbol{dH = C_P dT}, \qquad \boldsymbol{dS = C_P\frac{dT}{T}}$$

$$C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P, for\ ideal\ gas\colon\ C_P = C_V + Nk$$

Compressibility and thermal expansion coefficients

How much the volume changes upon changes in pressure at constant ***<u>temperature</u>*** *or* ***entropy****?*

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T > 0$$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S > 0$$

How much the volume changes upon changes in temperature at constant ***pressure****?*

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P > 0$$

Ideal gas: $\kappa_T = \frac{1}{P}, \alpha = \frac{1}{T}$

Thermodynamic stability

- *Response functions* $C_V, C_P, \kappa_T, \kappa_S, \alpha$ *are positive well-defined quantities*
- *An equilibrium state is stable upon thermal fluctuations as long as the system sponteneously returns to this state every time it is kicked away from it (by thermal fluctuations)*
- When this condition fails, the thermodynamic state becomes unstable and the system undergoes *a phase transition*

Thermodynamic stability

Spontaneous fluctuations in an ***isolated*** *system can bring the system out of its equilibrium state.*

Thermodynamic stability of an equilibrium state is that a spontaneous fluctuation will increase the energy of the *isolated* system $\mathrm{U_{final}} > \mathrm{U_{eq}}$. Then, the system will sponteneouly return to its favored equilibrium

Denote $\delta U = U_{final} - U_{eq}, \quad \delta S = S_{final} - S_{eq}, \ \delta V = V_{final} - V_{eq}$

$$\delta U = \left(\frac{\partial U}{\partial S}\right)_V \delta S + \left(\frac{\partial U}{\partial V}\right)_S \delta V + \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)\delta S^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)\delta S \delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)\delta V^2\right] \geq 0$$

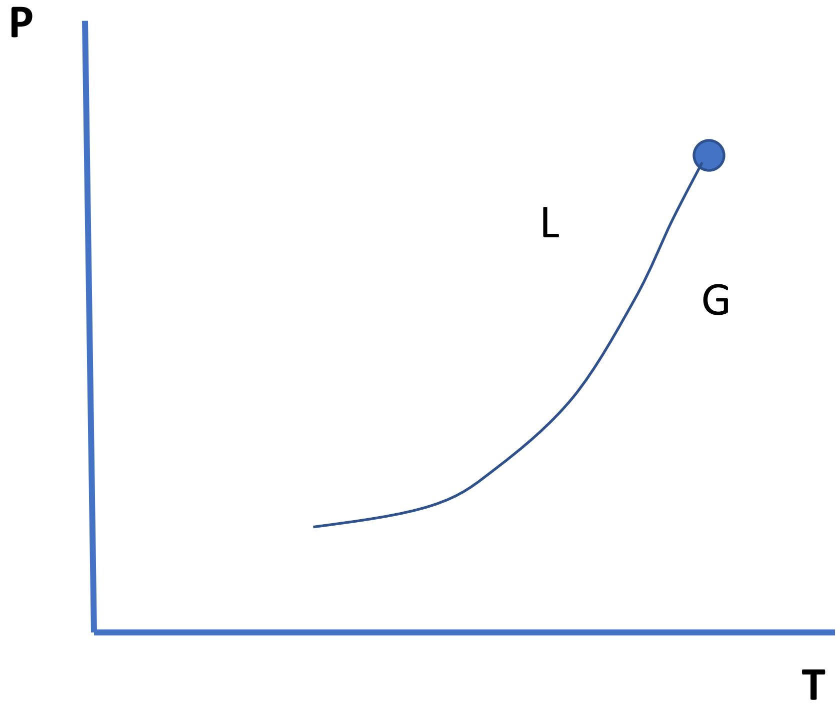
Using that $dU = TdS - PdV$

$$\left[\left(\frac{\partial^2 U}{\partial S^2}\right)\delta S^2 + 2\left(\frac{\partial^2 U}{\partial S \partial V}\right)\delta S \delta V + \left(\frac{\partial^2 U}{\partial V^2}\right)\delta V^2\right] \geq 0 \rightarrow$$

- $\left(\frac{\partial^2 U}{\partial S^2}\right) = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} \geq 0, \ \left(\frac{\partial^2 U}{\partial V^2}\right) = -\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V\kappa_S} \geq 0$
- $\left(\frac{\partial^2 U}{\partial S^2}\right)\left(\frac{\partial^2 U}{\partial V^2}\right) - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 \geq 0 \rightarrow \left(\frac{\partial T}{\partial V}\right)_S^2 \geq \frac{T}{V C_V \kappa_S}$

Phase transitions

Liquid-Gas coexistance phase boundary



Equilibrium conditions along the coexistance curb:

$$P_l = P_g, \qquad T_l = T_g, \qquad \mu_l = \mu_g$$

$$dG = 0$$

$$\mu_l(T,P) = \mu_g(T,P)$$

$$\mu_l(T+dT, P+dP) = \mu_g(T+dT, P+dP)$$

$$d\mu_l = d\mu_g$$

Using Gibbs-Duham equation

$$-s_l dT_l + v_l dP_l = -s_g dT_g + v_g dP_g$$

Clausius-Clapeyron equation

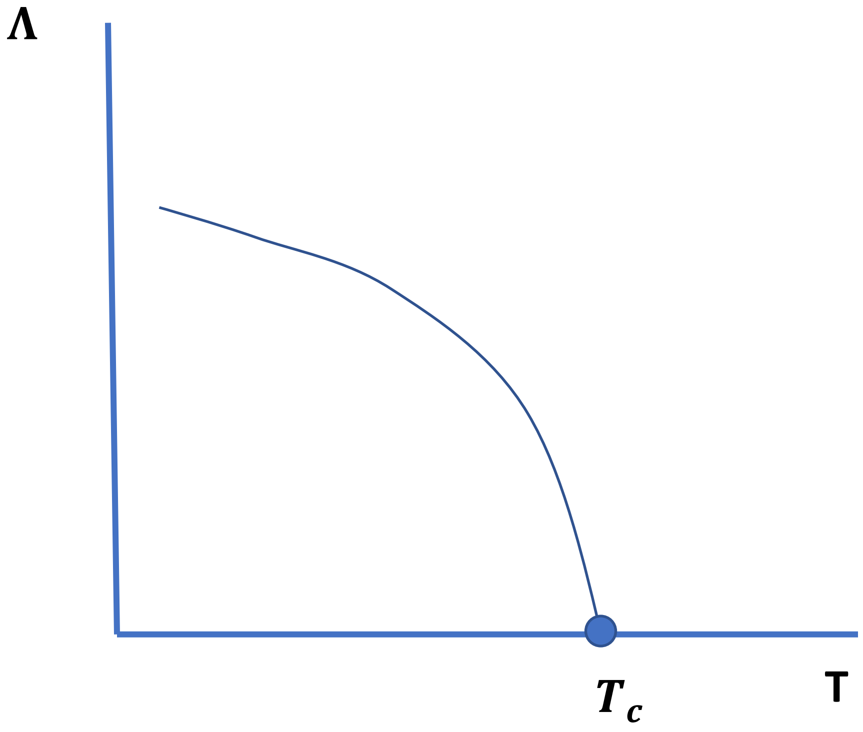
$$\frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l} = \frac{\Lambda}{T(v_g - v_l)}$$

For $v_l \ll v_g \approx \frac{kT}{P}$

$$\frac{dP}{dT} \approx \frac{\Lambda P}{kT^2} \rightarrow P = C\, e^{-\frac{\Lambda}{kT}}$$

Phase transitions

Liquid-Gas coexistance boundary



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$$\mu_l(T + dT, P + dP) = \mu_g(T + dT, P + dP) \leftrightarrow$$

$$d\mu_l = d\mu_g$$

Using Gibbs-Duham equation

$$-s_l dT_l + v_l dP_l = -s_g dT_g + v_g dP_g$$

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$$\boldsymbol{\frac{dP}{dT} = \frac{s_g - s_l}{v_g - v_l} = \frac{\Lambda}{T(v_g - v_l)}}$$

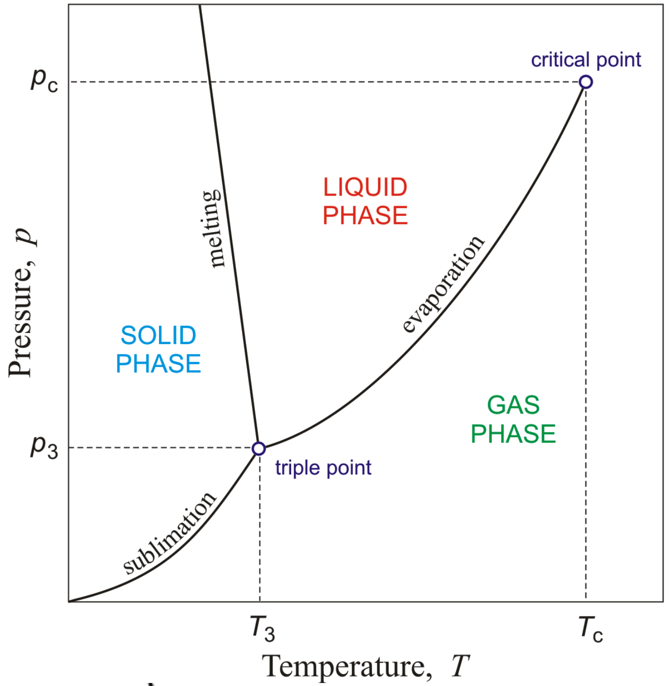
For $v_l \ll v_g \approx \frac{kT}{P}$

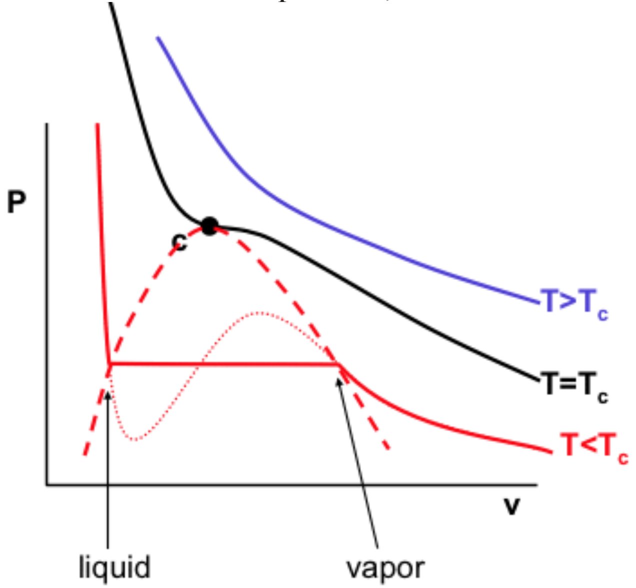
$$\frac{dP}{dT} \approx \frac{\Lambda P}{kT^2} \rightarrow P = C\, e^{-\frac{\Lambda}{kT}}$$

Phase transitions

- Discontinuous PT: first order derivative of the thermodynamic potential (TP) has a discontinuity across a phase boundary
  - $v_g \neq v_l$ this $\frac{\partial G}{\partial P}$ is discontinuous
  - $S_g \neq S_l$ this $\frac{\partial G}{\partial T} = -S$ is discontinuous

- *Continuous PT:* second order derivative of the thermodynamic potential has a singularity
  - Heat capacity at the critical point of fluids
  - Magnetic susceptibility at the para/ferromagnetic transition





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