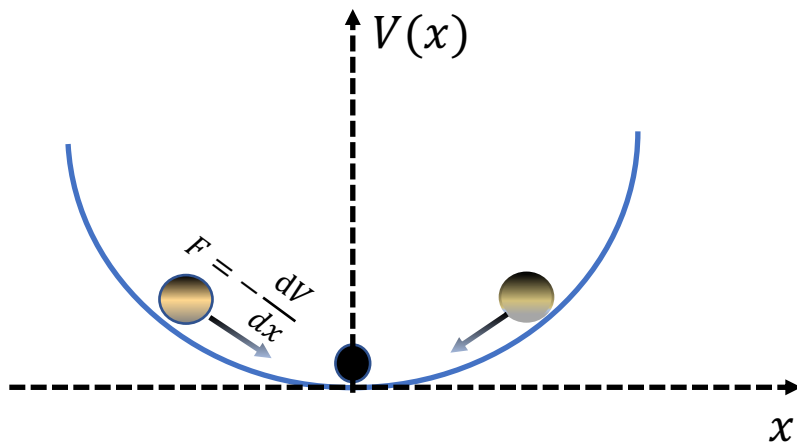# Lecture 10&11

19&24.09.2018

Free energies

# 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 | $F = -\nabla V$ |

## 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 it *interacts with its environment*

❑ When a system is **isolated**, the thermodynamic potential which is at **minimum at equilibrium** is its internal energy $U$

❑ 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

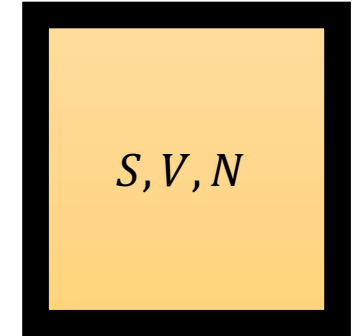❑ An infinitesimal dU is due to infinitesimal and independent changes in $S, V,$ or $N$

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

$$\boxed{S, V, N}$$

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

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

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

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

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

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

$$TdS \geq dU + PdV - \mu dN$$

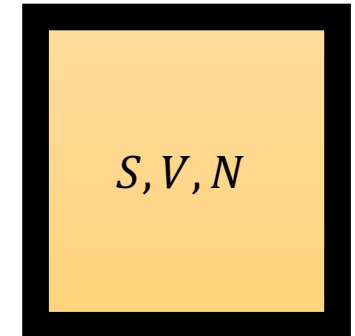Hence the change in the internal energy satisfies this **thermodynamic inequality**

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

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**:

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

$S, V, N$

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

❑ **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 $P$

$$H = U + PV$$

D. Schroeder

❑ 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 $S, P, N$

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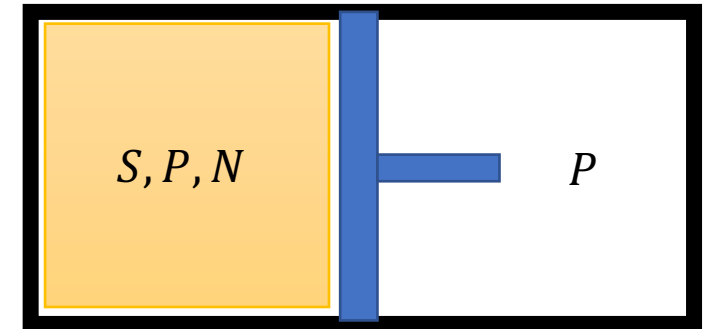
By defining $T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$, $V = \left(\frac{\partial H}{\partial P}\right)_{S,N}$ and $\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$

$S, P, N$

$P$

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

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

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

❑ Thermodynamic identity for an infinitesimal reversible process

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

Combing this with the 2nd law of thermodynamics,

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

D. Schroeder

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

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

$$\boldsymbol{dH \leq TdS + V\mathbf{d}P + \mu\mathbf{d}N}$$

➢ Any change in enthalpy H when $S, \mathrm{P},$ and $N$ are fixed is $\boldsymbol{dH}|_{\boldsymbol{S,P,N}} \leq \mathbf{0}$. This is to *lower* $\boldsymbol{H}$ to its **miminum value at equilibrium**

➢ Reversible process at fixed $S, \boldsymbol{P},$ and N means that $\boldsymbol{H}$ **is conserved**: $dH|_{S,P,N} = 0$

➢ Reversible process at fixed $\boldsymbol{P},$ and N means that : $dH|_{P,N} = TdS = \delta Q_{rev}$
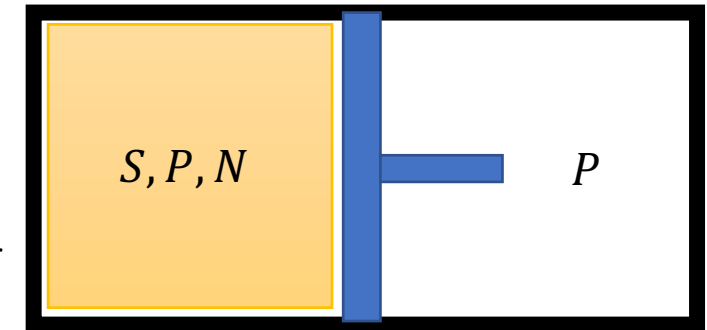
# Systems at constant $P$ and Enthaly $H(S, P, N)$

❑ System + surrounding at constant pressure = isolated system

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

D. Schroeder

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

❑ **Principle of maximum work**

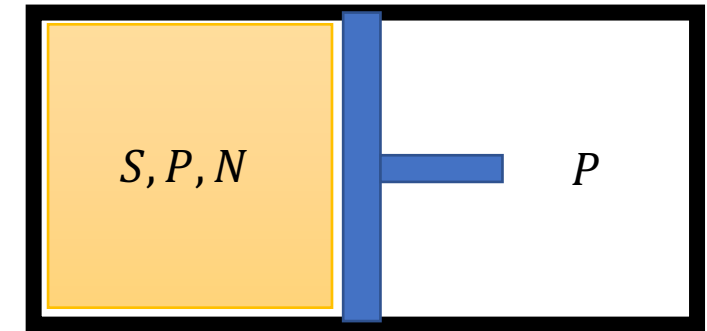$$\delta W \leq -PdV \rightarrow dU \leq -PdV$$

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

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

$S, P, N$ ⟶ $P$

❑ *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

$$Q = 0 \rightarrow \Delta U = W$$
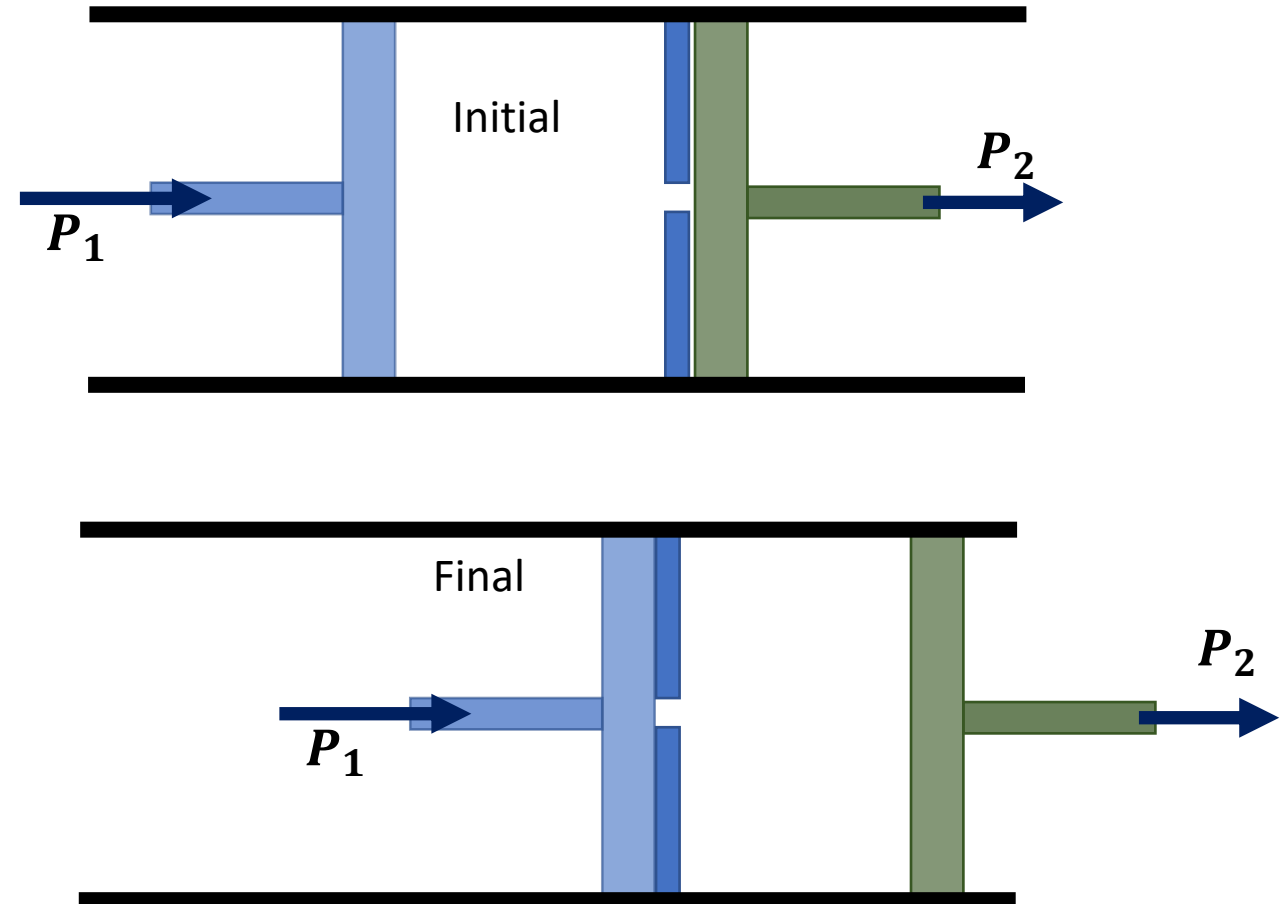
Work done on the gas at $P_1$ =const:

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

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

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

Initial

$P_1$

$P_2$
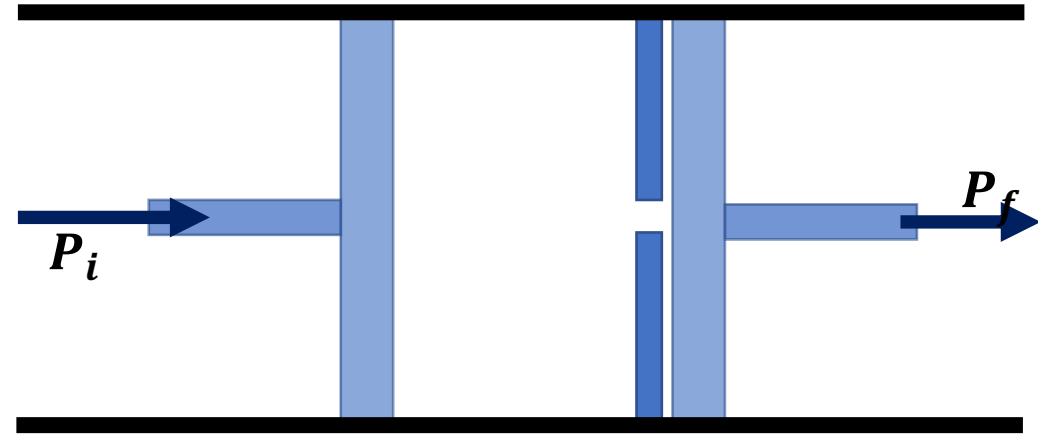
Final

$P_1$

$P_2$

# Joule-Thomson expansion

$$\mathbf{\Delta U = W} \rightarrow$$

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

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

*This expansion is at constant enthalpy*

$$\mathbf{\Delta H = \Delta(U + PV) = 0}$$

# 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 $T$
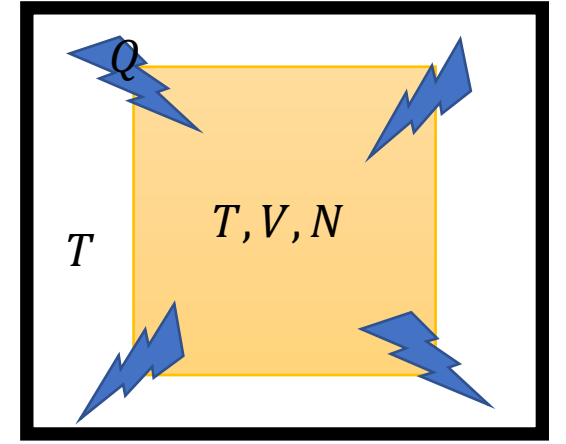
$$F = U - TS$$

❑ 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 $T, V, N$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

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

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

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

# 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,

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

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

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

$$\boldsymbol{dF \leq -SdT - PdV + \mu dN}$$

> Any change in $F$ when T, V, and $N$ are fixed must be $\boldsymbol{dF}|_{T,V,N} \leq \boldsymbol{0}$. 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.
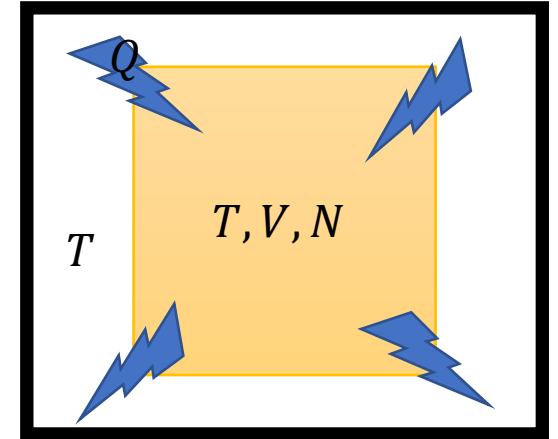
❑ The system + its thermal bath = isolated system. Hence total internal energy is conserved

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

❑ System can exchange heat with its thermal bath, while both mentained the same temperature $T$. Using the conservation of energy and Clausius inequality

$$\delta Q_{bath} = -\delta Q \rightarrow \delta Q_{bath} = -\frac{dU}{T} \leq dS_{bath}$$
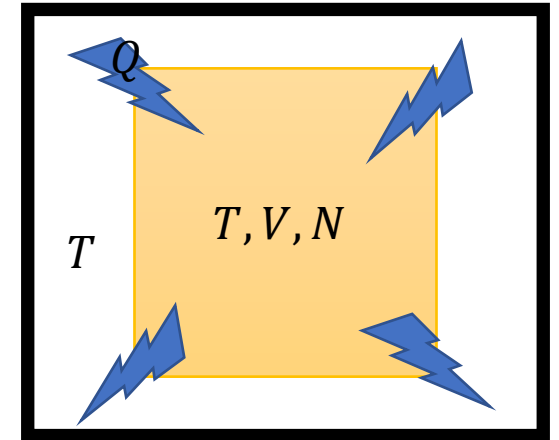
❑ Hence, the change in the total entropy, $S_t = S + S_{bath}$, is

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

❑ *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**
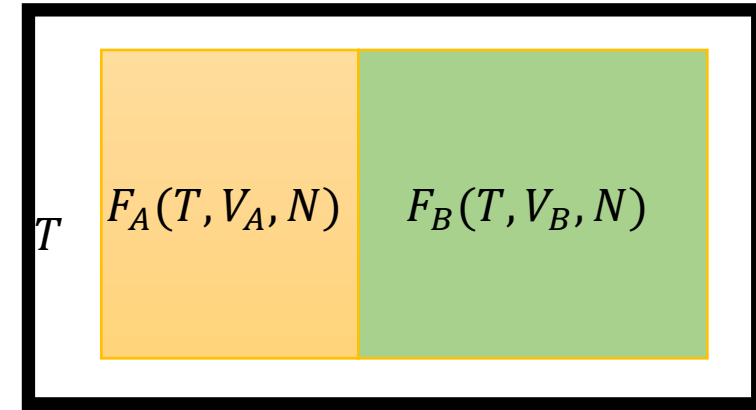
# Helmholtz free energy $F(T, V, N)$ in the ideal gas

☐ $F = U - TS \rightarrow F = \frac{3NkT}{2} - NkT \left[ \ln\left(\frac{V}{N}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} + \frac{5}{2} \right]$
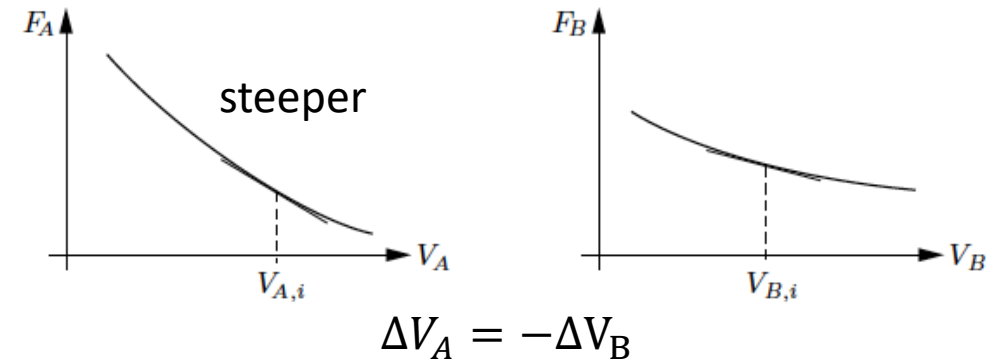
$$F(T, V, N) = -NkT \left[ \ln\left(\frac{V}{N}\right) + \ln\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} + 1 \right]$$

☐ $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \rightarrow P = NkT \left(\frac{\partial}{\partial V} \ln V\right)_{T,N} \rightarrow P = \frac{NkT}{V}$

$T$  $F_A(T, V_A, N)$   $F_B(T, V_B, N)$

➤ Slopes are negative (higher volume, higher entropy, lower F)

➤ $-\frac{\partial F_A}{\partial V_A} > -\frac{\partial F_B}{\partial V_B} \rightarrow$ gas A expands into gas B to lower its free energy $F_A$

➤ $P_A > P_B$ the gas with higher pressure expands

➤ The reduction in $F_A$ is larger than the increase in $F_B$

$$-\Delta F_A > \Delta F_B \rightarrow \Delta(F_A + F_B) < 0$$

$F_A$  $F_B$

steeper

$V_A$  $V_B$

$V_{A,i}$  $V_{B,i}$

$$\Delta V_A = -\Delta V_B$$

# Systems at constant $T$ $and$ $P$ and Gibbs free energy $G(T, P, N)$

❑ ***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
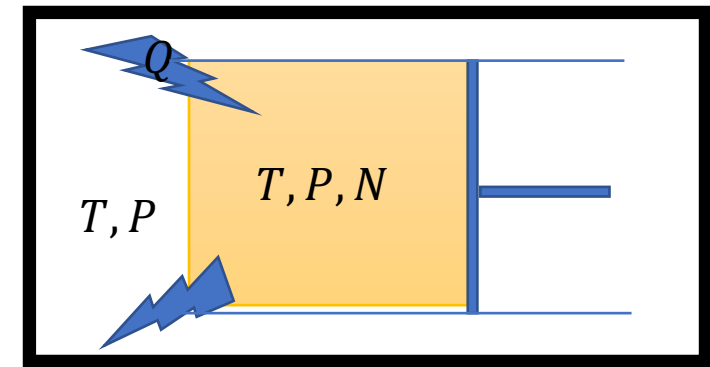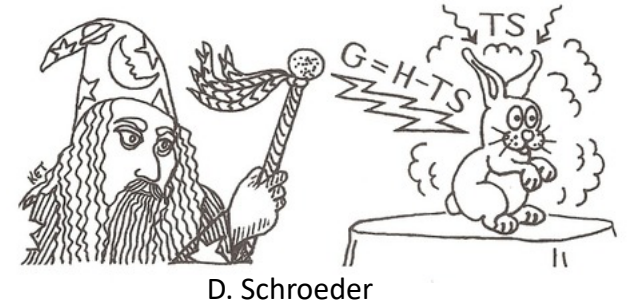
$$G = U - TS + PV$$

❑ 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 $T, P, N$

D. Schroeder

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

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

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

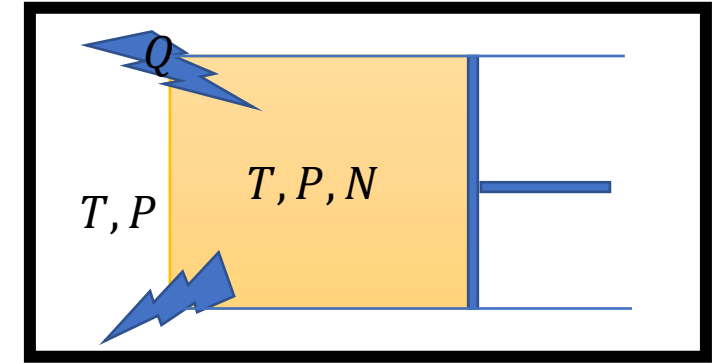$$\boldsymbol{dG = -SdT + VdP + \mu dN}$$

# Systems at constant $T$ and $P$ and Gibbs free energy $G(T, P, N)$

❏ Thermodynamic identity for an infinitesimal reversible process

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

Combing this with the 2nd law of thermodynamics,

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

❏ **Thermodynamic inequality** for any infitesimal process (reversible «=», irreversible «>»)

$$dU - d(TS) + d(PV) \leq -TdS + VdP + \mu dN$$

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

❏ Any change in the Gibbs free energy $G$ when T, 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**

# Gibbs free energy $G(T, P, N)$ and chemical potential $\mu$

❑ 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

$T, P, N$
$G_N = N\mu$

$\mu$

➢ This means that when we add a particle to the system, its Gibbs enery increases by one unit equal to $\mu$
➢ By adding more particles we dont change the value of $\mu$: *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, $\mu$ can vary with N
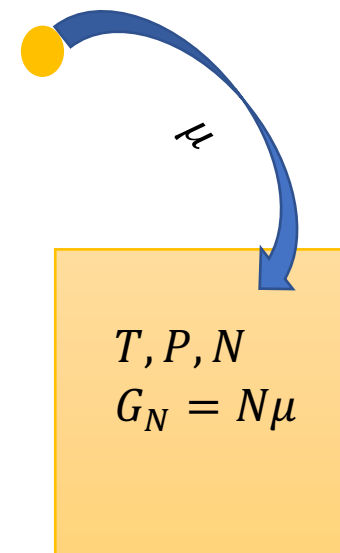
# Ideal gas: $G(T, P, N)$ and $\mu$

❑ Gibbs free energy $G(T, P, N)$

$$G = U - TS + PV = F + PV$$

$$G(T, P, N) = -NkT \left[ \ln \left[ \frac{V}{N} \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] + 1 \right] + NkT$$
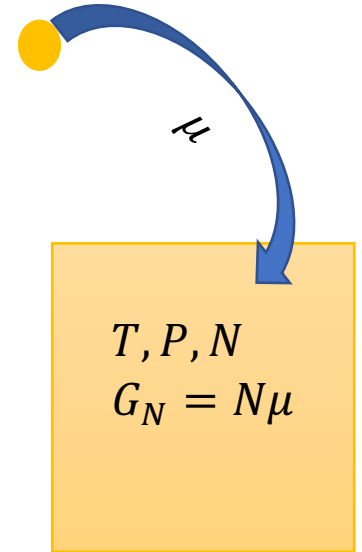
$$G(T, P, N) = -NkT \ln \left[ \frac{kT}{P} \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right]$$

❑ Chemical potential $\mu(T, P)$

$$\mu(T, P) = \frac{G}{N} = -kT \ln \left[ \frac{kT}{P} \left( \frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right]$$

❑ Change in chemical potential $\Delta\mu(P)$ at fixed $T$

$$\Delta\mu(P) = \mu(P) - \mu(P_0) = kT \ln \left[ \frac{P}{P_0} \right]$$

$\mu$

$$T, P, N$$
$$G_N = N\mu$$

# Thermodynamic potentials are related by <u>Legendre transforms</u>

- The extensive variables $(S, V, N)$ and intensive variables $(T, P, \mu)$ 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 $H(S, P, N)$

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

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

**Example in mechanics:**

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

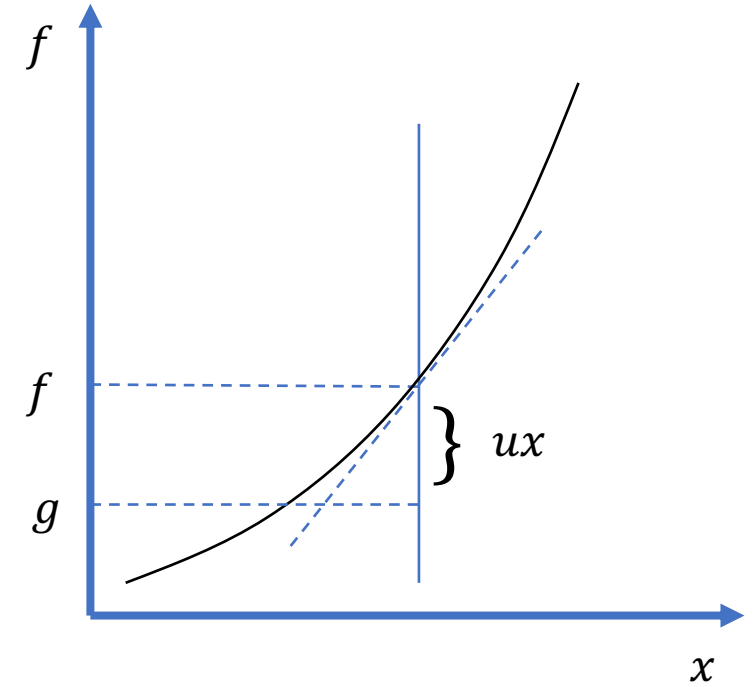$$\boldsymbol{-H(p, q) = L(q, \dot{q}) - p\,\dot{q} \rightarrow H(p, q) = K + U}$$

# Legendre transform: graphic intepretation

*Given a function of x with the slope u*

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

**The Legendre transform is**

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

# Legendre transform

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

$$G(z, y) = F(x, y) - zx$$

**Proof:**

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

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

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

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

## Legendre transforms:

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

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

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

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

### Thermodynamic identities

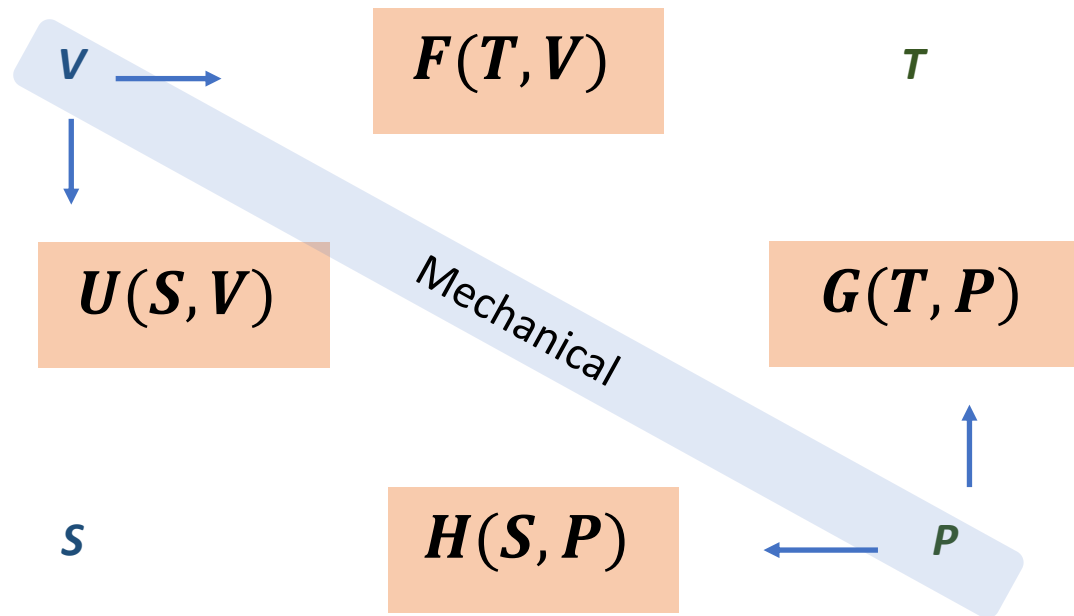$$dU = TdS - PdV + \mu dN$$

$$dF = -SdT - PdV + \mu dN$$

$$dH = TdS + VdP + \mu dN$$

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

# Thermodynamic square
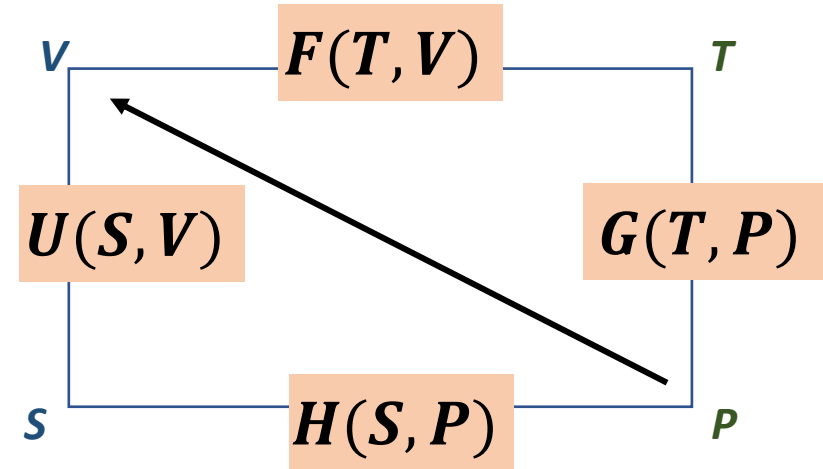
Extensive variables

Intensive variables

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

Mechanical

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

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

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

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

# Thermodynamic square

$V$      $F(T,V)$      $T$
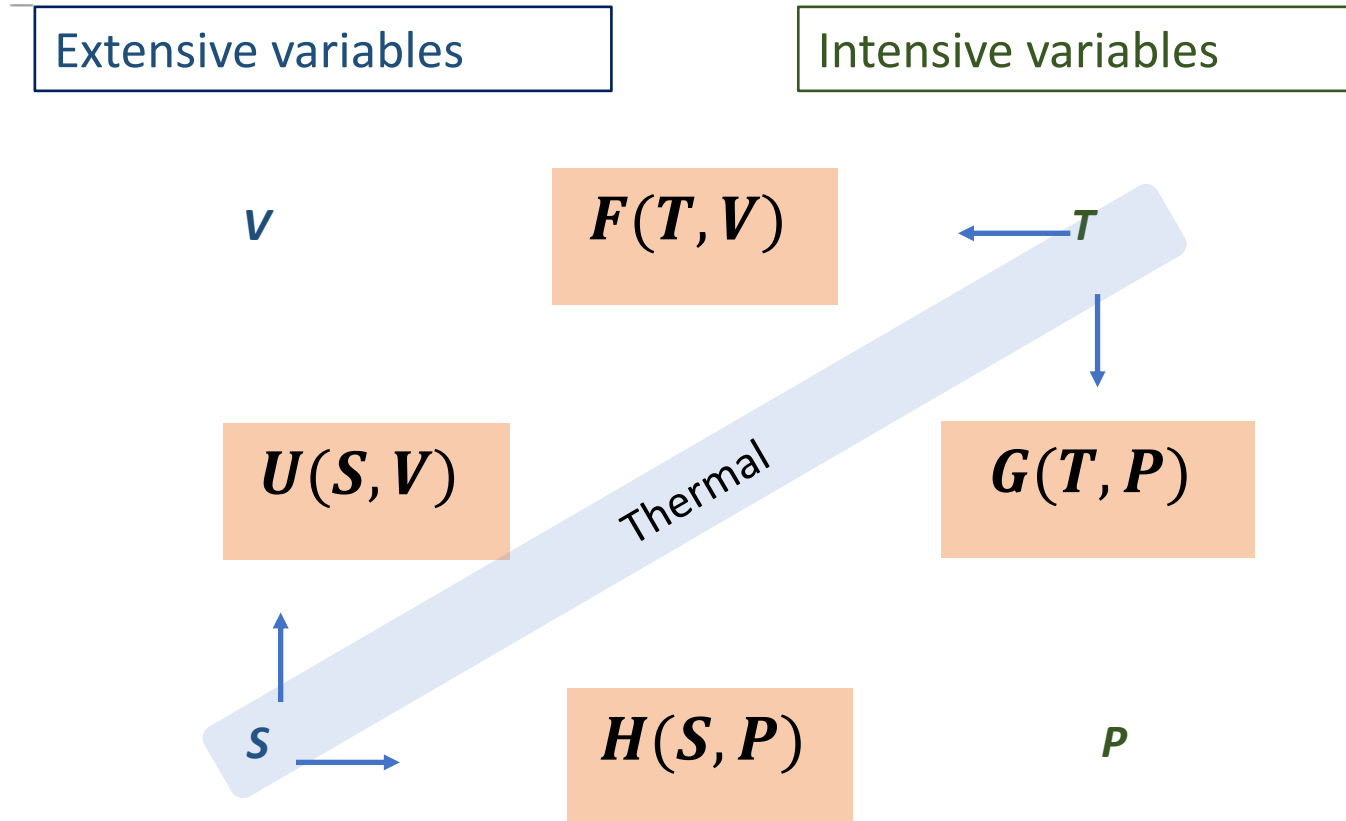
$U(S,V)$           $G(T,P)$

$S$      $H(S,P)$      $P$

❑ 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

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

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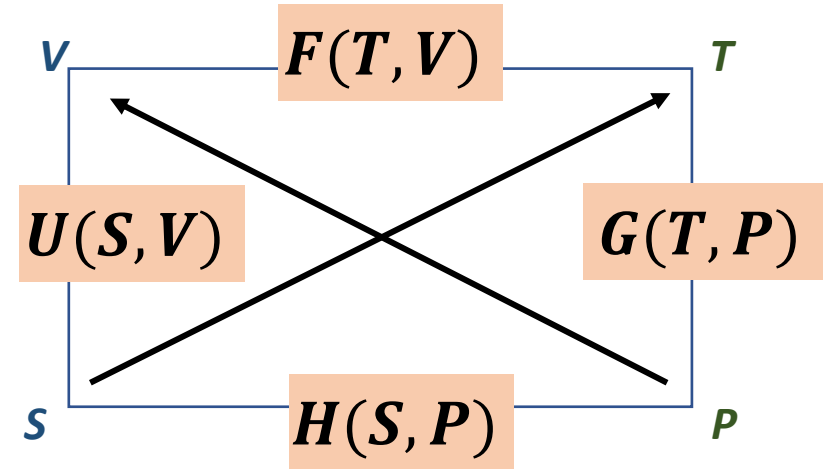
# Thermodynamic square

$V$

$F(T,V)$

$T$

Thermal

$U(S,V)$

$G(T,P)$

$S$

$H(S,P)$

$P$

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

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

# Thermodynamic square

$$V \quad\quad \boxed{F(T,V)} \quad\quad T$$

$$\boxed{U(S,V)} \quad\quad\quad\quad \boxed{G(T,P)}$$

$$S \quad\quad \boxed{H(S,P)} \quad\quad P$$

❑ 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