RECAP:

① Combined first and second laws of thermo:

$$\boxed{dU = TdS + \sum_i Y_i dX_i}$$

$Y_i \longrightarrow$ intensive STATE variable

$X_i \longrightarrow$ extensive STATE variable

$\delta w_{reversible} = Y dX$] General expression for reversible Work.

② Legendre transforms:

$$dU = TdS + \sum_i Y_i dX_i \Rightarrow U(S, X_1, X_2, \cdots)$$

NATURAL VARIABLES OF U

if we control some intensive variables in experiment we need to perform Legendre transforms to compute the CHARACTERISTIC POTENTIAL under the experimental boundary conditions.

$$\Lambda = U - \sum_i Y_i X_i$$

sum over the experimentally controlled intensive variables.

EXAMPLES:

★ Constant V, T: $F = U - TS$;

$$dF = -SdT - pdV$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p$$

eg IDEAL GAS: from statistical mechanics.

$$F(T,V) = -nRT\left[\log V - \frac{3}{2}\log T + \frac{3}{2}\log\left(\frac{m}{2\pi k_B \hbar^2}\right)\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{nRT}{V}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = nR\left[\log V - \frac{3}{2}\log T + \frac{3}{2}\log\left(\frac{m}{2\pi\hbar^2 k_B}\right)\right] - \frac{3}{2}nR$$

$$U = F + TS = \frac{3}{2}nRT = U(T)$$

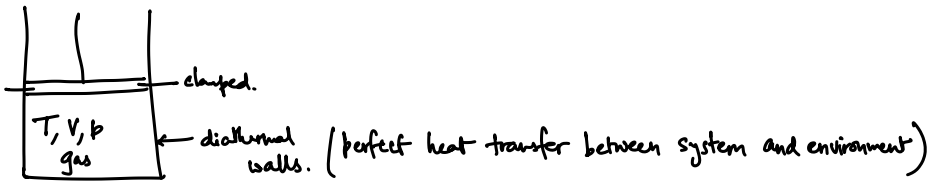
Whenever an INTENSIVE variable is experimentally controlled, we have to perform a LEGENDRE TRANSFORM

In general: $\phi = U - Y_i X_i$ (chor. potential under the experimental conditions.)

$\begin{cases} X_i = \text{extensive} \\ Y_i = \text{intensive.} \end{cases}$

EXAMPLES:

* Constant T, V:



* start with fundamental equation:

$dU = TdS - pdV \longrightarrow U(S,V)$ (need to replace this with conjugate T; good ✓)

Legendre transform:

$F = U - TS$ → Legendre transform.

$dF = dU - TdS - SdT$

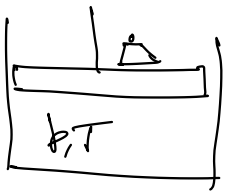
$= TdS - pdV - TdS - SdT$

$$\boxed{dF = -SdT - pdV} \longrightarrow F(T,V)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \Rightarrow \boxed{\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -p}$$

EQUATIONS of STATE

2. Constant T, p



fundamental equation: $dU = TdS - pdV$

$U(S, V)$ ⟶ replace both variables with their conjugates

$$G = U - TS + pV$$

↳ sign because $Y_i = -p$

$$dG = -SdT + Vdp$$

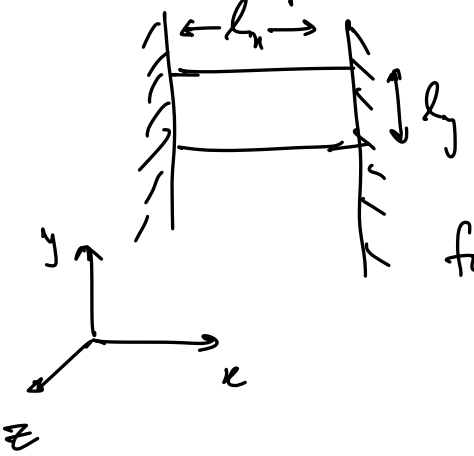
$G(T, p)$ ⟶ GIBBS FREE ENERGY

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

EQUATIONS OF STATE:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \qquad V = \left(\frac{\partial G}{\partial p}\right)_T$$

4. Clamped block of material @ constant T, p



generalized stress/strain work

$$\sum_i \sum_j V_0 \sigma_{ij} d\varepsilon_{ij}$$

for simplicity, assume no shear stress/strain

$$\delta W = V_0 \left(\sigma_{xx} d\varepsilon_{xx} + \sigma_{yy} d\varepsilon_{yy} + \sigma_{zz} d\varepsilon_{zz} \right)$$

fundamental equation:

$$dU = T dS + V\sigma_{xx} d\varepsilon_{xx} + V\sigma_{zz} d\varepsilon_{zz} + V\sigma_{yy} d\varepsilon_{yy}$$

$$U\left(S, V\varepsilon_{xx}, V\varepsilon_{zz}, V\varepsilon_{yy}\right)$$

we control:

$$\left(T, V\varepsilon_{xx}, \underbrace{\sigma_{zz}, \sigma_{yy}}_{-p}\right)$$

$V\varepsilon_{xx}$: extensive

$$\Lambda = U - TS - V\sigma_{yy}\varepsilon_{yy} - V\sigma_{zz}\varepsilon_{zz} = U - TS + pV\left(\varepsilon_{yy} + \varepsilon_{zz}\right)$$

$$d\Lambda = -S dT + \sigma_{xx} V d\varepsilon_{xx} - V\left(\varepsilon_{yy} + \varepsilon_{zz}\right) dp$$

EQUATIONS OF STATE:

$$S = -\left(\frac{\partial \Lambda}{\partial T}\right)_{V\varepsilon_{xx}, p} \qquad \sigma_{xx} = \left(\frac{\partial \Lambda}{\partial \varepsilon_{xx}}\right)_{T,p} \frac{1}{V}$$

$$V\left(\varepsilon_{xx} + \varepsilon_{yy}\right) = -\left(\frac{\partial \Lambda}{\partial p}\right)_{T, V\varepsilon_{xx}}$$

SECOND DERIVATIVES OF CHARACTERISTIC POTENTIAL

— Related to "RESPONSE FUNCTION"

Response functions:

(eg) control T, p experimentally

* fix p, change T ⟶ look at response of the system.

1. $\delta Q \rightsquigarrow C_p = \left(\frac{\delta Q}{dT}\right)\Big|_p = T\left(\frac{\partial S}{\partial T}\right)_p$ [$\exists$ Laws]

2. $\Delta V \rightsquigarrow \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

* fix T, change p ⟶ look at response

1. $\Delta V \rightsquigarrow \underline{K} = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

In general: response function $\sim$ $\frac{\partial(\text{freely varying state variable})}{\partial(\text{expt. controlled state variable})}$

Usually $\sim$ $\frac{\partial(\text{extensive})}{\partial(\text{intensive})}$

* Coming back to char. potentials:

(example) constant T, p ⟶ char. potential $G(T,p)$

$G = U - TS + pV$

$dG = -SdT + Vdp$

* EOS:

$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = \left(\frac{\partial G}{\partial p}\right)_T$

S, V are allowed to freely vary in experiment

* second derivatives of G (Hessian):

$$\left(\frac{\partial^2 G}{\partial T^2}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right) = -\left(\frac{\partial S}{\partial T}\right)_p = -\frac{1}{T}T\left(\frac{\partial S}{\partial T}\right)_p = -\frac{C_p}{T}$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right) = -V\underline{K}$$

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T = V\beta$$

↑ Maxwell's relation.

Hessian: $\begin{bmatrix} \frac{\partial^2 G}{\partial T^2} & \frac{\partial^2 G}{\partial T \partial P} \\ \frac{\partial^2 G}{\partial P \partial T} & \frac{\partial^2 G}{\partial P^2} \end{bmatrix} = \begin{bmatrix} -(C_P/T) & V\beta \\ V\beta & -V\bar{K} \end{bmatrix}$

(eg) control $T, V \longrightarrow F = U - TS = F(T,V)$

$$dF = -S\,dT - P\,dV$$

* EOS: $\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$

* second derivative: $\begin{bmatrix} \frac{\partial^2 F}{\partial T^2} & \frac{\partial^2 F}{\partial T \partial V} \\ \frac{\partial^2 F}{\partial V \partial T} & \frac{\partial^2 F}{\partial V^2} \end{bmatrix} = \begin{bmatrix} -C_V/T & -\beta/\bar{K} \\ -\beta/\bar{K} & \frac{1}{V\bar{K}} \end{bmatrix}$

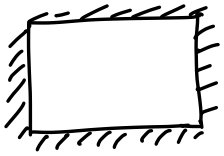
EQUILIBRIUM CRITERIA:

Second Law of Thermodynamics

$$dS \geq \frac{\delta Q}{T}$$

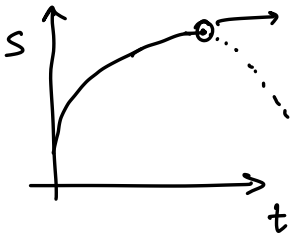
Consider an isolated system:

Consider an isolated system ⟶ all extensive variables are constant



(eg) Volume cant change ⇒ no p-V work

II Law: $dS \geq 0$



⟶ cannot evolve since entropy would decrease

$$dS = \frac{dU}{T} + \frac{p}{T} dV$$

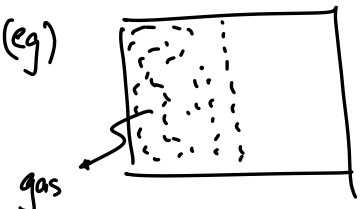
U ⟶ constant

V ⟶ constant

what are we maximizing over?

FIND EQUILIBRIUM STATE BY MAXIMIZING S OVER SOME INTERNAL EXTENSIVE VARIABLES

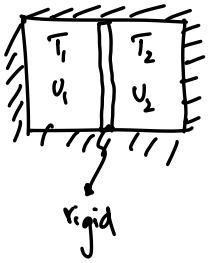
(eg)



"internal" degree of freedom ⟶ volume of the gas

S ⟶ maximized when gas fills the whole volume.

① THERMAL EQUILIBRIUM:



$U = U_1 + U_2 = \text{constant}$ since no work or heat exchange with the environment

$dV_1 = dV_2 = 0$

Let U_1 be the independent internal extensive variable

$$dU_1 = T\,dS_1 - p\,dV_1 \quad (dV_1 = 0)$$

$$\boxed{dU_1 = T_1\,dS_1}$$

$dU = 0$

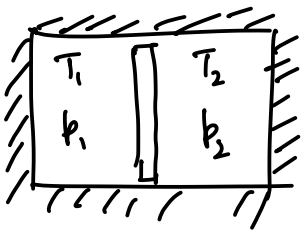
$\Rightarrow dU_1 = -dU_2$

$$S = S_1 + S_2 \Rightarrow dS = dS_1 + dS_2 = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = dU_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$S(U_1) \longrightarrow \boxed{\frac{dS}{dU_1} = \frac{1}{T_1} - \frac{1}{T_2}}$$

only if $T_1 = T_2 \Rightarrow \boxed{dS = 0}$ $\longrightarrow$ ENTROPY MAXIMIZED

② THERMAL & MECHANICAL AND THERMAL EQUILIBRIUM:



U = Constant

$= U_1 + U_2$

$dU = 0 \Rightarrow dU_1 = -dU_2$

V = Constant

$dV = 0 \Rightarrow dV_1 = -dV_2$

fundamental equation:

$$dS_1 = \frac{dU_1}{T_1} + \frac{p_1}{T_1}dV_1 \quad \& \quad dS_2 = \frac{dU_2}{T_2} + \frac{p_2}{T_2}dV_2$$

2 independant internal extensive variables:

U_1 & V_1

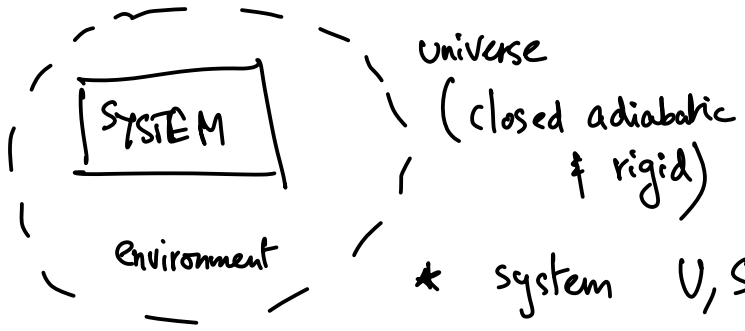
$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)dU + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)dV_1$$

$dS = 0 \longrightarrow$ max entropy.

$$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{V_1} = 0 \Rightarrow T_1 = T_2 \; ; \; \left(\frac{\partial S}{\partial V_1}\right)_{U_1} = 0 \Rightarrow p_1 = p_2$$

INTENSIVE VARIABLES CONJUGATE TO FREELY VARYING INTERNAL EXTENSIVE VARIABLES ARE EQUAL BETWEEN ALL SUBSYSTEMS

★ GENERAL EQUILIBRIUM CRITERIA:



★ system U, S, T, X_i, Y_i

★ environment $U^{env}, S^{env}, T^{env}, X_i^{env}, Y_i^{env}$

$U^{env} + U = \text{constant}$

$X_i^{env} + X_i = \text{Constant}$ ← Conserved extensive variables

initial state:

$T_2 T^{env}$

$Y_i = Y_i^{env}$

find eqm state

$T = T^{env}$

$Y_i = Y_i^{env}$

] environment is large enough such that transformation in the system does not affect intensive variables.

CHANGE OF STATE OF THE SYSTEM

$\Delta U, \Delta X_i, \Delta S, \dots$

for the environment: (EULER)

$$\Delta U^{env} = T^{env} \Delta S^{env} + \sum_i Y_i^{env} \Delta X_i^{env}$$

$\Delta U^{env} = -\Delta U$

$\Delta X^{env} = -\Delta X$

$$\Rightarrow -\Delta U = T^{env}\Delta S^{env} - \sum_i Y_i^{env}\Delta X_i$$

II Law $\quad \Delta S^{env} + \Delta S \geq 0$

$$\Rightarrow \Delta S^{env} \geq -\Delta S$$

$$T^{env}\Delta S^{env} \geq -T^{env}\Delta S$$

$$-\Delta U + \sum_i Y_i^{env}\Delta X_i \geq -T^{env}\Delta S$$

$$\Rightarrow \boxed{0 \geq \Delta U - T^{env}\Delta S - \sum_i Y_i^{env}\Delta X_i}$$

- all freely varying extensive variables are system variables
- intensive variables are set by the environment

$$\Rightarrow \boxed{0 \geq \Delta U - T\Delta S - \sum_i Y_i \Delta X_i}$$

change of state can be irreversible
only end points need to be in eq^m

EQ^m UNDER DIFFERENT BOUNDARY CONDITIONS:

① fix all extensive variables

S_i, X_i = Constant

$\Rightarrow \Delta U \leq 0 \longrightarrow$ U has to be minimal] U is the characteristic potential.

② fix T and all extensive mechanical variables

$\Delta X_i = 0$, since X_i is fixed.

$$\Delta U - T\Delta S \leq 0$$

$\Delta f \leq 0 \longrightarrow$ minimize the characteristic potential $f(T,V)$

③ fix T & p:

$$\Delta U - T\Delta S + p\Delta V \leq 0$$

$\boxed{\Delta G \leq 0} \longrightarrow$ minimize the characteristic potential $G(T,p)$

IN GENERAL: Given boundary conditions $(Y_i, X_j) \rightarrow$ minimize $\boxed{\Lambda = U - \sum_i Y_i X_i}$

PHASE TRANSITIONS & ONE COMPONENT SYSTEMS:

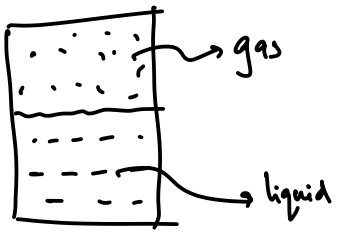
We will control T, p $\longrightarrow$ look for states (phases) with lowest G

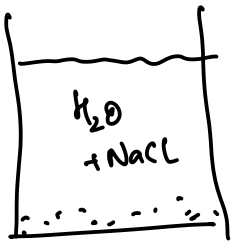
To find the lowest energy state we need to know how G changes with T, p.

$$\Rightarrow \boxed{dG = -S\,dT + V\,dp}$$

* Reminder:

What is a phase?





Both containers have "distinct portions" with properties that are markedly different

(eg) ρ_{liquid} v/s ρ_{solid} $\longrightarrow$ densities

each "distinct portion" $\longrightarrow$ PHASE

* The shape of the Gibbs free energies:

$dG = V\,dp - S\,dT$

$$\left(\frac{\partial G}{\partial p}\right)_T = V > 0$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S < 0$$

Curvature

$$\left(\frac{\partial^2 G}{\partial T^2}\right) = -\left(\frac{\partial S}{\partial T}\right)_p$$

$$= -C_p/T < 0$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_T = \left(\frac{\partial V}{\partial p}\right)_T = -V\bar{K}$$

$$< 0$$