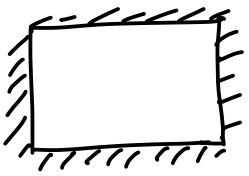
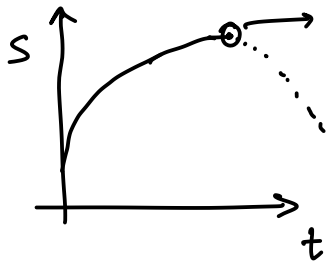
EQUILIBRIUM CRITERIA

Consider an isolated system ⟶ all extensive variables are constant



(eg) Volume can't change ⇒ no p-V work

II Law: $dS \geq 0$



⟶ cannot evolve since entropy would decrease

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

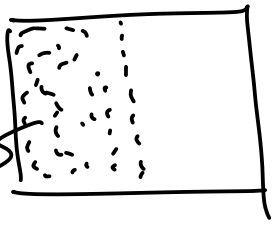
U ⟶ constant

V ⟶ constant

what are we maximizing over?

FIND EQUILIBRIUM STATE BY MAXIMIZING S OVER SOME INTERNAL EXTENSIVE VARIABLES

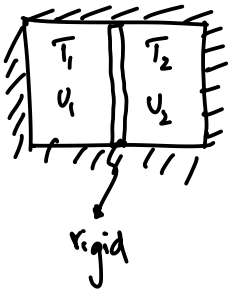
(eg)



"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

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

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

$dU = 0$

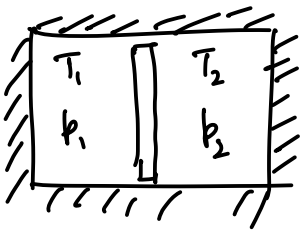
$\Rightarrow dU_1 = -dU_2$

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

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

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

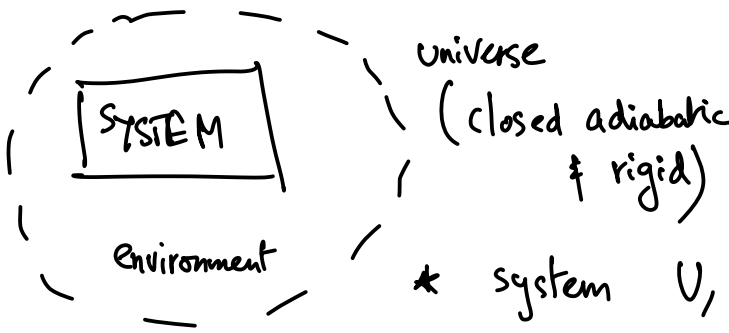
$$dS = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1$$

$dS = 0 \longrightarrow$ 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 $U^{env}, S^{env}, T^{env}, X_i^{env}, Y_i^{env}$

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

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

initial state:

$$T = T^{env}$$

$$Y_i = Y_i^{env}$$

find eqm state

$$\left.\begin{aligned} T &= T^{env} \\ Y_i &= Y_i^{env} \end{aligned}\right] \quad \begin{array}{l}\text{environment is large enough such that transformation in the system does not affect intensive variables.}\end{array}$$

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.

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

$$\Delta F \leq 0$$

③ fix T & p:

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

$$\boxed{\Delta G \leq 0}$$

CHEMICAL POTENTIALS & CHEMICAL WORK:

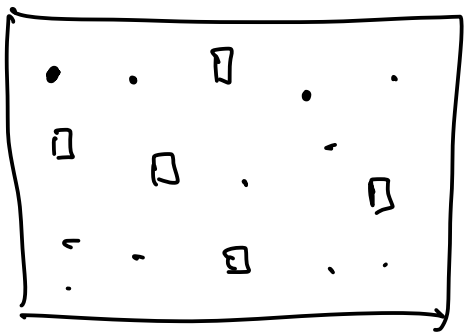
Work terms we have discussed so far:

p-V work, τ-ε work $\rightarrow$ mechanical

E-P work $\rightarrow$ electrical

What about chemical?

Consider:



• $\rightarrow$ Oxygen

□ $\rightarrow$ nitrogen

$p \longleftrightarrow V$ conjugate

p: intensive, V: extensive

$\mu_i \longleftrightarrow N_i \rightarrow$ number of moles or atoms of specie i

μ_i: intensive, N_i: extensive

μ_i: chemical potential

$$\delta W_{chemical} = \sum_{i=1} \mu_i \, dN_i$$

FUNDAMENTAL EQUATION OF THERMO: Assume p-V & μ_i-N_i work

$$dU = TdS - pdV + \sum_{i=1}^{c} \mu_i \, dN_i$$

★ EULER RELATION WITH GIBBS FREE ENERGIES

Consider a system with C chemical species where we control T, p, and N_i:

characteristic potential:

$$G(T, p, N_1, N_2, \cdots, N_C) = U - TS + pV$$

$$dG = V\,dp - S\,dT + \sum_{i=1}^{C} \mu_i\,dN_i \Rightarrow \text{Derive EOS}$$

Say we multiply the number of atoms of each specie by α $\Rightarrow$ size of the system changes by a factor α

$$\Rightarrow \alpha\, G(T, p, N_1, N_2, \cdots, N_C)$$

$$= G(T, p, \alpha N_1, \alpha N_2, \cdots, \alpha N_C)$$

Differentiating both sides of the equation with respect to α at fixed T, p

$$\text{LHS} = \frac{\partial}{\partial \alpha}\left(\alpha\, G(T, p, N_1, \cdots, N_C)\right) = G(T, p, N_1, N_2, \cdots N_C)$$

$$\text{RHS} = \frac{\partial G(T, p, \alpha N_1, \alpha N_2, \cdots)}{\partial \alpha} = \sum_{i=1}^{C} \frac{\partial G}{\partial(\alpha N_i)} \cdot \left(\frac{\partial(\alpha N_i)}{\partial \alpha}\right)$$

$$RHS = \sum_{i=1}^{c} \frac{\partial G}{\partial(\alpha N_i)} N_i$$

evaluate LHS and RHS at $\alpha = 1$

$$\Rightarrow G = \left(\frac{\partial G}{\partial N_1}\right)_{T,p,N_{j\neq 1}} N_1 + \left(\frac{\partial G}{\partial N_2}\right)_{T,p,N_{j\neq 2}} N_2 + \cdots = \sum_{i=1}^{c} \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}} N_i$$

FROM THE Equation of state for G

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}$$

$$\Rightarrow \boxed{G = \sum_{i=1}^{c} \mu_i N_i}$$

— Pure substance that forms a single phase

(g) A block of copper at room temperature and ambient pressure

$G = N\mu$ → chemical potential

↑ number of moles

$$\boxed{\mu = \frac{G}{N}}$$

PHASE TRANSITIONS & ONE COMPONENT SYSTEMS:

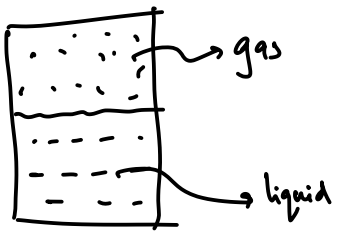
We will control $T, p \longrightarrow$ look for states (phases) with lowest G

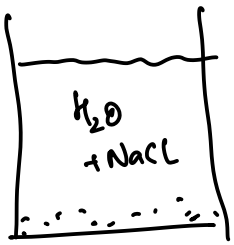
To find the lowest energy state we need to know how G changes with T, p.

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

★ Reminder:

What is a phase?





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

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

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

$$= -C_p/T < 0$$

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

$$< 0$$

The phases and phase diagram of water:

Water is commonly known to have 3 PHASES

- Solid
- Liquid
- Gas

Let $\alpha \longrightarrow$ denote one of these phases of water

$G^\alpha = U^\alpha - TS^\alpha + pV^\alpha \longrightarrow$ we control T & p

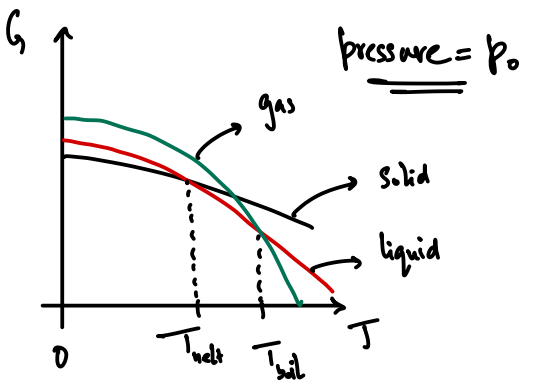
$$\boxed{G^\alpha = \mu^\alpha - TS^\alpha}$$

Notice @ $T=0$

$G^\alpha = \mu^\alpha$

Usually $\left[S^{gas} > S^{liquid} > S^{solid} \right.$

$\left. \mu^{gas}(T=0) > \mu^{liquid}(T=0) > \mu^{solid}(T=0) \right]$



Recall for eq^m: $dG \leq 0$ @ G (the characteristic potential) is minimized

$\Rightarrow$ At any given temperature the phase with the lowest Gibbs free energy is the eq^n phase

$T < T_{melt} \longrightarrow$ solid

$T_{melt} < T < T_{boil} \longrightarrow$ liquid

$T_{boil} < T \longrightarrow$ gas

[REPEAT FOR SUBLIMATION]

At $T = T_{melt}$

$$\left(G^{solid} = G^{liquid}\right) < G^{gas}$$

At $T = T_{boil}$

$$\left(G^{liquid} = G^{gas}\right) < G^{solid}$$