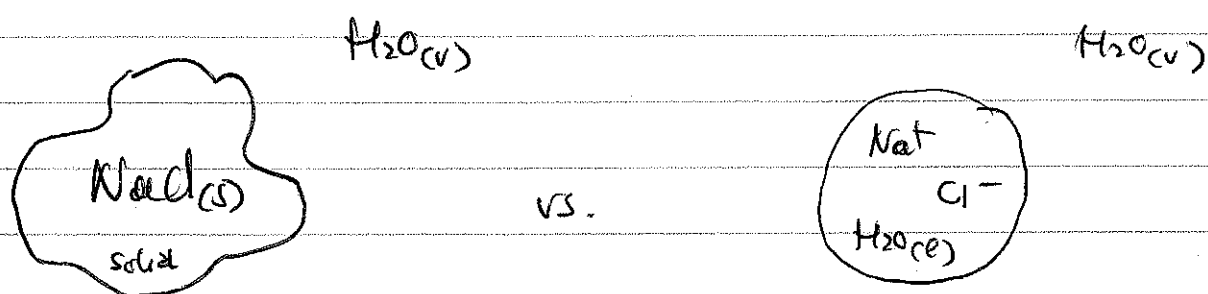


→ How useful are these equilibrium conditions? Very!

Example: Aerosol particle in equilibrium with water vapor.



Which one of the two states will occur for a given level of water vapor and  $T$ ?

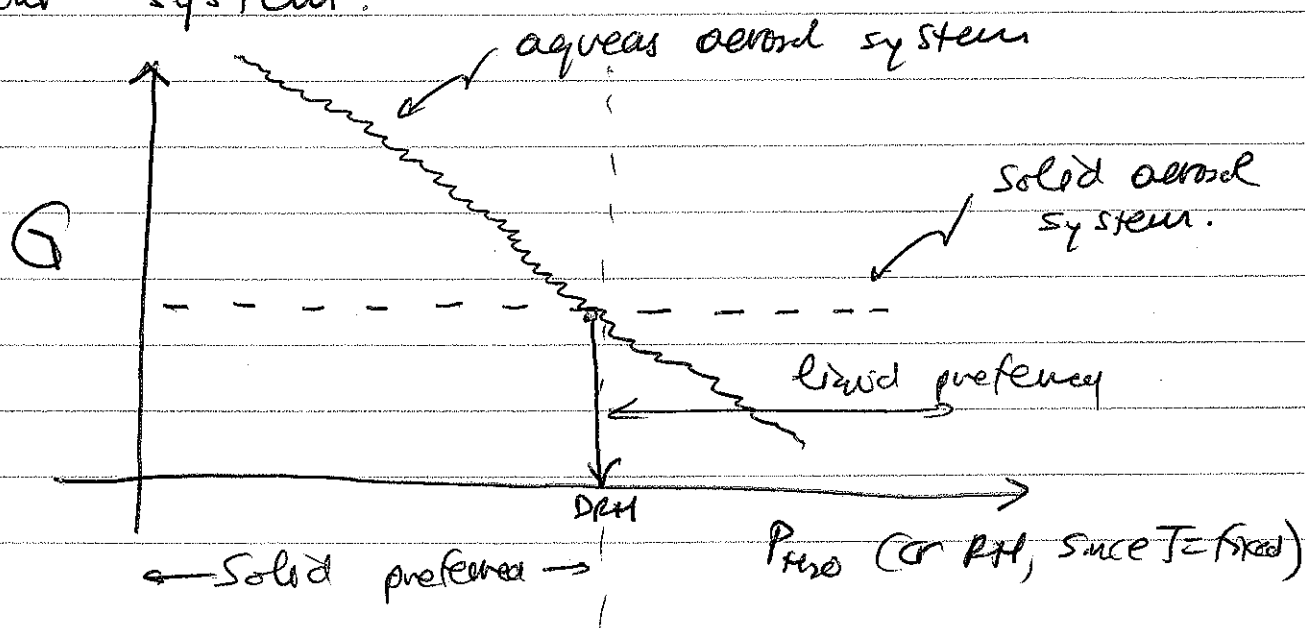


defines a  $P_{\text{H}_2\text{O}}$

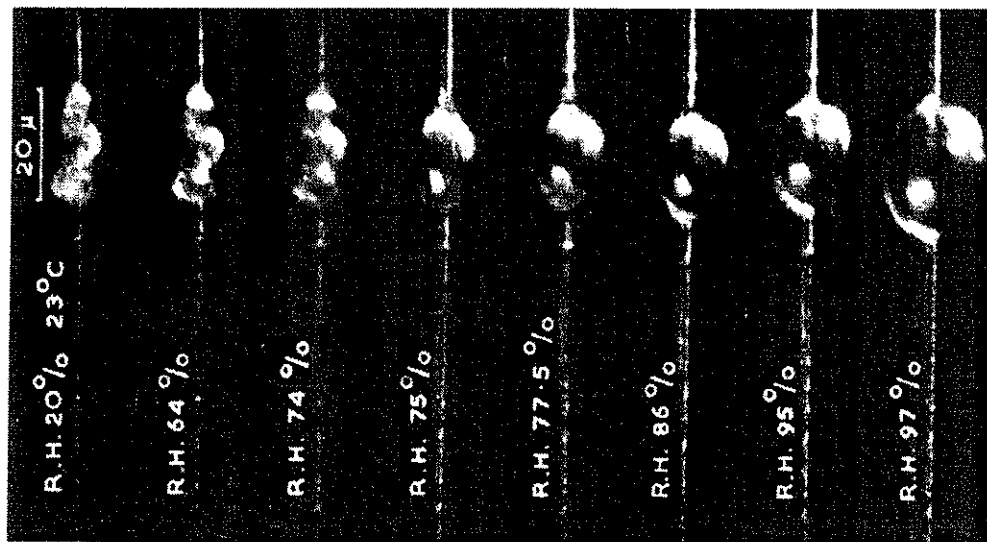
means  $P = \text{const}$   
 $T = \text{const.}$

$\Rightarrow$  we equilibrium definition based on Gibbs free energy.

So, just say  $dG=0$  or  $G=0$  for our system:



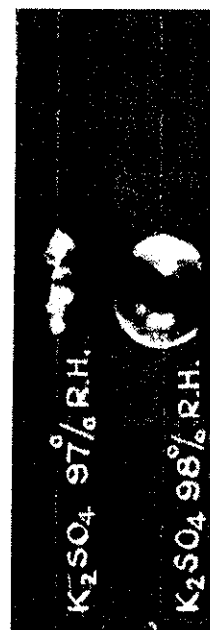
# PARTICLE DELIQUESCENT



Sea Salt Particle: DRH ~ 75%



Dust Particle: no DRH



K<sub>2</sub>SO<sub>4</sub> particle: DRH = 98%

Recall: We are looking at systems that:

- have only one work "mode" (changes in volume)
- have only one heat transfer mode (conduction)
- No chemical reactions (yet.)

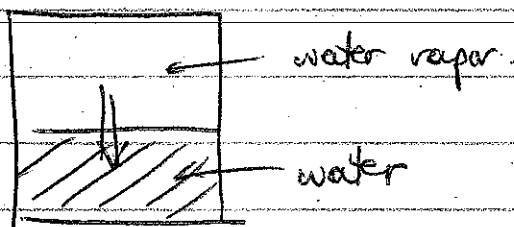
→ Thermodynamic equilibrium is then:

i) Mechanical equilibrium:  $P = P_{\text{ext}}$  (or const).

This ensures no net bulk mass transfer or change of volume.

ii) Thermal equilibrium: no net heat transfer  $T = T_{\text{ext}}$   
temperature of system with its surroundings are equal

iii) Diffusional equilibrium: no net transfer of mass within the system, i.e.:



no net change in  
water vapor amount or  
liquid water amount  
with time.

→ We also know that for a pure component (e.g. a gas), the state depends on two properties.  
e.g.  $P(v, T)$  or  $v(T, P)$ .

→ What if we have many components in our system? Gibbs Phase Rule tells us how

In addition, we have  $(P-1)$  phases in equilibrium with the phase we are looking at, so each needs a constraint of mechanical, thermal and diffusional equilibrium (for each component). This adds another  $(P-1)(C+2)$  constraints  $\Leftarrow \begin{cases} \text{mechanical} \\ \text{thermal} \\ C \times \text{diffusional} \end{cases} (P-1)$

Total constraints:  $P + (P-1)(C+2)$ .

$$\text{So } F = P(C+2) - [P + (P-1)(C+2)] =$$

$$\Rightarrow \boxed{P + F = C + 2}$$

Pure substance:  $C = 1$

$$\text{so: } F = 3 - P$$

$$P = 1 \Rightarrow F = 2 \quad \checkmark$$

$$P = 2 \Rightarrow F = 1$$

$$P = 3 \Rightarrow F = 0 \quad \text{triple point}$$

Worksheet.

many independent properties on which the state depends.

→ The # of independent properties  $F$  is obtained by counting the # of interactions available to the system and take away # of constraints:

$$F = \left\{ \begin{array}{l} \# \text{ of interactions} \\ \text{available to all} \\ \text{phases} \end{array} \right\} - \left\{ \begin{array}{l} \text{total \# of} \\ \text{constraints} \end{array} \right\}$$

⊗ Standard practice is to consider a system composed of  $C$  components among  $P$  phases.

Components: water, ethanol, benzene, salt

Phases: gas, liquid, solid

So # of interactions can be as follows:

for each phase, we have  $C+2$  interactions:

- one to change amount of each component
- one to change the  $P-V$  work
- one to change energy by heat conduction

total # :  $P(C+2)$  interactions

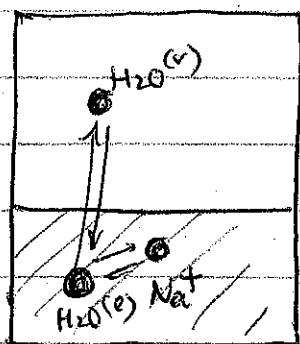
Total # of constraints: we are interested in intensive properties: so we have  $\downarrow$  for total mass in each phase

Extending everything to multiphase systems  
(with multiple components.)

So, now  $G$  will not depend only on  $T, P$ , but also on the amount of material (component) and the amount of each phase:

$$G = G(T, P, n_{11}, n_{12}, \dots, n_{ij}, \dots)$$

phase component



There are interactions of all molecules with each other and with all phases. Therefore changing  $n_{ij}$  will also change the  $G$ :

$$dG = -SdT + Vdp + \frac{\partial G}{\partial n_{11}} dn_{11} + \frac{\partial G}{\partial n_{12}} dn_{12} + \dots$$

$$+ \frac{\partial G}{\partial n_{ij}} dn_{ij} \quad (\text{from math})$$

or:

$$dG = -SdT + Vdp + \sum_{i=1}^P \sum_{j=1}^C \frac{\partial G}{\partial n_{ij}} dn_{ij}$$

definition || we define  $\frac{\partial G}{\partial n_{ij}}$  as chemical potential of component  $j$  in phase  $i$   $:= \mu_{ij}$

so:

$$dG = -SdT + Vdp + \sum_{i=1}^P \sum_{j=1}^C \mu_{ij} dn_{ij} \quad (2)$$

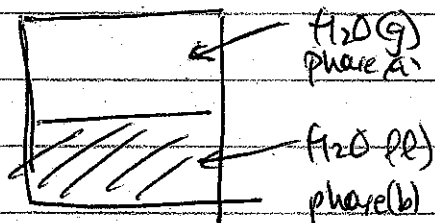
Now, if  $(T, P)$  are fixed:

$$dG = \sum_{i=1}^P \sum_{j=1}^C \mu_{ij} dn_{ij} \quad \text{fixed } (T, P)$$

let's see what we can do to derive an equilibrium criterion, involving the chemical potentials. At Thermodynamic equilibrium for the whole system.

$$dG = -SdT + VdP = 0 \quad (\text{whole system}).$$

Since  $G$  is extensive, it is the sum of contributions of each phase. For simplicity, let's take 2 phases and one component within a closed volume:



$$dG = dG^{(a)} + dG^{(b)} = 0$$

We express the intensive properties in terms of moles:  $G = ng$

So:

$$dG = d(n^a g^a) + d(n^b g^b) = 0$$

$$= n^a dg^a + g^a dn^a + g^b dn^b + n^b dg^b = 0$$

$$= g^a dn^a + g^b dn^b + n^a dg^a + n^b dg^b$$

Since we keep  $P, T$  const the intensive  $g$ 's do not change when we add some material into one phase (much like you don't change the  $P$  of water when you add some liquid into a flask).



Therefore,  $dg^a = dg^b = 0$  and:

$$dG = g^a dn^a + g^b dn^b = 0 \quad (3)$$

Since we are talking about a closed volume:  $n^a + n^b = \text{const} \rightarrow$   
 $\Rightarrow d(n^a + n^b) = 0 \Rightarrow dn^a = -dn^b$

$$\Rightarrow dG = (g^a - g^b) dn^a = 0$$

Now,  $dn^a$  is arbitrary, so for the above to hold, you must always have  $g^a = g^b$

i.e.: for thermodynamic equilibrium between multiple phases,  $g^a = g^b$  always.

How does this relate to chemical potentials?  
 Go to equation (3):

$$dG = g^a dn^a + g^b dn^b$$

from eq. 1

$$dG = \underbrace{S}_{T=\text{const}} dT + \underbrace{P}_{P=\text{const}} dV + \mu^a dn^a + \mu^b dn^b$$

$$\Rightarrow g^a = \mu^a \quad \text{and} \quad g^b = \mu^b$$

So for equilibrium between phases we need  $\mu^a = \mu^b$  for each component

distributed amongst each phase. This is the "diffusional" equilibrium we were talking about:

For thermodynamic equilibrium:

- Mechanical equilibrium

$P = \text{const with time, or } P^a = P^b$

- Thermal equilibrium

$T = \text{const with time, or } T^a = T^b$

- "Diffusional" (or chemical) equilibrium:

$$\mu^a = \mu^b$$

$G$  however is also the sum of its partial contributions. For constant  $T, P$ :

$$G = \sum g_i n_i \leftarrow \text{\# of moles of substance } i$$

$\uparrow$  GFE per unit mol of substance  $i$

and, since we showed already that  $p_i = g_i$

$$G = \sum \mu_i n_i \quad \text{at } T, P.$$

Total GFE of the system is given by the sum of the chemical potentials  $\times$  # of moles of each constituent.