# Chemical Potential



definitions: $dE = TdS - pdV + \mu dN$

$$\mu = \left.\frac{\partial E}{\partial N}\right)_{S,V} \quad \text{or} \quad \mu = -T\left.\frac{\partial S}{\partial N}\right)_{E,V}$$

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

$$\mu = \left.\frac{\partial F}{\partial N}\right)_{T,V}$$

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

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

## Gibbs-Duhem relation:

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

$$G = E - TS + PV = \mu N$$

$$dG = \mu dN + N d\mu$$

$$\cancel{\mu dN} + N d\mu = -SdT + VdP \cancel{+ \mu dN}$$

$$\boxed{-SdT + VdP - N d\mu = 0}$$

* role of chemical potential:
  - describing phase equilibria
  - describing chemical equilibrium

# Phase equilibria

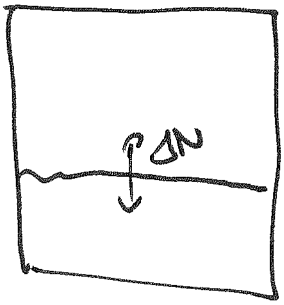


- if we have two phases of the same material in the same container: in general we will have two chemical potentials $\mu_1$ and $\mu_2$

- if the sample is kept at constant temperature T, and constant pressure P ⇒

$$dG = -SdT + VdP + \mu_1 dN_1 + \mu_2 dN_2$$

- if the system is isolated by an impermeable wall (no particles of either phase can escape)




⇒ $dN_1 = -dN_2$

- constant pressure/temperature

⇒ $dG = (\mu_1 - \mu_2) dN$

equilibrium ⇒ $dG = 0$ ⇒ $\boxed{\mu_1 = \mu_2}$

$$\boxed{\mu_1(P,T) = \mu_2(P,T)}$$

* how many phases can coexist?

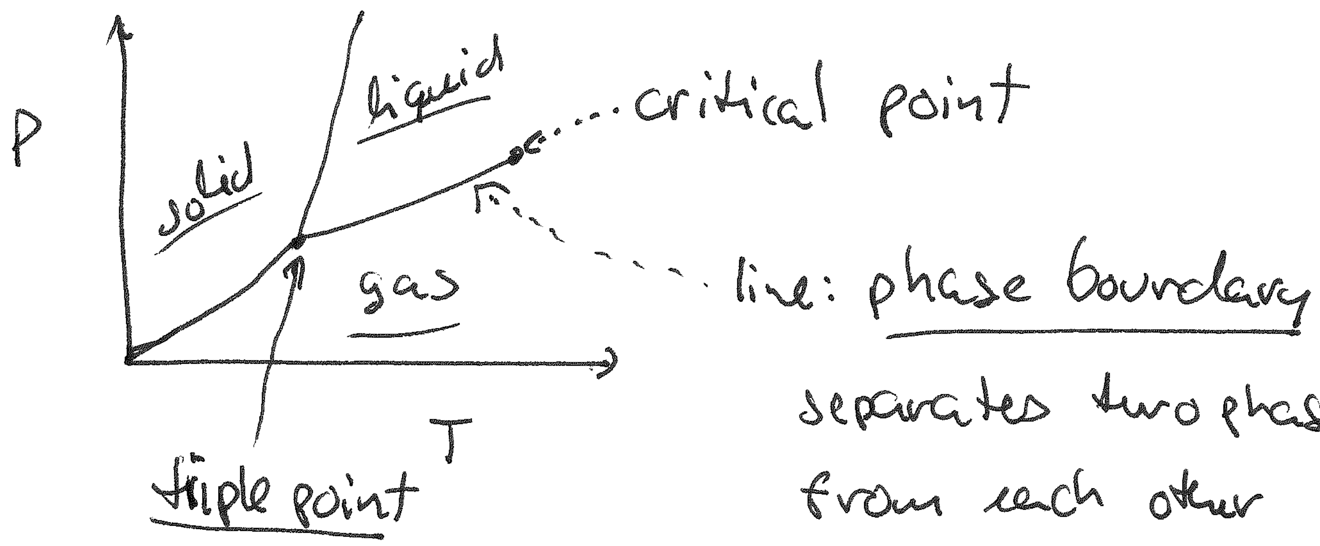
$\mu_1(P,T) = \mu_2(P,T)$ ⇒ defines a <u>line</u>

$$\underline{P = P(T)}$$

two phases can coexist at lines

$\mu_1(p,T) = \mu_2(p,T) = \mu_3(p,T) \Rightarrow$ defines a <u>point</u>

three phases can coexist at points




line: <u>phase boundary</u>

separates two phases from each other

<u>triple point</u>

three phases coexist

* suppose we have more than one type of substance in the container
  - suppose we have <u>r</u> substances

how many phases can coexist?
  - let this number be <u>l</u>

- in each phase r substances $\Rightarrow$

$$\sum_{j=1}^{r} x_j^{(i)} = 1$$

(i) – phase index

j – substance index

$x_j^{(i)} \rightarrow$ mole fraction of substance j in phase (i) chemical potential of phase (i) substance j: $\mu_j^{(i)}$

- depends on $P, T, x_1^{(i)}, \dots, x_{r-1}^{(i)}$

for each substance chemical potential for each phase should be equal (phase equilibrium)

$$\mu_1^{(1)}(P, T, x_1^{(1)}, \dots x_{r-1}^{(1)}) = \mu_1^{(2)}(P, T, x_1^{(2)}, \dots, x_{r-1}^{(2)}) = \dots$$

$$\dots = \mu_1^{(l)}(P, T, x_1^{(l)}, \dots, x_{r-1}^{(l)})$$

$$\mu_2^{(1)}(P, T, x_1^{(1)}, \dots, x_{r-1}^{(1)}) = \mu_2^{(2)}(P, T, x_1^{(2)}, \dots, x_{r-1}^{(2)}) = \dots$$

$$\dots = \mu_2^{(l)}(P, T, x_1^{(l)}, \dots, x_{r-1}^{(l)})$$

$$\vdots$$

$$\mu_r^{(1)}(P, T, x_1^{(1)}, \dots, x_{r-1}^{(1)}) = \mu_r^{(2)}(P, T, x_1^{(2)}, \dots, x_{r-1}^{(2)}) = \dots$$

$$\dots \mu_r^{(l)}(P, T, x_1^{(l)}, \dots, x_{r-1}^{(l)})$$

number of unknowns: $P, T, x_1^{(1)}, \dots, x_{r-1}^{(1)}, x_1^{(2)}, \dots, x_{r-1}^{(2)}, \dots, x_1^{(l)}, \dots, x_{r-1}^{(l)}$

$$\Rightarrow 2 + l(r-1)$$

number of equations: $r(l-1)$

well-defined if $2 + l(r-l) \geq r(l-1)$

$$2 - l \geq -r \Rightarrow \boxed{r + 2 \leq l}$$

Gibbs phase rule

as a consequence of phase equilibrium for a single substance, we can derive an equation for $\left.\frac{dP}{dT}\right)_{coex}$ ⇒ the derivative of the pressure with respect to the temperature along the coexistence curve

$$\mu_1(T,P) = \mu_2(T,P)$$

$$dg_1 = -s_1 dT + v_1 dP + \mu_1$$

$$dg_2 = -s_2 dT + v_2 dP + \mu_2$$

$$\Rightarrow \mu_1 = \mu_2 \Rightarrow -s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

Clausius-Clapeyron equation:

$$\left.\frac{dP}{dT}\right)_{coex} = \frac{(s_2 - s_1)}{(v_2 - v_1)}$$

in terms of latent heat: $\left.\frac{\partial P}{\partial T}\right)_{coex} = \frac{\Delta H}{T \Delta V}$

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- qualitatively: consider ⇒

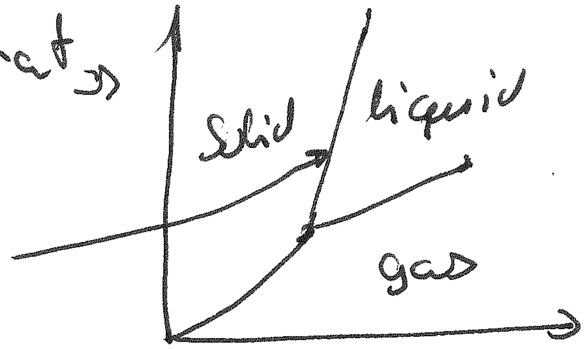
| solid | | liquid |
|---|---|---|
| $S_s$ | < | $S_e$ |
| $V_s$ | < | $V_e$ |

expect: solid more ordered than liquid → $S_s < S_e$

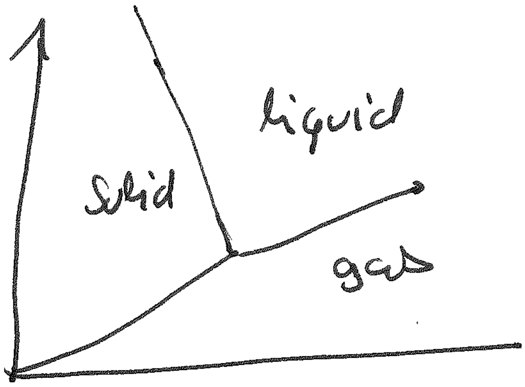
volume of solid less than volume of liquid → $V_s < V_e$

$$\Rightarrow \left.\frac{\partial P}{\partial T}\right)_{coex} > 0$$

thus expect that ⇒ solid-liquid phase line has positive slope




BUT there are exceptions: water-ice




because volume of liquid is less than volume of solid