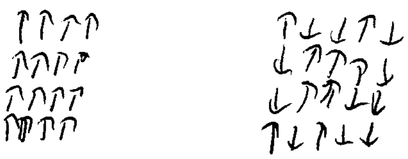
Thermodynamics of phase transitions

II.1 Examples

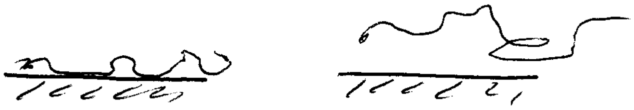
Phase transition: Through a change of external parameters a substance changes from one phase to another

liquid - gas
solid - gas
liquid - solid
conductor - superconductor
ferromagnet - paramagnet



denatured - globular

gas - Bose-Einstein-condensate
absorbed - desorbed



isotropic - nematic

II.2 Gibbs phase rule

Single component system:
three degrees of freedom, say N, Y, T
At phase transition:
two phases coexistence
$\Rightarrow Y^{I} = Y^{II}, \; T^{I} = T^{II}, \; \mu^{I} = \mu^{II}$

Gibbs - Duham relation

$\mu^{I} = \mu^{I}(Y,T)$ $\qquad$ $\mu^{II} = \mu^{II}(Y,T)$

two completely different functions

$\Rightarrow$ condition for phase coexistence of two phases

$$\mu^{I}(Y,T) = \mu^{II}(Y,T)$$

reduces number of degrees of freedom by one

$\rightarrow$ can solve for $Y = Y(T)$ "coexistence curve";

one intensive degree of freedom

<u>three phase coexistence</u>:

$$Y^{I} = Y^{II} = Y^{III} \equiv Y \qquad T^{I} = T^{II} = T^{III} \equiv T$$

$$\mu^{I}(Y,T) = \mu^{II}(Y,T) = \mu^{III}(Y,T)$$

reduces number of degrees of freedom by two

$\Rightarrow$ no intensive degree of freedom

$\Rightarrow$ (Y_3, T_3) isolated points

<u>four phase coexistence</u>

$$\mu^{I}(Y,T) = \mu^{II}(Y,T) = \mu^{III}(Y,T) = \mu^{IV}(Y,T)$$

three equations for two unknowns

$\rightarrow$ four phases cannot coexist in a single component system general rule for multi component systems

l components

$\to$ $l+1$ intensive degrees of freedom in each phase

$Y, T, x_1, x_2, \ldots, x_{l-1}$ $\qquad x_i = \dfrac{n_i}{\sum_{j=1}^{l} n_j}$

coexistence of r phases:

Y, T the same in all phases but x_i can be different

$\Rightarrow 2 + r(l-1)$ intensive degrees of freedom

coexistence conditions

$$\mu_1^{I}(Y, T, x_1^{I}, \ldots, x_{l-1}^{I}) = \mu_1^{II}(Y, T, x_1^{II}, \ldots, x_{l-1}^{II}) = \ldots = \mu_1^{(r)}(Y, T, x_1^{(r)}, \ldots, x_{l-1}^{(r)})$$

$$\mu_2^{I}(Y, T, x_1^{I}, \ldots, x_{l-1}^{I}) = \mu_2^{II}(Y, T, x_1^{II}, \ldots, x_{l-1}^{II}) = \ldots = \mu_2^{(r)}(Y, T, x_1^{(r)}, \ldots, x_{l-1}^{(r)})$$

$$\vdots$$

$$\mu_l^{I}(Y, T, x_1^{I}, \ldots, x_{l-1}^{I}) = \mu_l^{II}(Y, T, x_1^{II}, \ldots, x_{l-1}^{II}) = \ldots = \mu_l^{(r)}(Y, T, x_1^{(r)}, \ldots, x_{l-1}^{(r)})$$

$l(r-1)$ equations

$\Rightarrow$ A r-phase coexistence region of an l-component system has $2 + r(l-1) - l(r-1) = 2 + l - r$ intensive degrees of freedom

"Gibbs phase rule"

$\downarrow$ 10/23