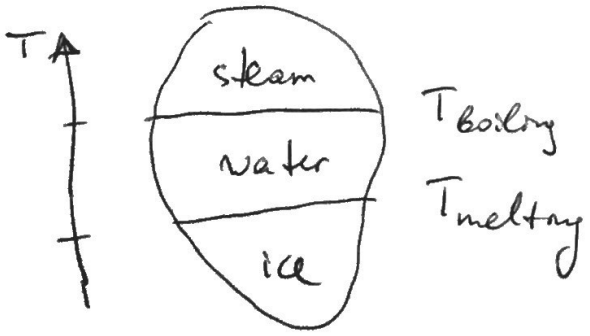
Phases

Phases are states of matter (in thermod. equilibrium) with properties changing smoothly under changes of external conditions, such as temp. T or pressure P.

Phases are distinguished through phase transitions: singular (discontinuous / nonsmooth) changes of properties under a change of T or P.

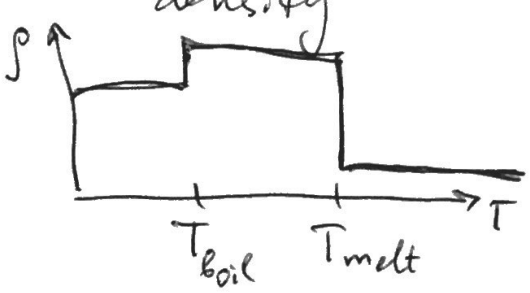
Order parameter(s): measure of degree of order across the boundary in a phase transition.

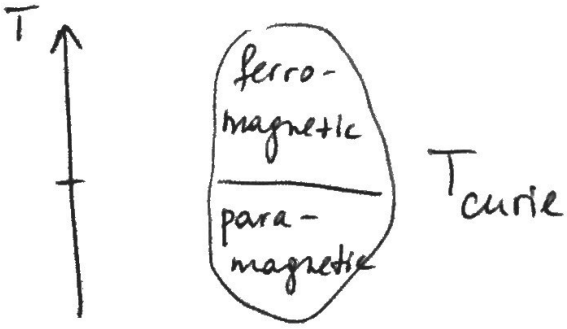
Examples:



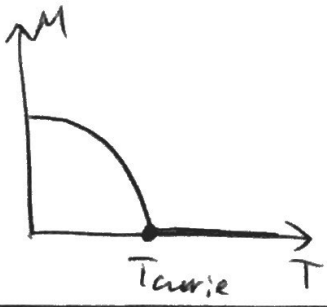
solid / liquid / gas

Order parameter: density





Order parameter: magnetization



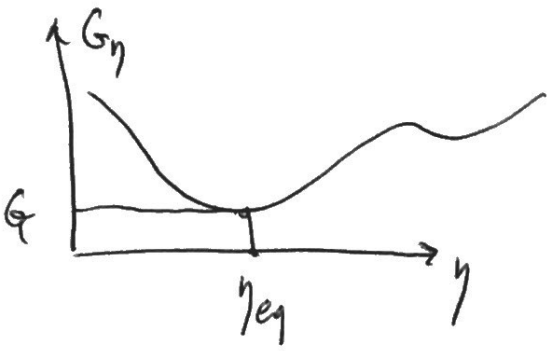
Phenomenological theory (Landau)

Let η be the order parameter.

Let us ~~introduce~~ consider the Gibbs free energy $G(T,P)$.

We know (material before) that $G \to \min$ in thermodinamic equilibrium at fixed temperature T and pressure P.

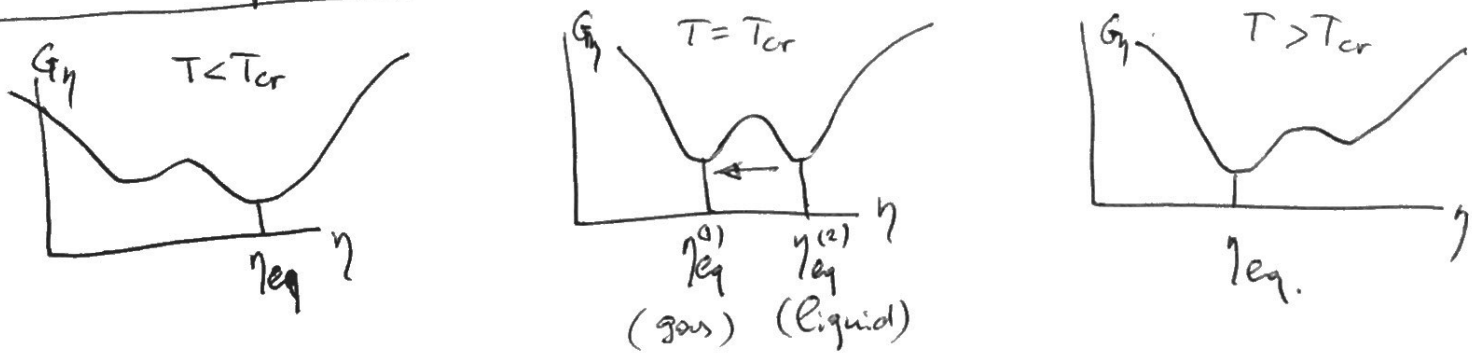
Let $G_\eta(T,P)$ be the Gibbs energy in partial equilibrium, under constraint that η is fixed $\Rightarrow \eta_{eq}$: $\min_\eta G_\eta$.



$$G(T,P) = \min_\eta G_\eta(T,P)$$

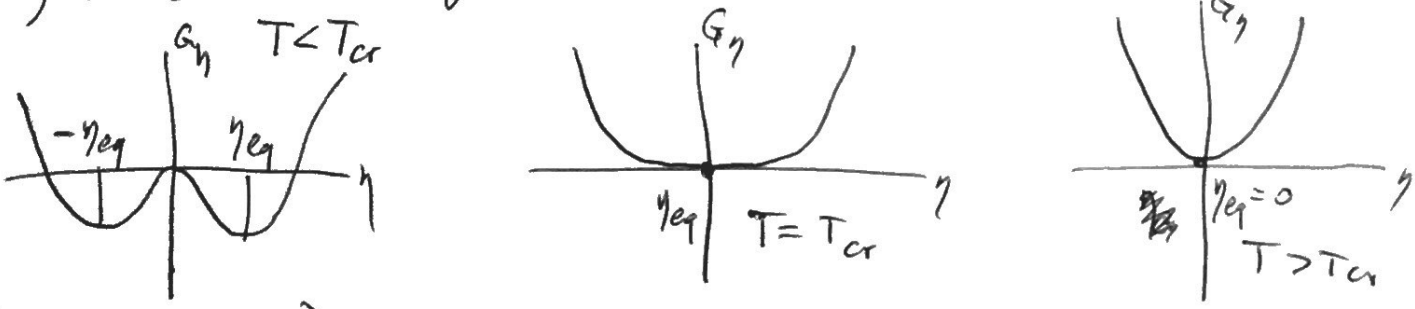
and η_{eq} is determined by this min.

1st-order phase transition (discontinuous):



2nd-order phase transition (continuous)

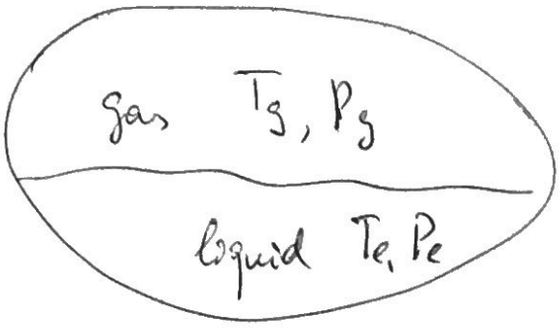
systems with symmetries



(magnetization)
$M>0$, direction is arbitrary

(paramagnetic
$M=0$)

Thermodynamics of phase equilibrium



In therm. equilibrium:

$S \longrightarrow \max$ (entropy)

$\Rightarrow \delta S = 0$ for any small variation in the system.

Internal energy:

$$\delta U_g = T_g \delta S_g - P_g \delta V_g + \mu_g \delta N_g \quad \text{(gas)}$$

$$\delta U_e = T_e \delta S_e - P_e \delta V_e + \mu_e \delta N_e \quad \text{(liquid)}$$

Exchange of energy: $\delta U_g = \varepsilon$, $\delta U_e = -\varepsilon$ $(\delta V = 0, \delta N = 0)$

$$\delta S = \delta S_g + \delta S_e = \frac{\delta U_g}{T_g} + \frac{\delta U_e}{T_e} = \left(\frac{1}{T_g} - \frac{1}{T_e}\right)\varepsilon = 0$$

$$\Rightarrow \boxed{T_g = T_e = T}$$ equal temperatures

Exchange of volume: $\delta V_g = \varepsilon$, $\delta V_e = -\varepsilon$ $(\delta U = 0, \delta N = 0)$

$$\delta S = \delta S_g + \delta S_e = \frac{P_g}{T}\delta V_g + \frac{P_e}{T}\delta V_e = (P_g - P_e)\frac{\varepsilon}{T} = 0$$

$$\Rightarrow \boxed{P_g = P_e = P}$$ equal pressures

Obs NOT TRUE if one takes into account energy of interface $\Rightarrow$ surface tension.

Exchange of mass: $\delta N_g = \varepsilon$, $\delta N_e = -\varepsilon$ $(\delta U = 0, \delta V = 0)$

similarly $\Rightarrow$ $$\boxed{\mu_g(T,P) = \mu_e(T,P)}$$ equilibrium condition

chemical potentials of phases in equilibrium are equal!

Obs: solution yields $T = T_{eq}(P)$.

Clausius - Clapeyron relation

$$\mu_\ell(T,P) = \mu_g(T,P) \Rightarrow P = P(T)$$

dependence of pressure on temperature for gas/liquid equilibrium (boiling point)

$$\frac{\partial \mu_\ell}{\partial T} + \left(\frac{\partial \mu_\ell}{\partial P}\right)_T \frac{dP}{dT} = \frac{\partial \mu_g}{\partial T} + \left(\frac{\partial \mu_g}{\partial P}\right)_T \frac{dP}{dT} \qquad (*)$$

Recall that $G = \mu N$ (Gibbs free energy) and

$$dG = -S\,dT + V\,dP \quad \text{(at fixed } N\text{)}$$

Hence, $\left(\frac{\partial \mu}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{N} = \tilde{s}$ (entropy per particle)

$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_T = \frac{V}{N} = \tilde{v}$ (volume per particle)

$$(*) \Rightarrow \quad -\tilde{s}_\ell + \tilde{v}_\ell \frac{dP}{dT} = -\tilde{s}_g + \tilde{v}_g \frac{dP}{dT}$$

$$\frac{dP}{dT} = \frac{\tilde{s}_g - \tilde{s}_\ell}{\tilde{v}_g - \tilde{v}_\ell} \approx \frac{q}{T\tilde{v}_g}$$

(a) $\tilde{v}_g - \tilde{v}_\ell \approx \tilde{v}_g$ (because $\tilde{v}_g \gg \tilde{v}_\ell$ in gas vs. liquid)

(b) $q = T\Delta s = T(\tilde{s}_g - \tilde{s}_\ell)$ heat of phase transition (vaporization)

In ideal gas : $PV = k_B N T \Rightarrow \tilde{v}_g = \frac{V}{N} = \frac{k_B T}{P}$.

So, $$\frac{dP}{dT} = \frac{qP}{k_B T^2} = \frac{QP}{RT^2}.$$

where $Q = q N_A$ (heat of phase transition per 1 mole)

$R = k_B N_A$ (ideal gas constant)

$$\boxed{d \log P = -Q \, d\frac{1}{RT}}$$

If $Q \approx$ const (neglecting dependence on P and T)

$$\log P = -\frac{Q}{RT} + \text{const} \Rightarrow P = A \exp\left(-\frac{Q}{RT}\right)$$

At $P = P_{atm}$ (atmospheric), T_b^{atm} (atm. boiling temperat.)

$$\Rightarrow A = P_{atm} \exp\left(\frac{Q}{R T_b^{atm}}\right)$$

$$\Rightarrow \boxed{P = P_{atm} \exp\left[-\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_b^{atm}}\right)\right]}$$

value of pressure P corresponding to the boiling temperature T.

Multiple components

Particles of type A, B, C (etc.)

For example, air $= N_2 + O_2 + H_2O + \ldots$

78% 21% 1% ...

$N_{tot} = N_A + N_B + N_C$, $s_A = \frac{N_A}{N_{tot}}$, $s_B = \frac{N_B}{N_{tot}}$, etc. molar saturations.

Gibbs energy: $G = G(T, P, N_A, N_B, N_C)$

Chemical potentials: $\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B,N_C}$, etc.

<u>Exercise</u>: show that in phase equilibrium (liquid / gas), chemical potentials of each component are equal:

$$\mu_A^g(T, P, s_A, s_B, s_C) = \mu_A^l(T, P, s_A, s_B, s_C)$$

$$\mu_B^g(\text{——}) = \mu_B^l(\text{——})$$

etc.

<u>Exercise</u>: In ideal gas $P_A = s_A P = \rho_A RT$ (partial pressure)

For air-water equilibrium, show that

air $\begin{pmatrix} N_2, \\ O_2, \\ H_2O, \text{etc.} \end{pmatrix}$

water (H_2O)

$$P_{H_2O} = P_{atm} \exp\left(-\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_b^{atm}}\right)\right).$$

partial pressure of H_2O-vapor over water at given temperature T.

Gibbs' phase rule

Consider a system in thermodynamic equilibrium, which consists of c components (A, B, etc.) and p phases. All components may be present in all phases.

We know that all phases must have the same T and P (assuming no surface effects).

In each phase (i), the composition depends on $c-1$ concentrations $\xi_1^{(i)}, \dots, \xi_{c-1}^{(i)}$ because $\xi_1^{(i)} + \dots + \xi_c^{(i)} = 1$

Hence, total number of unknowns is $\underset{(T,P)}{2} + \underbrace{p(c-1)}_{\text{concentrations in } p \text{ phases}}$

For each ~~(j)~~ components (j), the equilibrium condition is

$$\mu_j^{\text{phase 1}} = \mu_j^{\text{phase 2}} = \dots = \mu_j^{\text{phase } p} \Rightarrow c(p-1) \text{ equations}$$

Hence, a general solution of ~~eqs~~ $c(p-1)$ eqs with $2+p(c-1)$ unknowns ~~depends~~ depends on

$$\boxed{f = 2 + p(c-1) - c(p-1) = 2 + c - p}$$

number of degrees of freedom.

Obs: $f \geq 0 \Rightarrow p \leq c+2$ (max. number of phases)

Example:

air (N_2, O_2, H_2O)

water (H_2O)

$c = 3, \quad p = 2$

$f = 2+3-2 = 3$

Can be: T, P, ξ_{O_2}

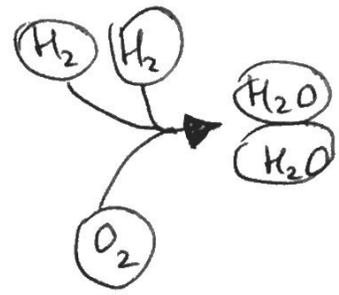
Chemical reactions

$$\nu_A A + \nu_B B \longrightarrow \nu_C C \qquad (\text{in fact, } \rightleftarrows)$$

ν_A, ν_B, ν_C are stoichiometric coefficients

Examples

$C + O_2 \rightarrow CO_2$ $\qquad$ $2H_2 + O_2 \rightarrow 2H_2O$



$\nu_C = \nu_{O_2} = \nu_{CO_2} = 1$ $\qquad$ $\nu_{H_2} = 2,\ \nu_{O_2} = 1,\ \nu_{H_2O} = 2$

Consider a mixture in therm. equilibrium (reactions go in both sides at same rate).

$$G = G(T, P, N_A, N_B, N_C) \rightarrow \min \quad (\text{at constant } T \text{ and } P).$$

$$\Rightarrow \quad \delta G = \underbrace{\frac{\partial G}{\partial N_A}}_{\mu_A} \delta N_A + \underbrace{\frac{\partial G}{\partial N_B}}_{\mu_B} \delta N_B + \underbrace{\frac{\partial G}{\partial N_C}}_{\underline{\mu_C(T, P, S_A, S_B, S_C)}} \delta N_C = 0$$

$$\delta N_A = -\nu_A \underbrace{n_R}_{\text{number of reactions}}, \quad \delta N_B = -\nu_B n_R, \quad \delta N_C = +\nu_C n_R$$

(formula of reaction)

$$\Rightarrow \delta G = (-\nu_A \mu_A - \nu_B \mu_B + \nu_C \mu_C) n_R = 0$$

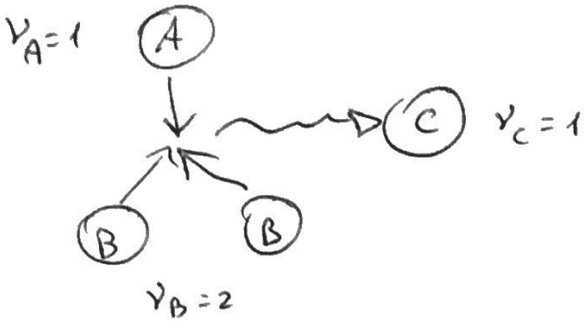
$$\boxed{\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C}$$

equilibrium condition

Obs: obvious generalization to other types of reactions.

Exercise: $A + B \rightarrow C + D$.

Reaction rate (in gases)



$$W_R \sim P_{collision} * P_{reaction}$$

reaction rate — probability of collision — probability of reaction.

$$P_{collision} \sim \rho_A^{\nu_A} \rho_B^{\nu_B}$$

(probability to be in the same place is proportional to (molar) density)

$P_{reaction}$: requires particles to have high speed, i.e., energy $\frac{mv^2}{2} \gtrsim e_{act}$ (activation energy per reaction)

In ideal gas, $\underbrace{\rho(q,p)}_{\text{prob. density function}} = \text{const} \cdot \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2mk_BT}\right) dp\,dq$

<u>Obs</u> Recall that $\rho = \text{const}\, e^{-\frac{H}{k_BT}}$ (Gibbs dist), $H = \sum_a \frac{p_a^2}{2m}$.

$\rho(p) = \text{const} \cdot \exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2mk_BT}\right) dp$ distribution w.r.t. momenta

$p_x = mv_x$, $p_y = mv_y$, $p_z = mv_z$, $dp_x dp_y dp_z = m^3 v^2 \sin\theta\, d\theta\, d\varphi\, dv$

where $v = \|(v_x, v_y, v_z)\|$.

$\xrightarrow[\text{w.r.t. angles}]{\text{integration}}$

$$\boxed{\rho(v) = \underbrace{4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}}_{\text{const: } \int \rho\, dv = 1} v^2 \exp\left(-\frac{mv^2}{2k_BT}\right) dv}$$

This is the Maxwell distribution.

$$P_{reaction} \sim P\left(\frac{mv^2}{2} \gtrsim e_{act}\right) \sim \int_{v \gtrsim \sqrt{\frac{2e_{act}}{m}}} \rho(v)\, dv \sim$$

(exercise)

$$\sim \text{const} \cdot \underbrace{\exp\left(-\frac{e_{act}}{k_B T}\right)}_{\text{strongly depends on temperature}}$$

neglecting (slow) power-law <u>prefactor T^{α}</u>.

For $E_{act} = N_A e_{at}$ (macroscopic activation energy), $R = k_B N_A$, we have

$$P_{reaction} \sim \text{const} \cdot \exp\left(-\frac{E_{act}}{RT}\right)$$

<u>Arrhenius law for the reaction rate:</u>

$$\boxed{W_R = \underbrace{k}_{\text{const. prefactor}} \rho_A^{\nu_A} \rho_B^{\nu_B} \exp\left(-\frac{E_{act}}{RT}\right).}$$

~~called temp~~