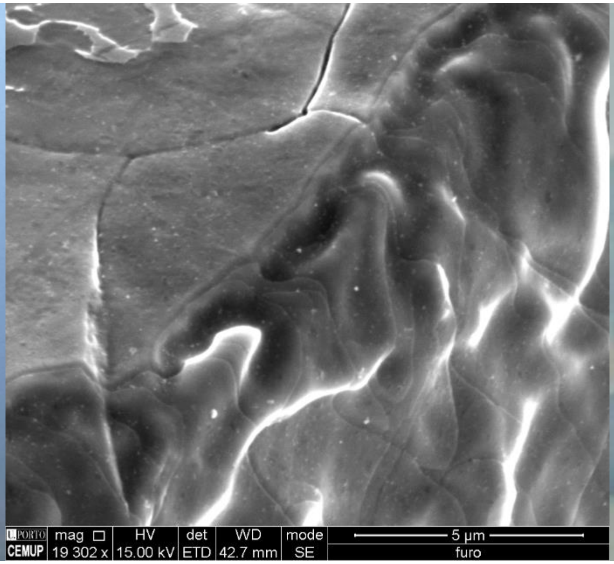
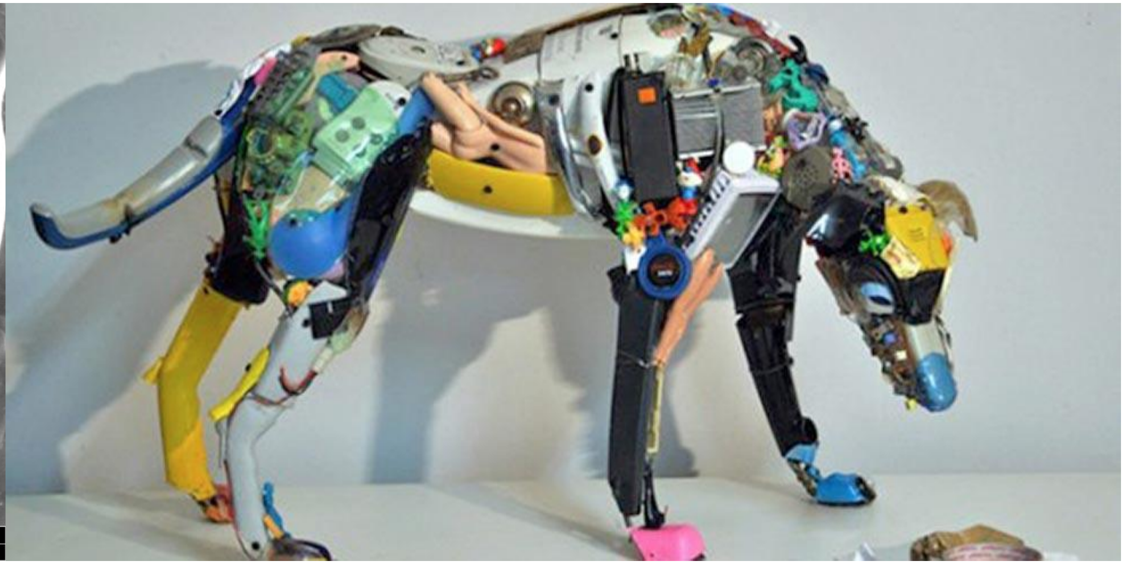
Physical Chemistry

... iremos explorar, refletir, aprender ?..

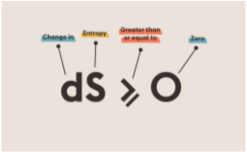
Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.





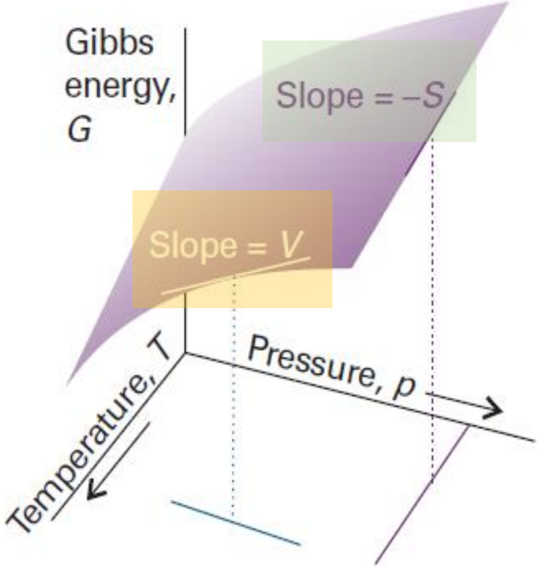
Second Law

$$dS - \frac{dq}{T} \geq 0$$

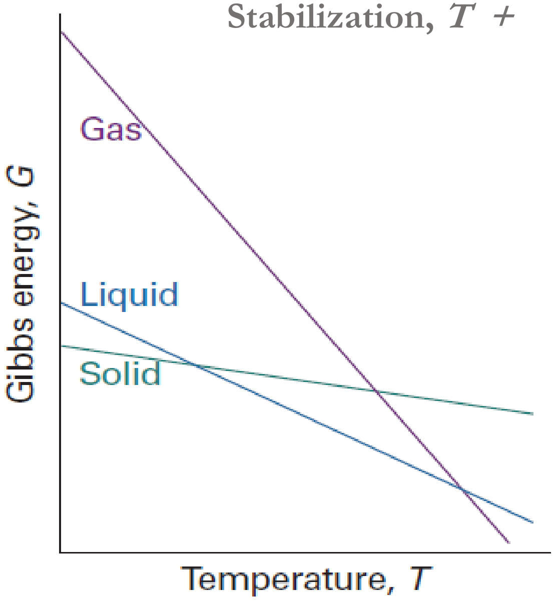


$$dG = Vdp - SdT$$

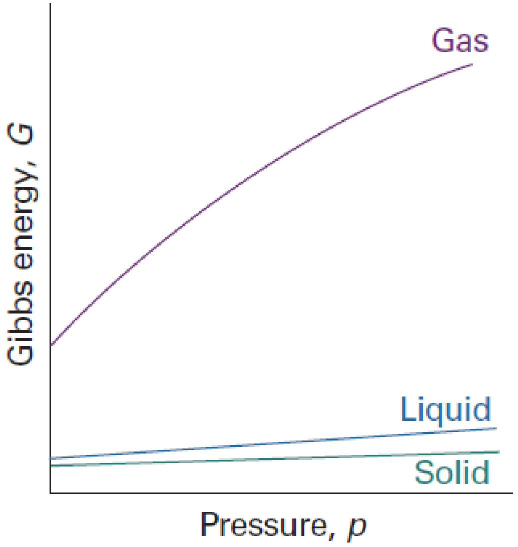
$$\left(\frac{\partial G}{\partial T}\right)_p = -S \qquad \left(\frac{\partial G}{\partial p}\right)_T = V$$



Stabilization, T +



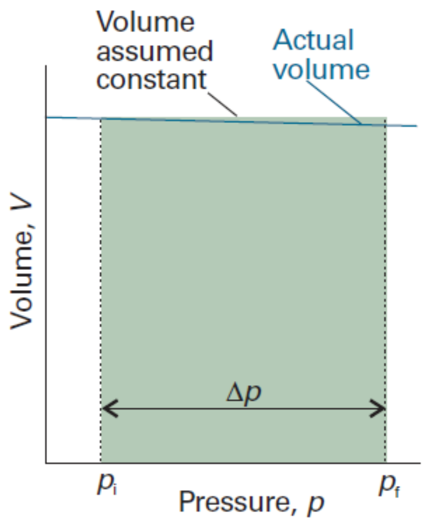
destabilization, p +



Variation of the Gibbs energy with pressure

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp$$



Condensed phase (liquids and Solids)
changes V_m is almost constante

$$G_m(p_f) = G_m(p_i) + V_m\int_{p_i}^{p_f} dp = G_m(p_i) + (p_f - p_i)V_m$$

Illustration 3.10 *Gibbs energies at high pressures*

Suppose that for a certain phase transition of a solid $\Delta_{trs}V = +1.0\ cm^3\ mol^{-1}$ independent of pressure. Then, for an increase in pressure to 3.0 Mbar (3.0×10^{11} Pa) from 1.0 bar (1.0×10^5 Pa), the Gibbs energy of the transition changes from $\Delta_{trs}G(1\ bar)$ to

$$\begin{aligned}\Delta_{trs}G(3\ Mbar) &= \Delta_{trs}G(1\ bar) + (1.0\times10^{-6}\ m^3\ mol^{-1})\times(3.0\times10^{11}\ Pa - 1.0\times10^5\ Pa)\\ &= \Delta_{trs}G(1\ bar) + 3.0\times10^2\ kJ\ mol^{-1}\end{aligned}$$

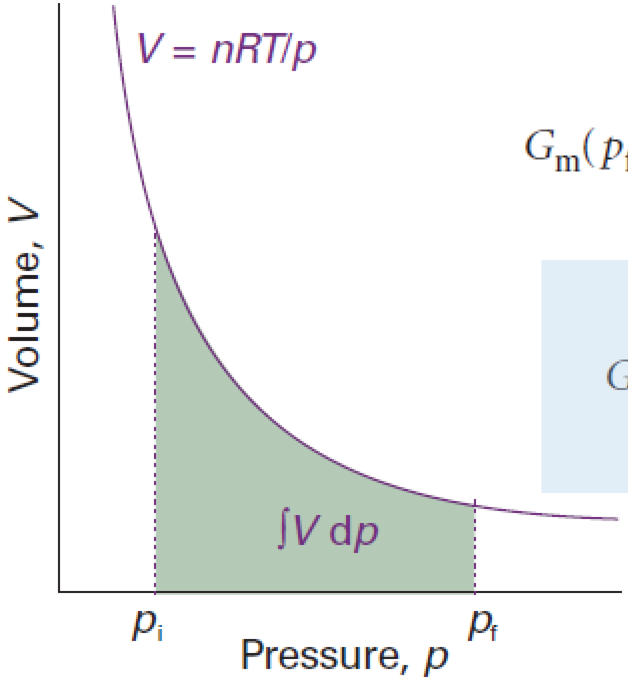
where we have used $1\ Pa\ m^3 = 1\ J$.

Variation of the Gibbs energy with pressure

V_m of Gas phase changes … $V_m = RT/p$

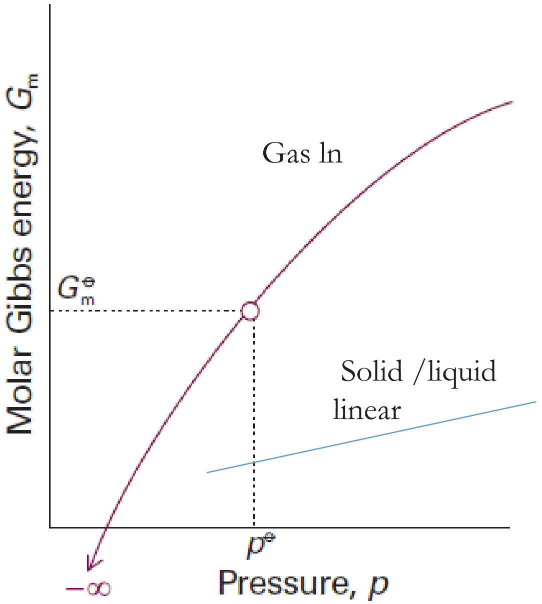
$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp$$



$$G_m(p_f) = G_m(p_i) + RT\int_{p_i}^{p_f}\frac{dp}{p} = G_m(p_i) + RT\ln\frac{p_f}{p_i}$$

$$G_m(p) = G_m^{\ominus} + RT\ln\frac{p}{p^{\ominus}}$$



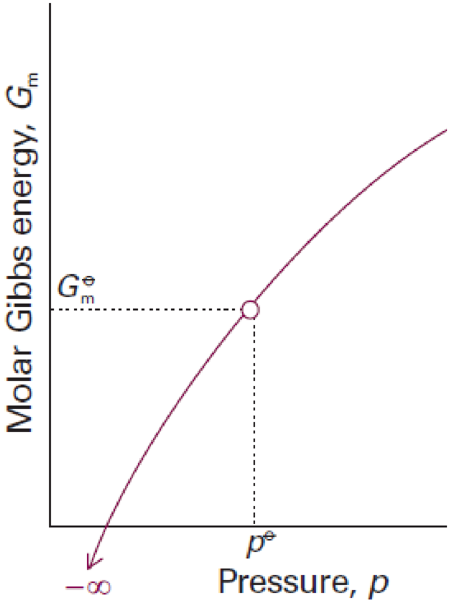
Variation of the Gibbs energy with pressure

V_m of Gas phase changes …

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

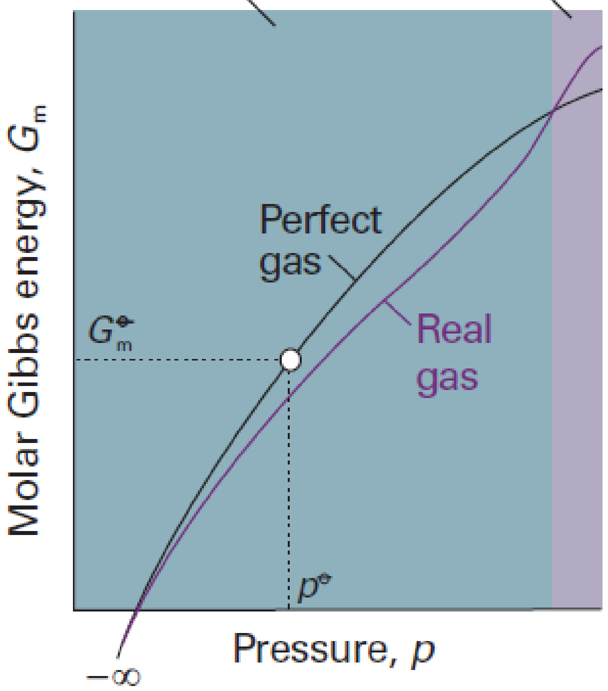
$$G(p_f) = G(p_i) + \int_{p_i}^{p_f} V\,dp$$

$$G_m(p_f) = G_m(p_i) + RT\int_{p_i}^{p_f}\frac{dp}{p} = G_m(p_i) + RT\ln\frac{p_f}{p_i}$$



$V_m = RT/p$ Perfect Gas

$$G_m(p) = G_m^\ominus + RT\ln\frac{p}{p^\ominus}$$



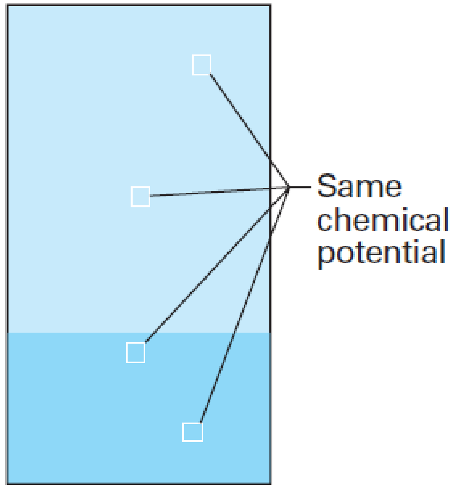
Higher Stability

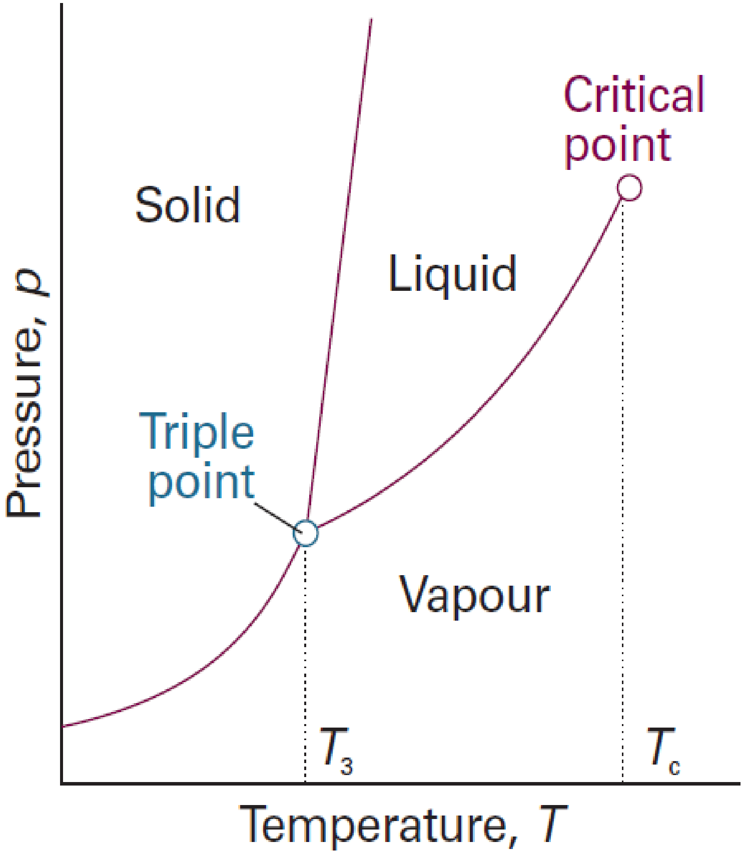
Phase

of a substance is a form of matter that is **uniform** throughout in **chemical composition** and **physical state**.

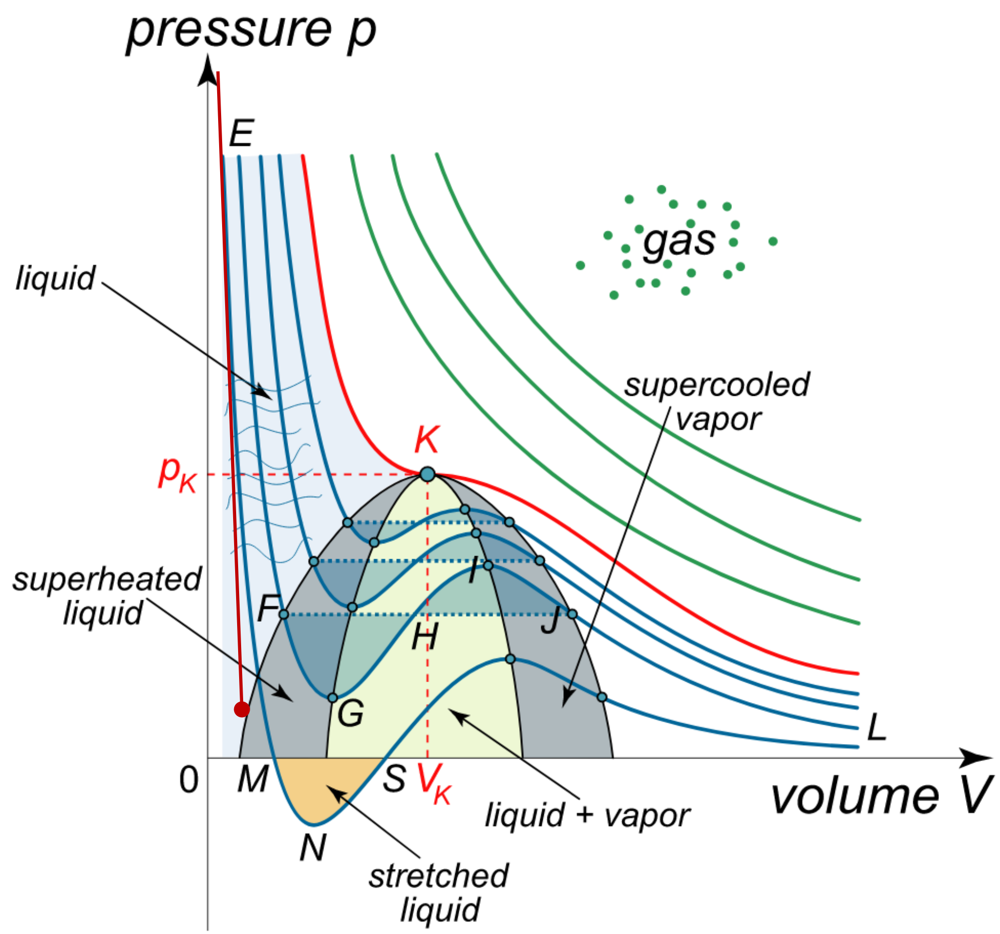
Phase transition,

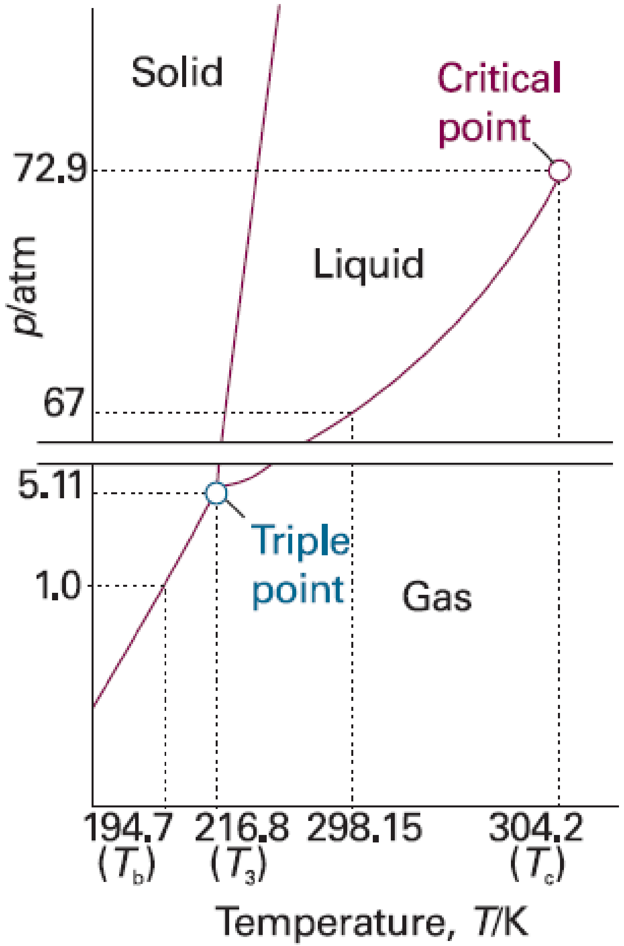
the spontaneous **conversion** of one **phase** into another phase, occurs at a characteristic ***T*** for a given ***p***



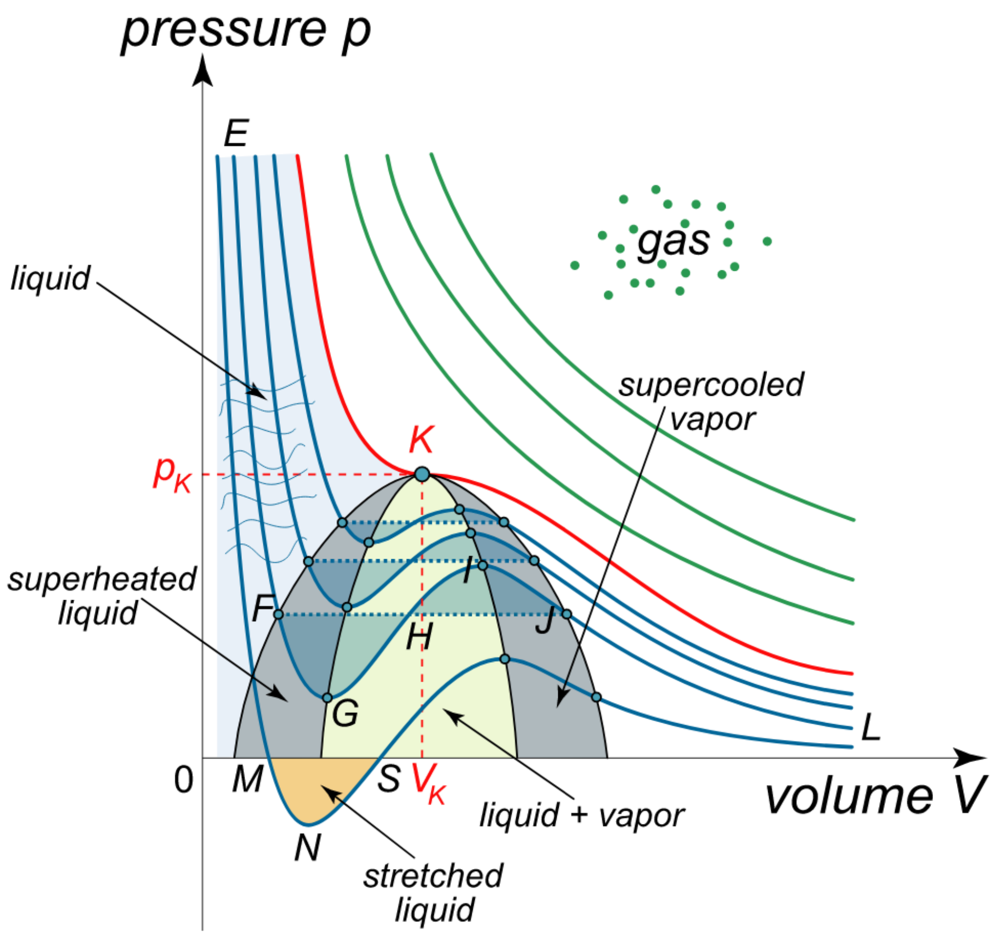


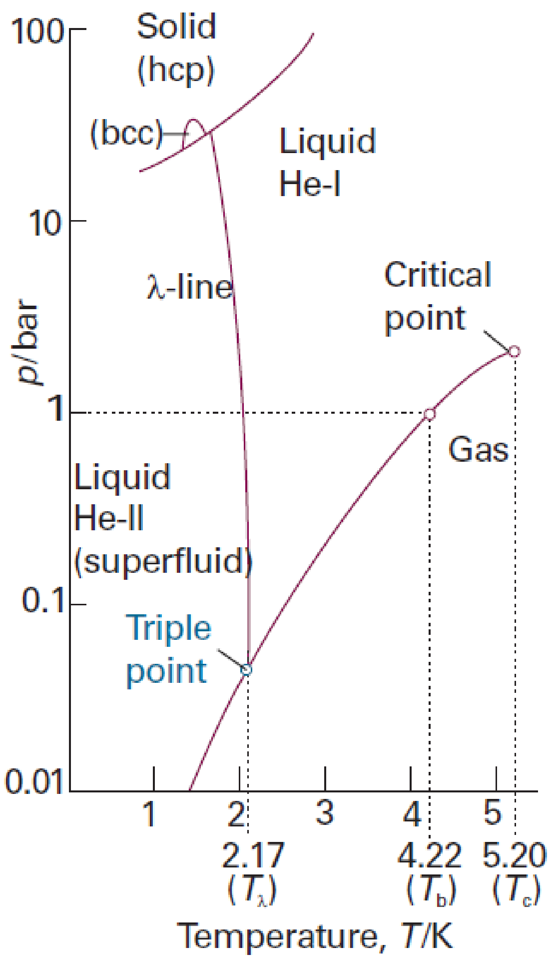
Water


pressure p
E
liquid
gas
supercooled vapor
K
p_K
superheated liquid
F
I
J
H
G
L
0
M
S
V_K
volume V
liquid + vapor
N
stretched liquid


Solid
Critical point
72.9
Liquid
p/atm
67
5.11
Triple point
1.0
Gas
194.7 (T_b)
216.8 (T_3)
298.15
304.2 (T_c)
Temperature, T/K

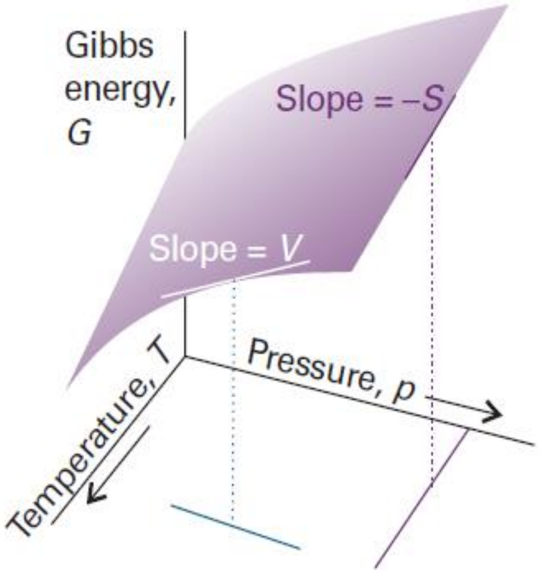
Helium

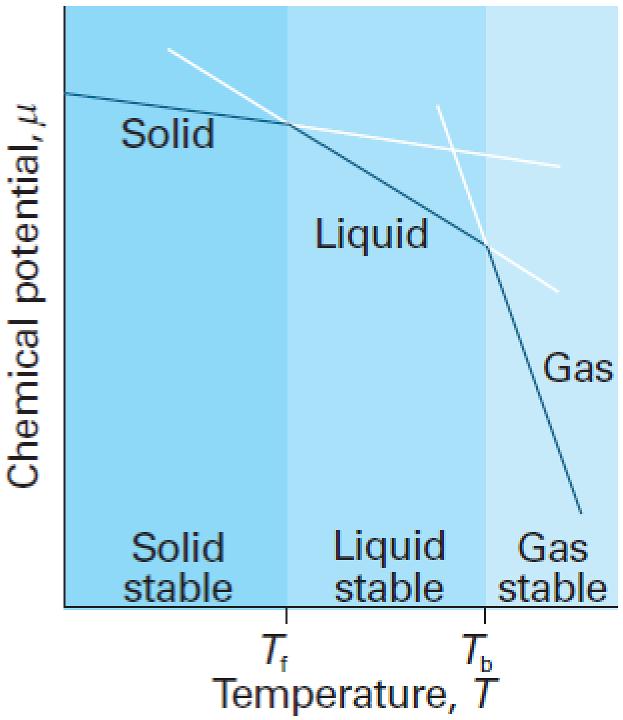

pressure p
E
liquid
gas
supercooled
vapor
p_K
K
superheated
liquid
F
H
I
J
G
L
0
M
S
V_K
N
volume V
liquid + vapor
stretched
liquid

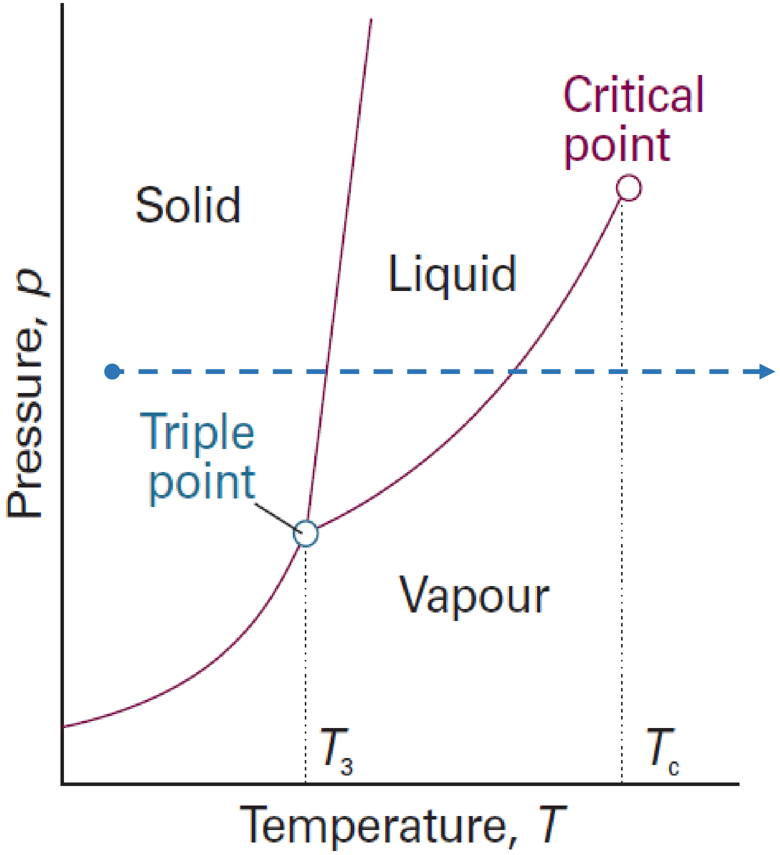

100
10
1
0.1
0.01
p/bar
Solid
(hcp)
(bcc)
Liquid
He-I
λ-line
Critical
point
Gas
Liquid
He-II
(superfluid)
Triple
point
1
2
3
4
5
2.17
($T_λ$)
4.22
(T_b)
5.20
(T_c)
Temperature, T/K

Physical transformations of pure substances

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







Physical transformations of pure substances

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

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$