Clase 52 23 Noviembre 2020

Título de la nota 23/11/2020

$$\lim_{p \to 0} \qquad pV = nRT$$

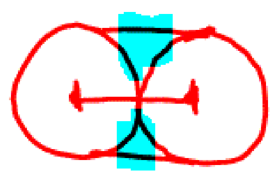
$$V = \frac{nRT}{P} \qquad P \to \infty$$

Esto no es un comportamiento real.

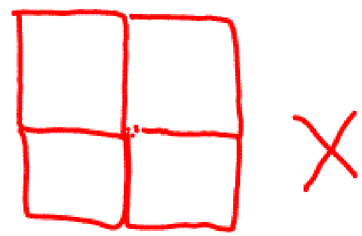
$T \to 0$

$V \to 0$

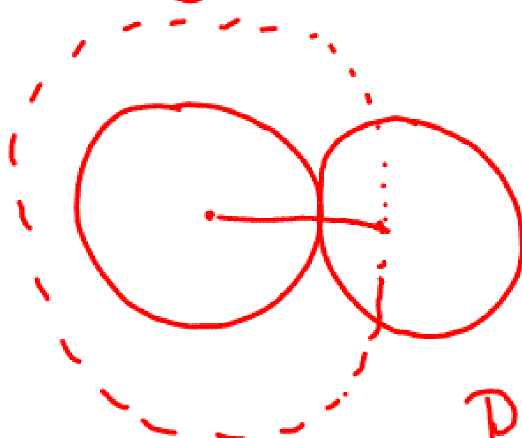
Van der Waals (1876)



Fundamento
- volumen exclusión



- presión no ejercida (atracción)



$$V_{\text{exclusión}} = \frac{4}{3}\pi d^3$$

$$\text{por mol.} = \frac{2}{3}\pi d^3$$

$$\boxed{\bar{V} = \frac{2}{3}\pi d^3 N} = b \quad \text{cte de}$$

Van der Waals

$$P = \frac{nRT}{V - nb} \checkmark \qquad b = \frac{L}{mol}$$

$$P = \frac{RT}{\bar{V} - b} \checkmark \qquad \boxed{b < \bar{V}}$$

$$b = \bar{V} \qquad P \to \infty$$

Presión no ejercida

$\lim V = nb$

$\bar{V} = b$

$T \to 0 \quad p \to \infty$

$F \propto C_1 C_2$ gas puro $C_1 = C_2$

$C = [\;] = \frac{n}{V}$

$F \propto C^2 \qquad F \propto [\;]^2$

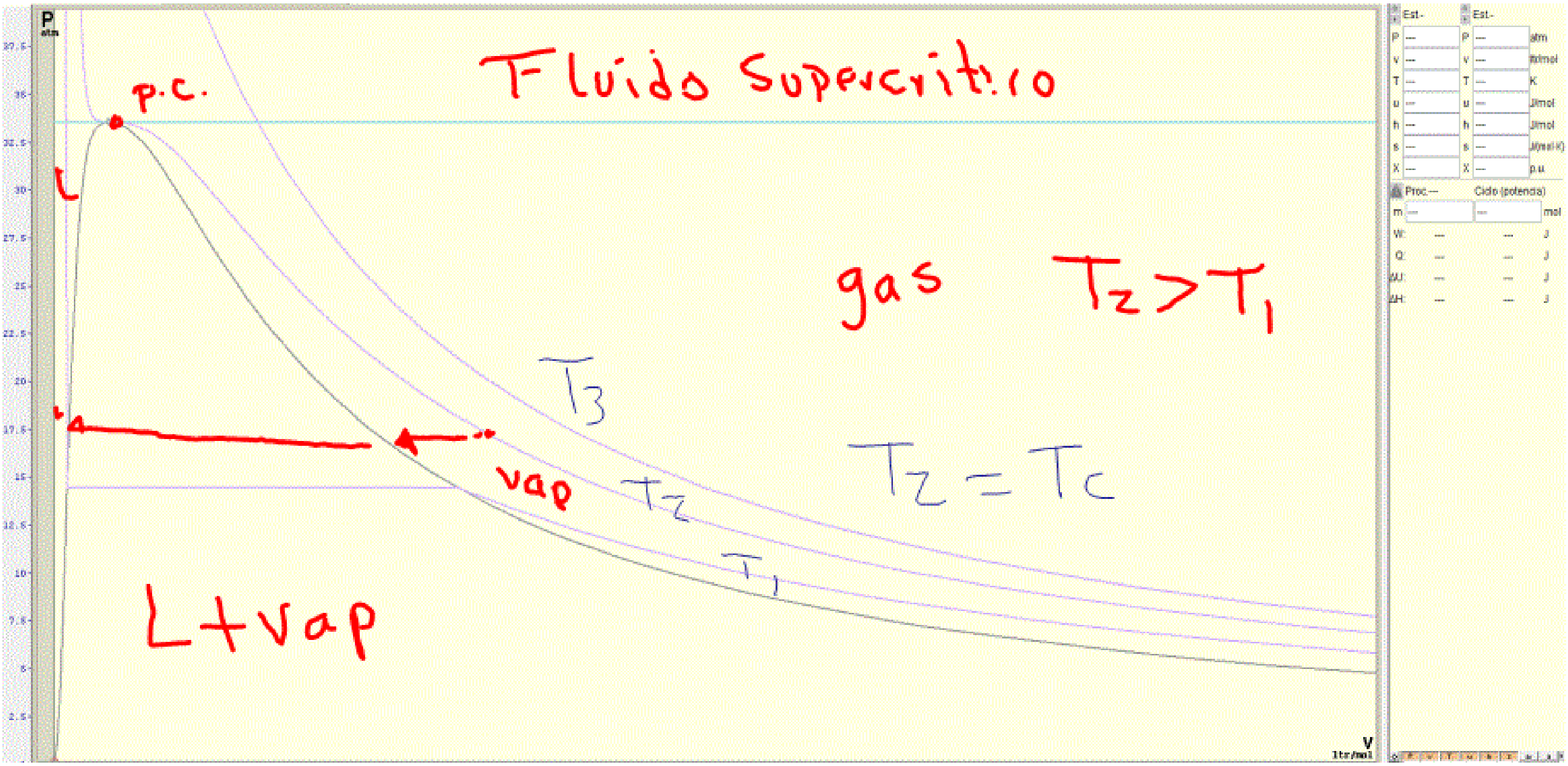
$$F \propto \frac{n^2}{V^2} \qquad F =$$

$$F = \frac{a' n^2}{V^2} \qquad P = \frac{F}{A}$$

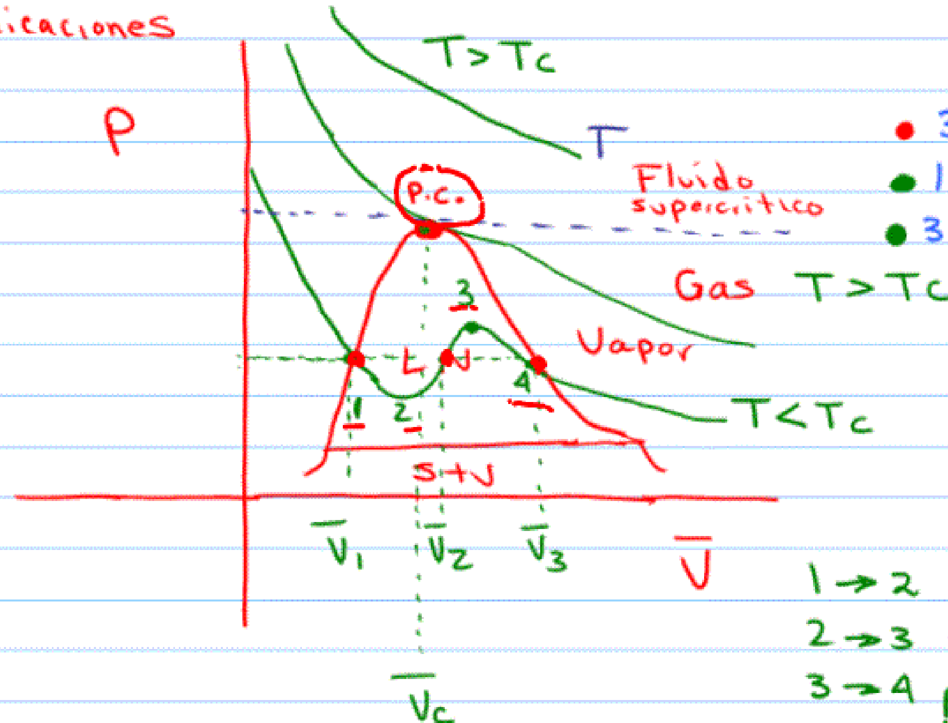
$$P = \frac{a' n^2}{V^2 A} = \frac{a n^2}{V^2}$$

$$\boxed{P = \frac{nRT}{V - nb} - \frac{a n^2}{V^2}} \qquad a = \frac{atm\,\cancel{L^2}}{\cancel{mol^2}}\left(\frac{\cancel{mol^2}}{\cancel{L^2}}\right)$$

$$\boxed{P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}} \qquad a = \frac{atm\,L^2}{mol^2}$$


P
atm
V
ltr/mol
Fluido Supercritico
p.c.
L
gas
$T_2 > T_1$
T_3
vap
T_2
$T_2 = T_c$
T_1
L+vap

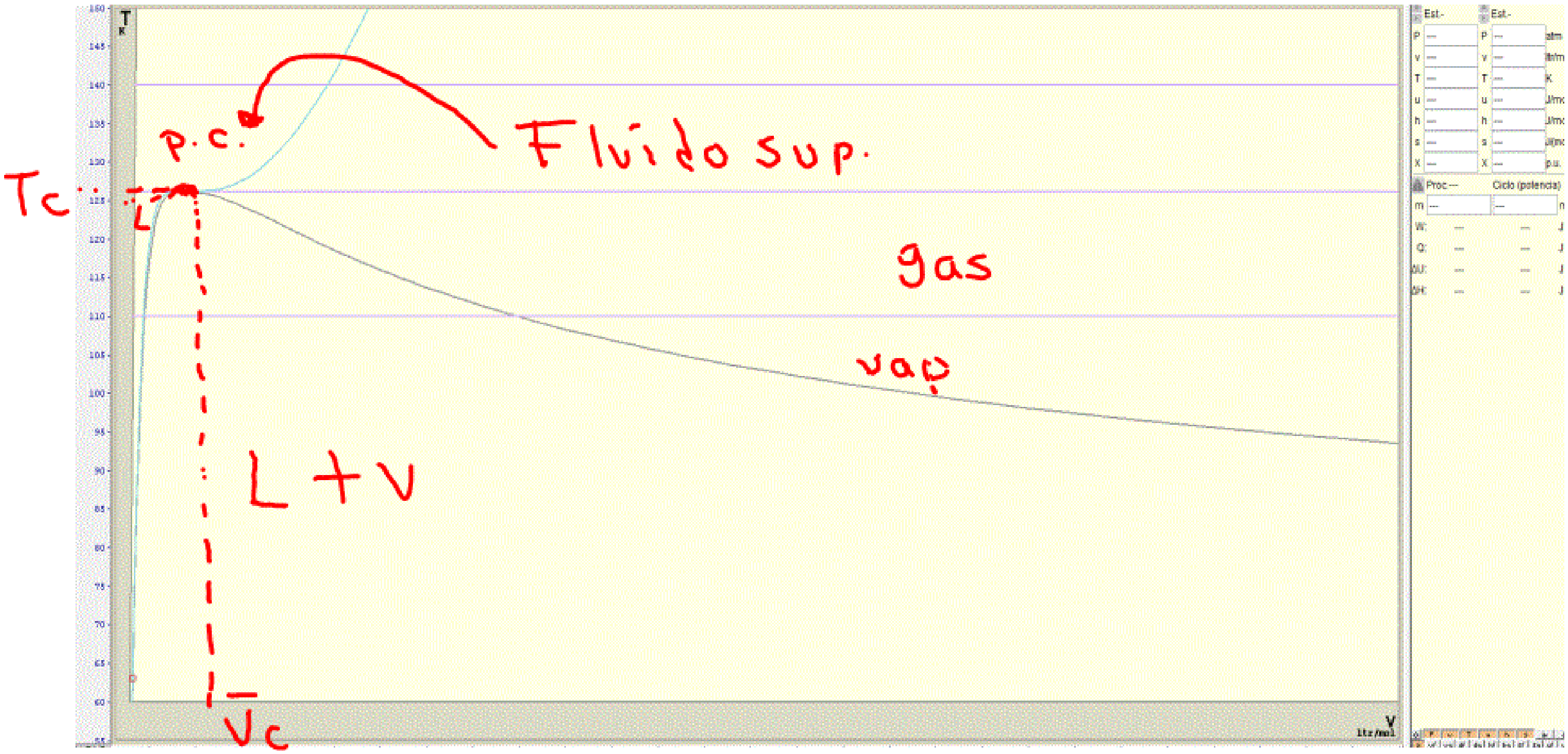
Implicaciones



esto implica que el volumen tiene:

- 3 raíces iguales reales
- 1 raíz real, 2 imaginarias
- 3 raíces reales ≠

1 → 2 metaestable
2 → 3 imposible
3 → 4 posible vapor condensado
1 → 4 transformación L→V


Tc
p.c.
Fluido sup.
gas
vap
L+V
$\bar{V}c$

p.c. $$\frac{\partial T_c}{\partial \bar{V}_c} = 0$$

$$\left(\frac{\partial T}{\partial \bar{V}}\right)_{p.c.} = 0$$

$$\frac{\partial^2 T_c}{\partial \bar{V}_c^2} = 0$$

$$\left(\frac{\partial^2 T}{\partial \bar{V}^2}\right)_{p.c.} = 0$$

$$P = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}$$

$$\boxed{P_c = \frac{RT_c}{\bar{V}_c-b} - \frac{a}{\bar{V}_c^2}} \rightarrow \text{Despejo } T_c$$

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$P + \frac{a}{\bar{V}^2} = \frac{RT}{\bar{V} - b}$$

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$$

$$RT = P\bar{V} - Pb + \frac{a\bar{V}}{\bar{V}^2} - \frac{ab}{\bar{V}^2}$$

$$RT = P\bar{V} - Pb + \frac{a}{\bar{V}} - \frac{ab}{\bar{V}^2}$$

$$RT = p\bar{v} - pb + \frac{a}{\bar{v}} - \frac{ab}{\bar{v}^2}$$

$$T = \frac{p\bar{v}}{R} - \frac{pb}{R} + \frac{a}{\bar{v}R} - \frac{ab}{\bar{v}^2R}$$

$$T_c = \frac{p_c\bar{v}_c}{R} - \boxed{\frac{p_cb}{R} + \frac{a}{\bar{v}_cR} - \frac{ab}{\bar{v}_c^2R}}$$

$$\left(\frac{\partial T_c}{\partial \bar{v}_c}\right)_{p.c.} = \frac{p_c}{R} - \frac{a}{\bar{v}_c^2R} + \frac{2\bar{v}_cab}{\bar{v}_c^4R} = 0$$

$$\left(\frac{\partial T_c}{\partial \bar{V}_c}\right)_{p.c.} = \frac{p_c}{R} - \frac{a}{\bar{V}_c^2 R} + \frac{2\bar{V}_c ab}{\bar{V}_c^4 R}$$

$$= \frac{p_c}{R} - \boxed{\frac{a}{\bar{V}_c^2 R} + \frac{2ab}{\bar{V}_c^3 R}}$$

$$\left(\frac{\partial^2 T_c}{\partial \bar{V}_c^2}\right) = \frac{2\bar{V}_c a}{\bar{V}_c^4 R} - \frac{6ab\bar{V}_c^2}{\bar{V}_c^6 R}$$

$$= \frac{2a}{\bar{V}_c^3 R} - \frac{6ab}{\bar{V}_c^4 R} = 0$$

$$\left[\frac{P_c}{R} - \frac{a}{\bar{V}_c^{2} R} + \frac{2ab}{\bar{V}_c^{3} R} = 0\right]\frac{3}{\bar{V}_c}$$

$$\frac{2a}{\bar{V}_c^{3} R} - \frac{6ab}{\bar{V}_c^{4} R} = 0$$

$$\frac{3P_c}{\bar{V}_c R} - \frac{3a}{\bar{V}_c^{3} R} + \frac{6ab}{\bar{V}_c^{4} R} = 0$$

$$\frac{2a}{\bar{V}_c^{3} R} - \frac{6ab}{\bar{V}_c^{4} R} = 0$$

$$\frac{3p_c}{R\bar{V}_c} - \frac{a}{\bar{V}_c^3 R} = 0$$

$$\frac{3p_c}{\cancel{R}\cancel{\bar{V}_c}} = \frac{a}{\bar{V}_c^{\cancel{3}\,2}\cancel{R}}$$

$$\boxed{a = 3p_c\bar{V}_c^2}$$

$$= 3\ \text{atm}\left(\frac{L}{\text{mol}}\right)^2$$

$$= \frac{3\ \text{atm}\ L^2}{\text{mol}^2}$$

$$\frac{2a}{\bar{V}_c^3 R} - \frac{6ab}{\bar{V}_c^4 R} = 0$$

$$\frac{2(3p_c\bar{V}_c^2)}{\bar{V}_c^3 R} = \frac{6(3p_c\bar{V}_c^2)b}{\bar{V}_c^4 R}$$

$$\frac{6\cancel{p_c}}{\bar{V}_c \cancel{R}} = \frac{18\cancel{p_c}b}{\bar{V}_c^2 \cancel{R}}$$

$$\boxed{b} = \frac{6}{18}\bar{V}_c = \boxed{\frac{1}{3}\bar{V}_c} = \frac{1}{3}\frac{L}{mol}$$