FISICOQUIMICA

I.- GASES

Ecuación de Estado: F(P,V,T) = 0

BOYLE $$PV = C(t°C)$$

GAY- LUSSAC $$V = a + bt(°C) = V_0 + \left(\frac{\partial V}{\partial t}\right)_P t(°C)$$

CHARLES (P = Cte., Masa Fija)

$$\alpha_0 = \frac{1}{V_0}\left(\frac{\partial V}{\partial t}\right)_P$$

La misma para todos los gases a 0°C

$$\therefore\ V = V_0(1+\alpha_0 t) = V_0\alpha_0\left(\frac{1}{\alpha_0}+t\right) = V_0\alpha_0 T$$

$$\frac{1}{\alpha_0} = 273.15\ ^\circ C$$

ESCALA ABSOLUTA DE TEMPERATURAS

——— o ———

$$\left.\begin{aligned} PV_0 &= C_0 \\ V &= \alpha_0 V_0 T \end{aligned}\right\} \rightarrow\quad V = \frac{\alpha_0 C_0 T}{P} = \frac{\alpha_0 A\omega T}{P}$$

Escoger $V_0 \leftrightarrow$ M = ω

$$V = \left(\frac{\omega}{M}\right)\frac{RT}{P} = \frac{nRT}{P}$$

$$R = \begin{cases} 0.08205\left(\dfrac{atm\times lt}{^\circ K\times mol}\right) \\ 1.987\left(\dfrac{cal}{^\circ K\times mol}\right) \end{cases}$$

$$V = 22.414\left(\frac{lt}{mol}\right)$$

Peso Molecular

$$PV = \left(\frac{\omega}{M}\right)RT = nRT$$

$$\Rightarrow \quad M = \left(\frac{\omega}{V}\right)\left(\frac{RT}{P}\right) = \left(\frac{\rho}{P}\right)RT$$

o

Sólo Gas Ideal

Dalton:

$$\sum P_i = P_T$$

$$P_i = n_i\left(\frac{RT}{V}\right) \quad \Rightarrow \quad P_i = x_i P_T$$

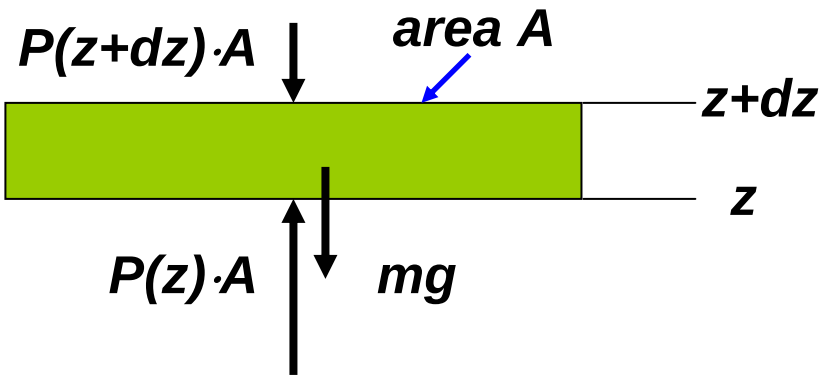
Amagat:

$$\sum V_i = V_T$$

$$V_i = n_i\left(\frac{RT}{P}\right) \quad \Rightarrow \quad V_i = x_i V_T$$

Ley Barométrica

- **Considerar que la temperatura de la atmósfera es independiente de la altura**
- **La masa molecular promedio es M**



$$P(z+dz)\cdot A + mg = P(z)\cdot A$$

$$P(z+dz) - P(z) = -\frac{mg}{A}$$

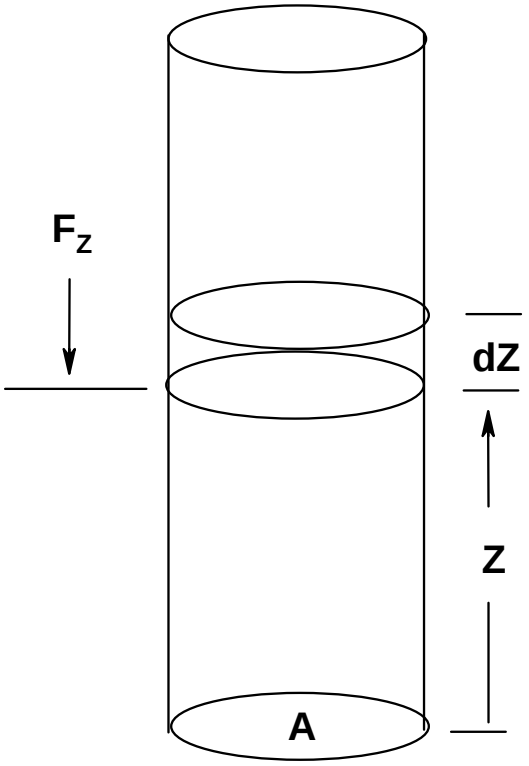
$$m = \rho A dz \quad \Rightarrow \quad \frac{dP}{dz} = -\rho g$$

Densidad del aire:

$$\rho = \frac{M}{V} = \frac{PM}{RT} \quad \Rightarrow \quad \frac{dP}{dz} = -\frac{Mg}{RT}P$$

$$\boxed{P(z) = P_0 \exp\left[-\frac{Mgz}{RT}\right]}$$

Ecuaciones Barométricas



$$F_{z+dz} + dF = F_z$$

$$dP = -\rho\, g\, dz$$

Líquidos

$$P = P_0 - \rho g Z$$

Gases

$$P = P_0\, e^{-\frac{MgZ}{RT}}$$

¿Cuál debe ser el peso molecular de un gas para que la presión del gas a 25ºC disminuya a la mitad a una distancia vertical de 1mt.?

$$Ln\frac{P}{P_0} = \frac{-MgZ}{RT} \qquad luego \qquad M = \frac{RT}{gZ} Ln\frac{P_0}{P} = \frac{RT}{gZ} Ln2$$

$$M = \frac{8.3144 \times 10^7 \times 298.15}{980 \times 100} Ln2 = 175333\ (gr/mol)$$

¿Cuál es la presión atmosférica, a 25ºC, a 4000 mts. de altura?

$$M_{aire} \approx 29 \qquad Ln\frac{P}{P_0} = \frac{-MgZ}{RT} = -\frac{29 \times 980 \times 4 \times 10^5}{8.3144 \times 10^7 \times 298.15} = -0.4588$$

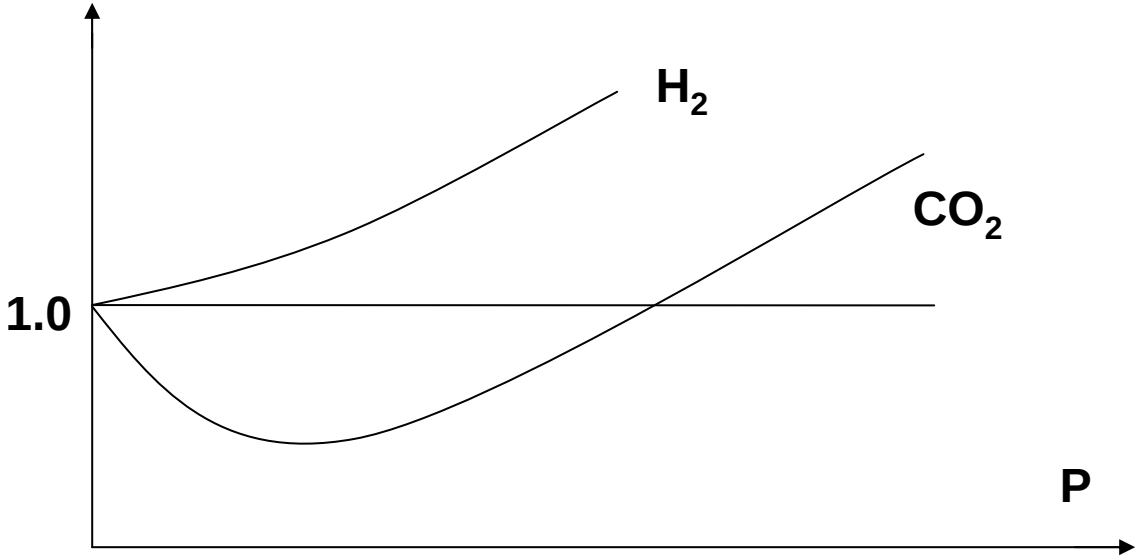
$$P = 0.632\ Atm$$

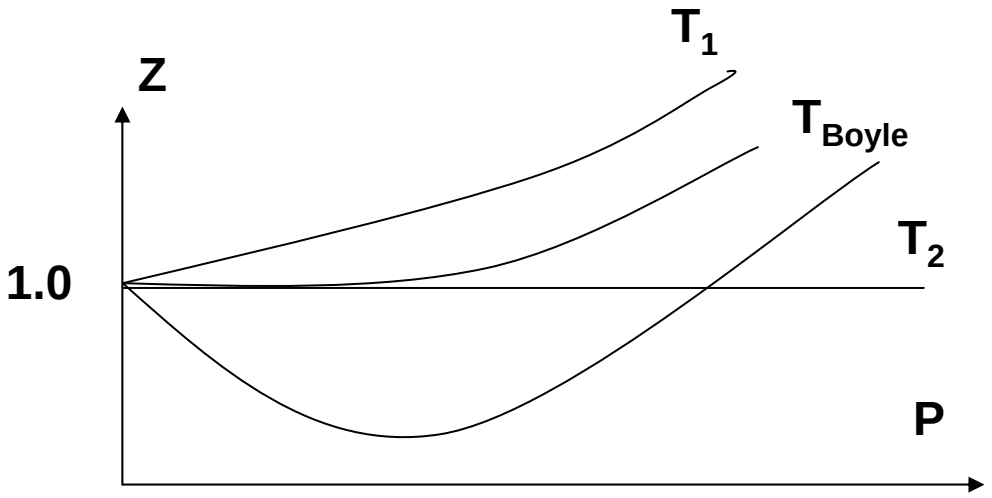
$$R = 8.3144 \times 10^7\ [erg/°K]$$

GAS REAL

Factor de Compresibilidad Z

$$Z = \frac{\overline{V}}{V_{id}} = \frac{P\overline{V}}{RT}$$

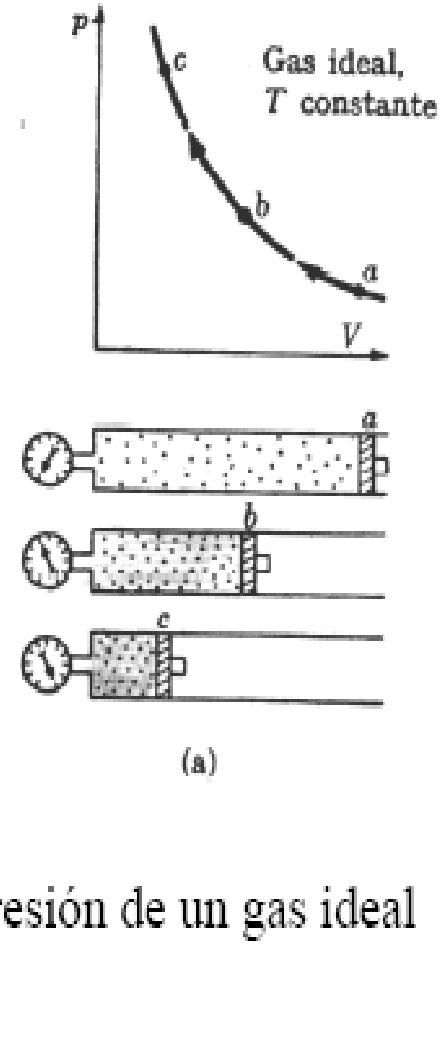




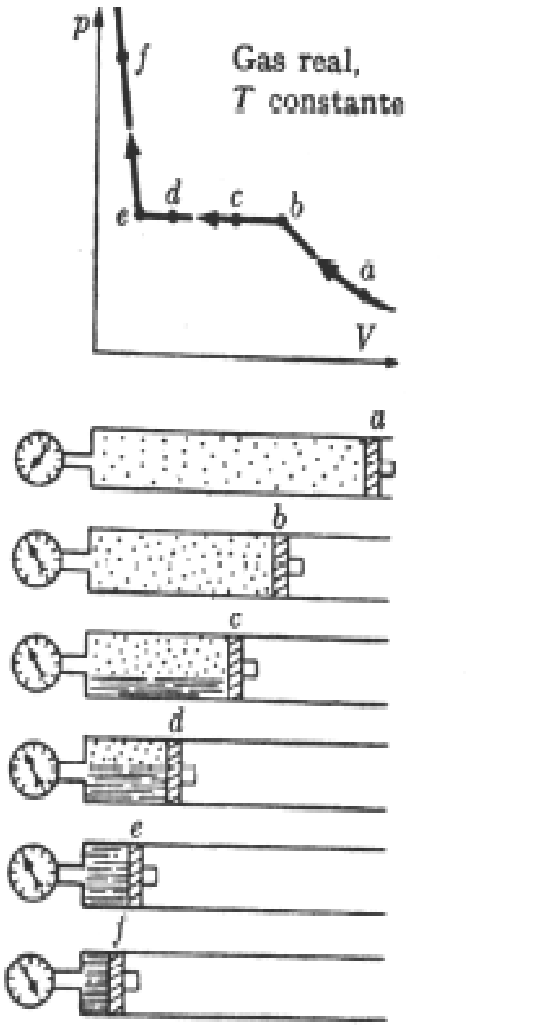
Para un mismo gas

$T_1 > T_B > T_2$

Isoterma de un Gas Real

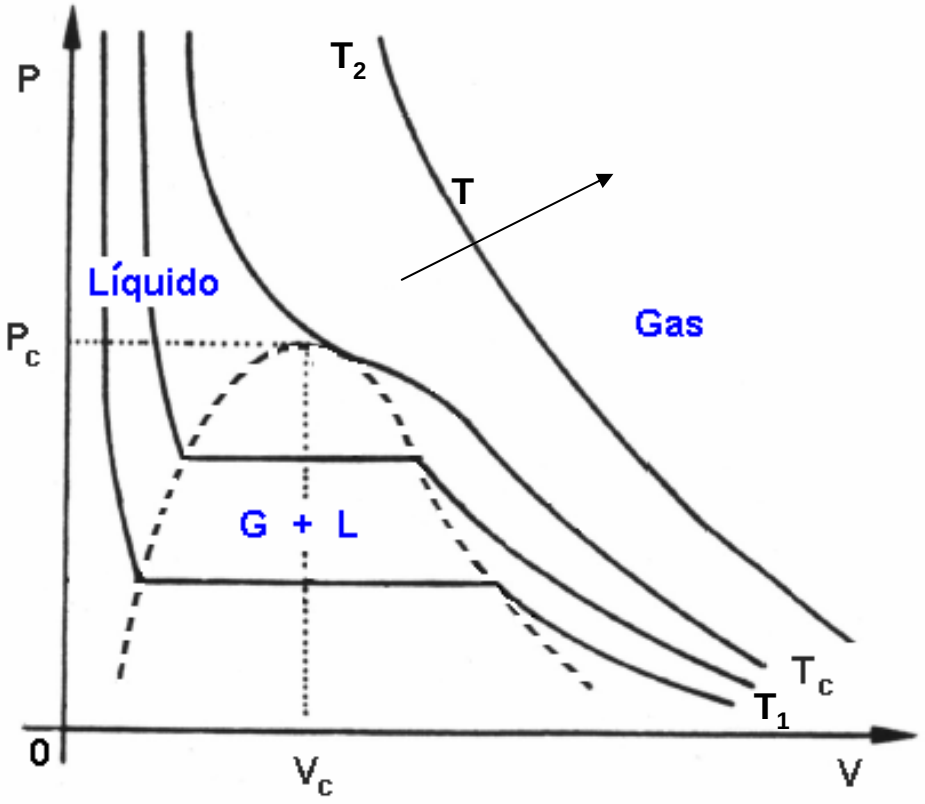


Compresión de un gas ideal



Compresión de un gas real

Isotermas en el gas real



CORRECCIONES AL GAS IDEAL

1) Volumen del gas ≠ 0

$$\overline{V} = b + \frac{RT}{P}$$

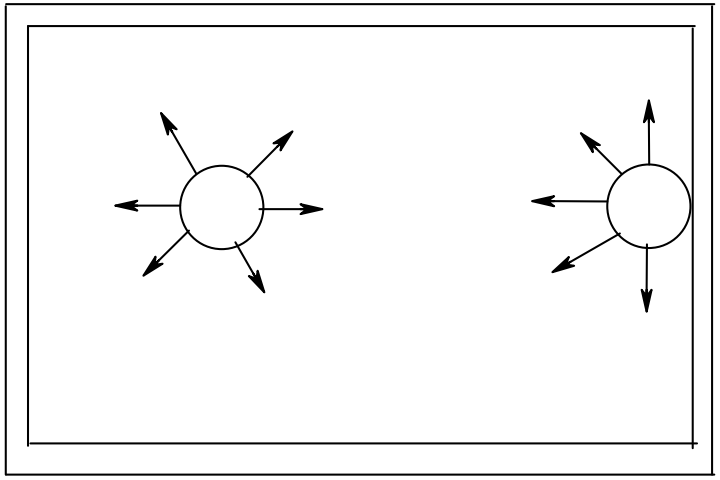
b ≈ Volumen molar del líquido

$$\therefore \quad Z = 1 + \frac{b}{RT} P$$

(Lineal)

$$P = \frac{RT}{(\overline{V} - b)}$$

2) Incluir interacción entre partículas



$$f_{interac.} \propto C^2 \left[\frac{mol^2}{litro^2}\right] \propto \frac{1}{\overline{V}^2}$$

Ec. Van der Waals

$$P = \frac{RT}{(\overline{V} - b)} - \frac{a}{\overline{V}^2}$$

$$\begin{cases} b \approx Volumen\ molar \\ a \approx Cte.interacción \end{cases}$$

Característico de cada gas

Algunas Constantes de Van der Waals

Substancia	a ($J \cdot m^3/mol^2$)	b (m^3/mol)	P_c (MPa)	T_c (K)
Aire	.1358	3.64×10^{-5}	3.77	133 K
Dióxido Carbono (CO_2)	.3643	4.27×10^{-5}	7.39	304.2 K
Nitrógeno (N_2)	.1361	3.85×10^{-5}	3.39	126.2 K
Hidrógeno (H_2)	.0247	2.65×10^{-5}	1.30	33.2 K
Agua (H_2O)	.5507	3.04×10^{-5}	22.09	647.3 K
Amoníaco (NH_3)	.4233	3.73×10^{-5}	11.28	406 K
Helio (He)	.00341	2.34×10^{-5}	0.23	5.2 K
Freón (CCl_2F_2)	1.078	9.98×10^{-5}	4.12	385 K

Z = Z(V)

$$\therefore \quad Z = \frac{P\bar{V}}{RT} = \frac{\bar{V}}{(\bar{V} - b)} - \frac{a}{RT\bar{V}}$$

$$\frac{b}{\bar{V}} << 1 \quad \rightarrow \quad Z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 + \ldots$$

——— o ———

Z = Z(P)

$$\frac{1}{\bar{V}} = \frac{P}{RTZ}$$

$$\alpha_1 + \alpha_2 P + \alpha_3 P^2 + \ldots = \left(b - \frac{a}{RT}\right)\frac{1}{RTZ} + \left(\frac{b}{RT}\right)^2 \frac{P}{Z^2} + \ldots = \frac{Z-1}{P}$$

$$P \to 0 \qquad Z \to 1 \qquad \alpha_1 = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

$$Z = 1 + \left(b - \frac{a}{RT}\right)\frac{P}{RT} + \left(2b - \frac{a}{RT}\right)^2 \frac{aP^2}{(RT)^3} + \ldots$$

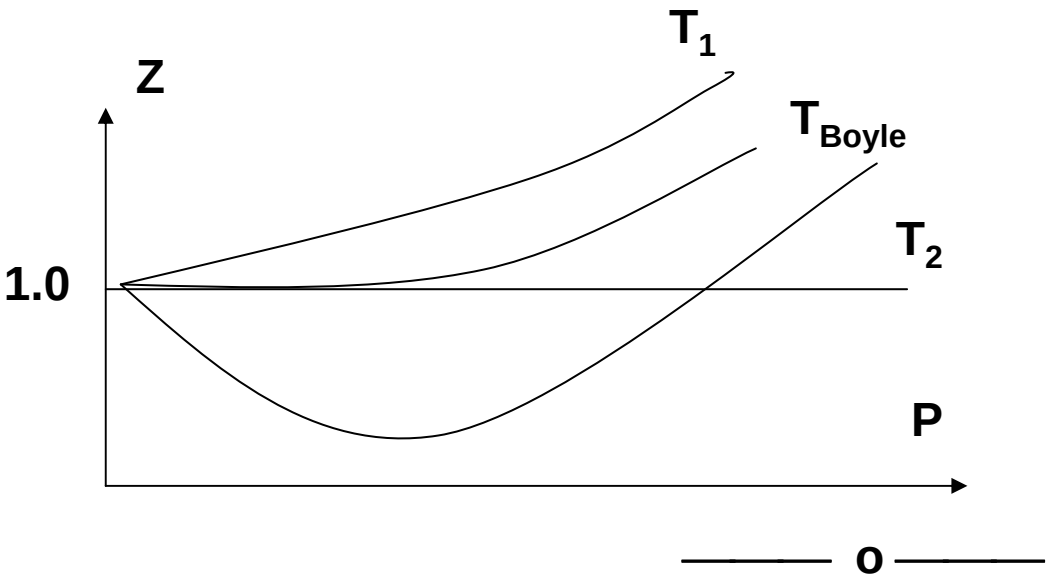
$$\lim_{P \to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{RT}\left(b - \frac{a}{RT}\right)$$

$$T_B = \frac{a}{Rb}$$

Temperatura de Boyle

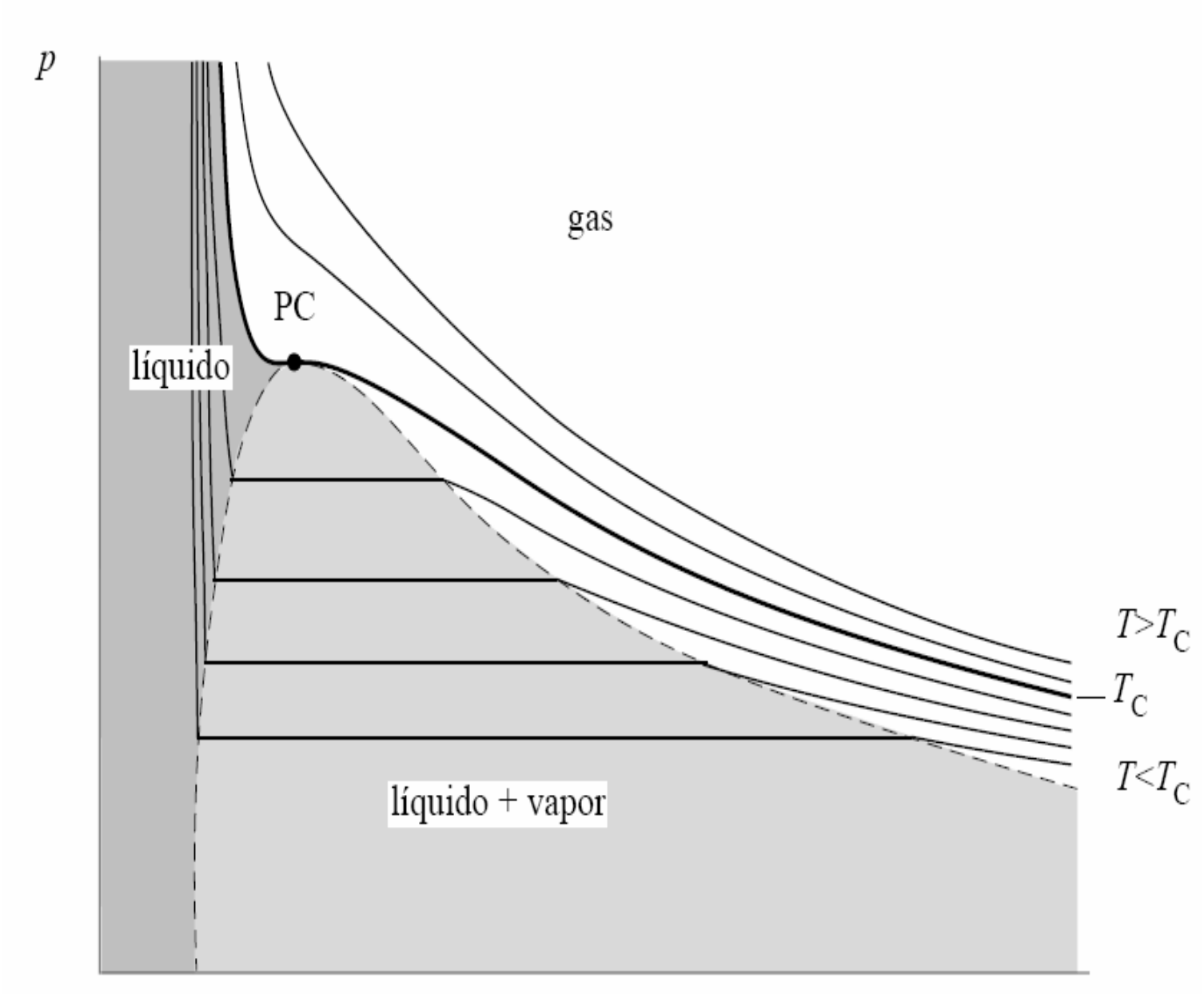
$$T_B = \frac{a}{Rb}$$

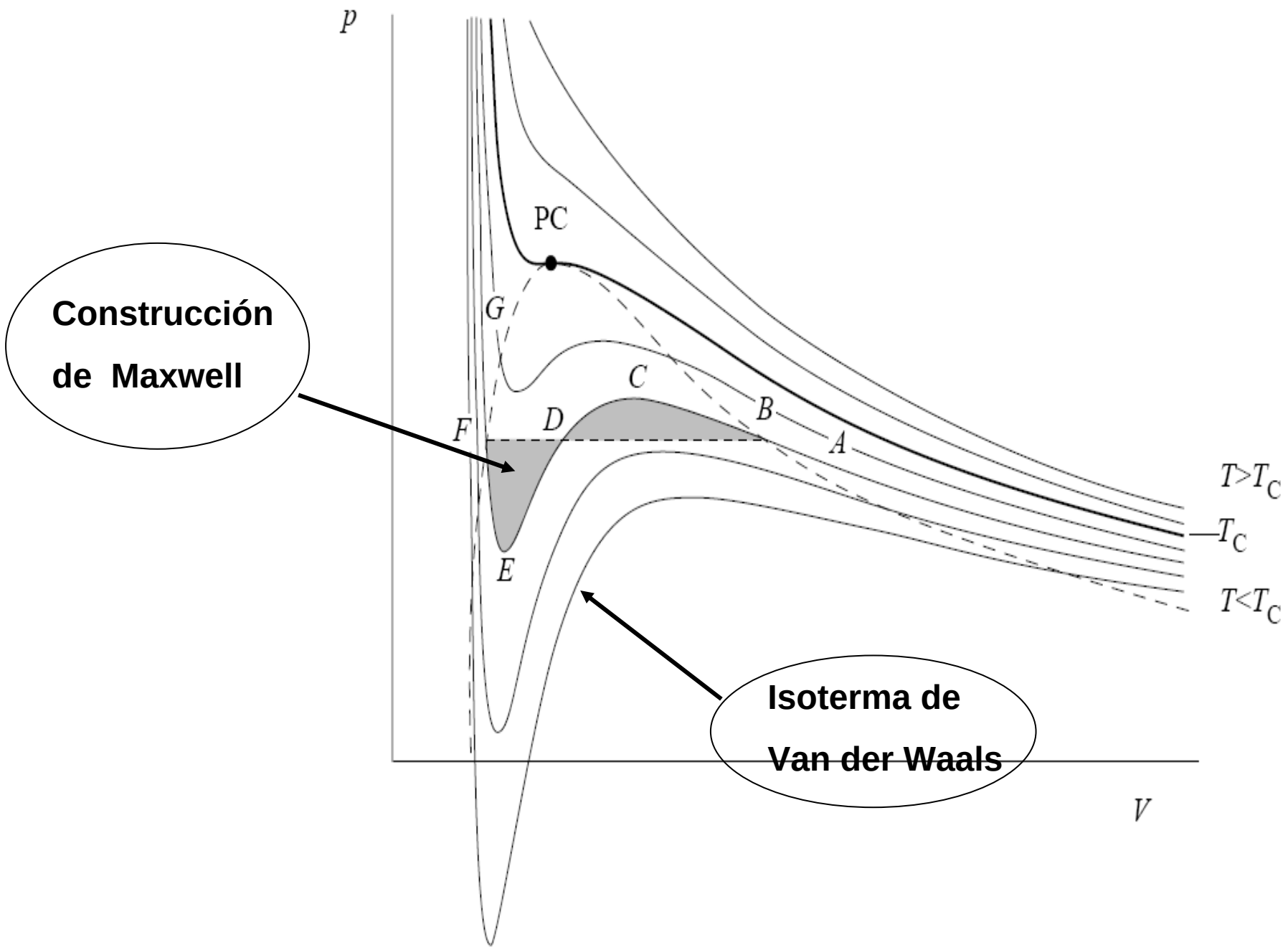
$$\begin{cases} b > \dfrac{a}{RT} & (+) \\ b < \dfrac{a}{RT} & (-) \end{cases}$$



$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + \frac{a}{(RT)^3}\left(2b - \frac{a}{RT}\right)P^2 + \ldots$$

Isotermas de un Gas Real




Construcción
de Maxwell
p
PC
G
C
B
A
F
D
E
$T>T_C$
T_C
$T<T_C$
Isoterma de
Van der Waals
V

Constantes críticas para algunas sustancias.

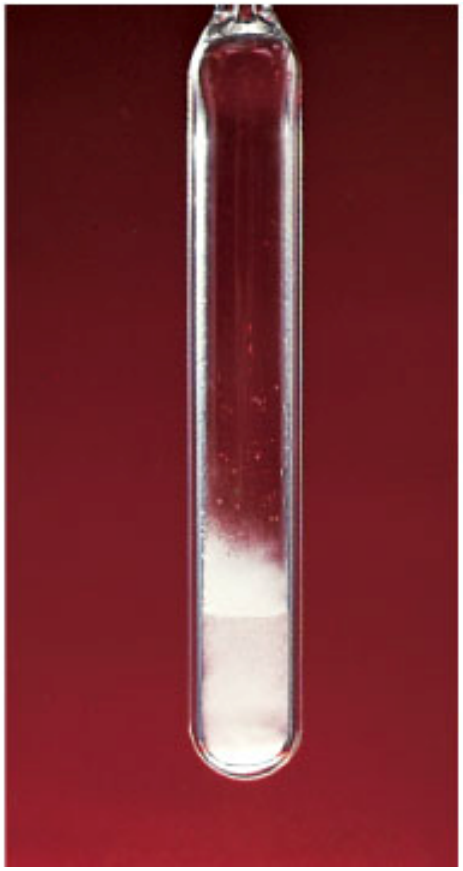
Sustancia	Presión crítica p_c (en atmósferas)	Temperatura crítica Tc °K	Volumen crítico molar Vc ml	Zc
He	2.26	5.2	60	3.18
H_2	12.8	33.2	68	3.28
N_2	33.5	126	90	3.42
CO_2	73.0	304.2	95	3.68
O_2	49.7	154.3	74	3.42
HCL	81.5	324.1	89	3.66
Cl_2	76.1	417.1	124	3.63
SO_2	77.6	430.3	125	3.64
CCl_4	45.4	556.2	275	3.68
C_6H_6	47.9	561.6	256	3.75

El fenómeno crítico de SF_6

$T < T_c$

$T > T_c$

$T \sim T_c$



$T < T_c$

Gas de Van der Waals

$$\left(\overline{V}-\overline{V}_1\right)\left(\overline{V}-\overline{V}_2\right)\left(\overline{V}-\overline{V}_3\right)=0$$

$$\left(\overline{V}-\overline{V}_c\right)^3=\overline{V}^3-3\overline{V}_c\overline{V}^2+3\overline{V}_c^2\overline{V}-\overline{V}_c^3=0$$

Comparar con:

$$\overline{V}^3-\left(b+\frac{RT_c}{P_c}\right)\overline{V}^2+\frac{a}{P_c}\overline{V}-\frac{ab}{P_c}=0$$

Luego:

$$\overline{V}_c=3b \quad\Leftrightarrow\quad a=3P_c\overline{V}_c^2$$

$$P_c=\frac{a}{27b^2} \quad\Leftrightarrow\quad b=\frac{1}{3}\overline{V}_c$$

$$T_c=\frac{8a}{27Rb} \quad\Leftrightarrow\quad R=\frac{8P_c\overline{V}_c}{3T_c}$$

Estados Correspondientes

$$P = \frac{8P_c\overline{V_c}T}{3T_c\left(\overline{V} - \frac{1}{3}\overline{V_c}\right)} - \frac{3P_c\overline{V_c}^2}{V^2}$$

$$\pi = \frac{8\tau}{3\phi - 1} - \frac{3}{\phi^2}$$

Ejemplo:

$$\pi = 1.3 \quad \tau = 1.85 \quad \phi = 1.1$$

He	$\frac{2.94}{2.26}$	$\frac{9.62}{5.2}$	$\frac{66}{60}$
O_2	$\frac{64.61}{49.7}$	$\frac{285.4}{154.3}$	$\frac{81}{74}$
C_6H_6	$\frac{62.3}{47.9}$	$\frac{1038.9}{561.6}$	$\frac{281.6}{256}$

OTRAS ECUACIONES DE ESTADO

Beathie-Bridgeman:

$$P\bar{V} = RT + \frac{\beta}{\bar{V}} + \frac{\gamma}{\bar{V}^2} + \frac{\delta}{\bar{V}^3} + \ldots.$$

Dieterici:

$$P = RT\frac{e^{-\frac{a}{RTV}}}{(\bar{V} - b)}$$

Virial:

$$P\bar{V} = RT\left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \frac{D}{\bar{V}^3} + \ldots\right)$$

$$B = B(T), \quad C = C(T), \ldots$$