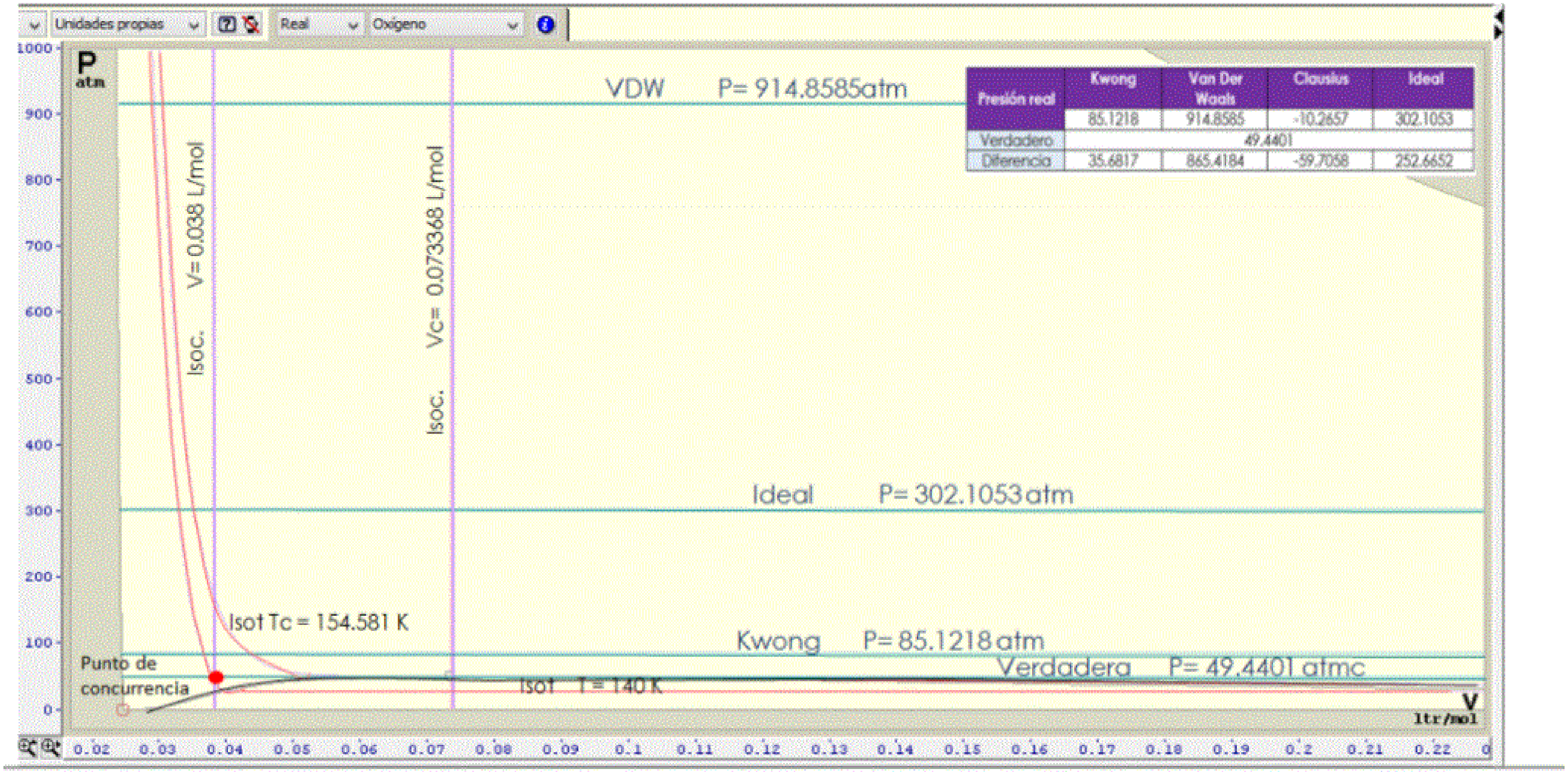
Clase 71 5 enero 2021

Título de la nota 15/12/2020

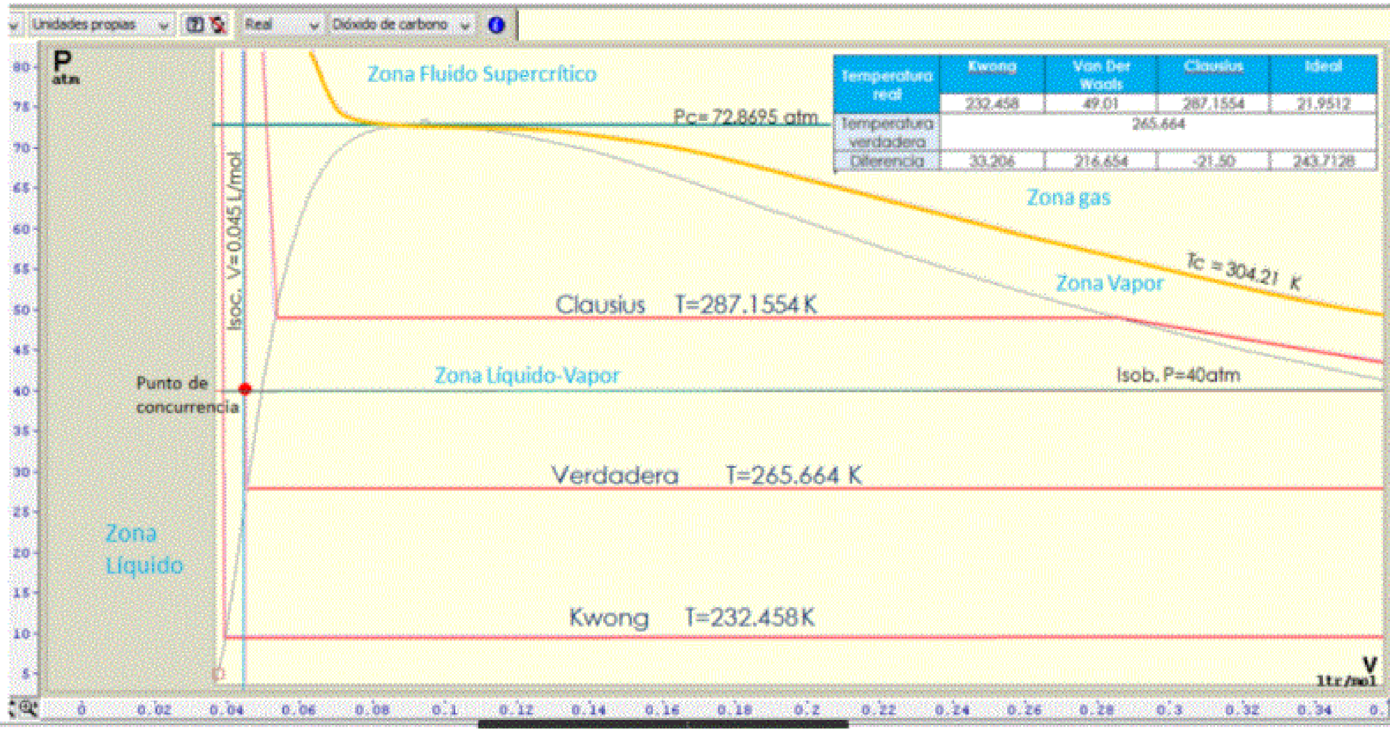
Tabla comparativa de presiones reales, verdadera y real

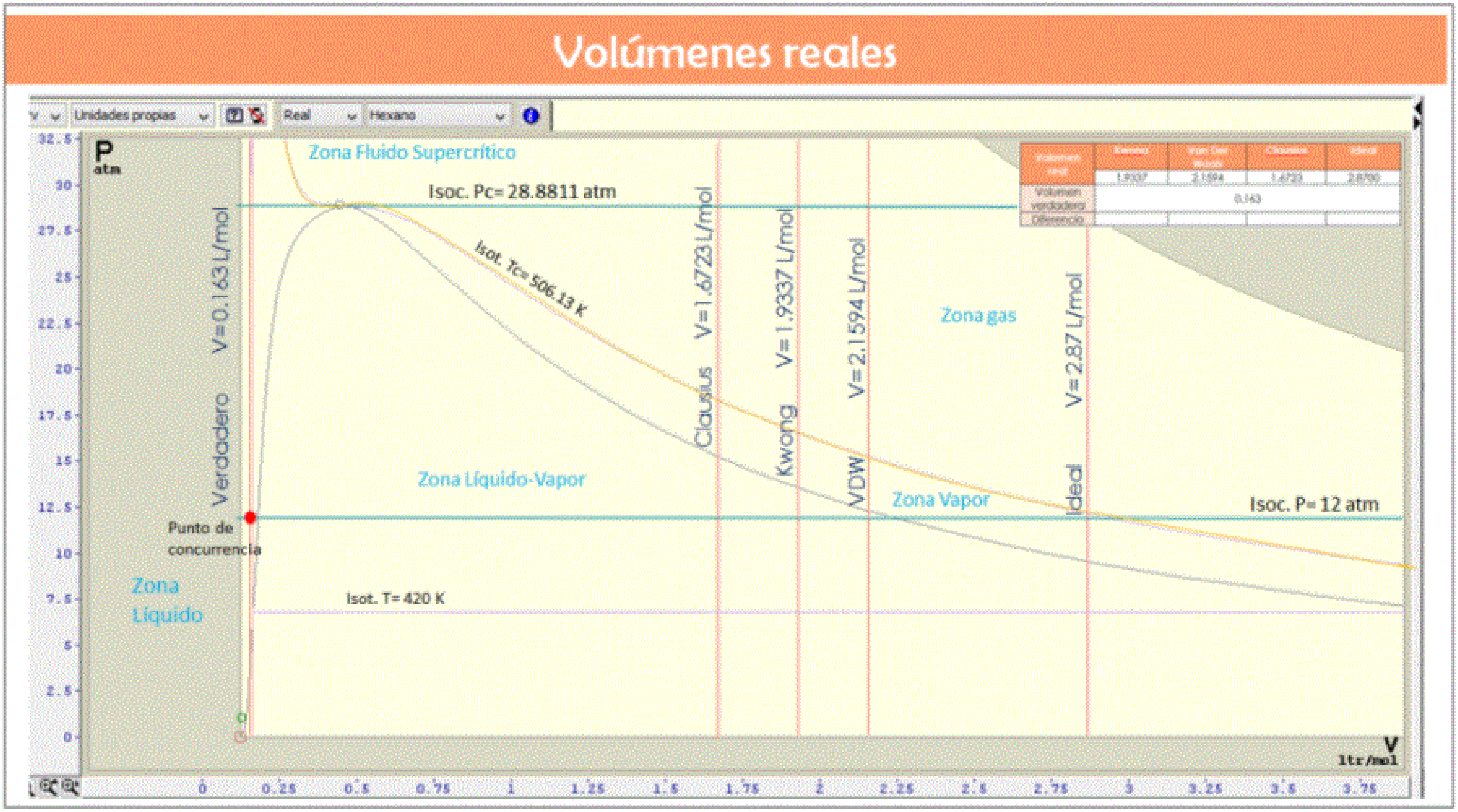
Presión real	Kwong	Van Der Waals	Clausius	Ideal
	85.1218	914.8585	-10.2657	302.1053
Verdadero	49.4401			
Diferencia	35.6817	865.4184	-59.7058	252.6652



Unidades propias
Real
Oxigeno
P
atm
VDW P= 914.8585atm
Presión real
Kwong
Van Der Waals
Clausius
Ideal
85.1218
914.8585
-10.2657
302.1053
Verdadero
49.4401
Diferencia
35.6817
865.4184
-59.7058
252.6652
Isoc. V= 0.038 L/mol
Isoc. Vc= 0.073368 L/mol
Ideal P= 302.1053 atm
Isot Tc = 154.581 K
Kwong P= 85.1218 atm
Verdadera P= 49.4401 atmc
Punto de concurrencia
Isot T = 140 K
V
ltr/mol

Temperaturas




Volúmenes reales
Unidades propias
Real
Hexano
P
atm
Zona Fluido Supercrítico
Isoc. Pc= 28.8811 atm
Isot. Tc= 506.13 K
V=0.163 L/mol
Verdadero
Clausius V=1.6723 L/mol
Kwong V= 1.9337 L/mol
VDW V= 2.1594 L/mol
Ideal V= 2.87 L/mol
Zona gas
Zona Líquido-Vapor
Zona Vapor
Isoc. P= 12 atm
Punto de concurrencia
Zona Líquido
Isot. T= 420 K
V
ltr/mol

Z Factor de compresibilidad

Z
- avance de Van der Waals
- gráfica generalizada

$$P\bar{V} = ZRT$$

$$PV = ZnRT$$

Z
- $= 1$ ideal.
- < 1 atracción
- > 1 repulsión

$$Z = \frac{\bar{V}\,\text{real}}{\bar{V}\,\text{ideal}}$$

- ecuación virial
- Fugacidad

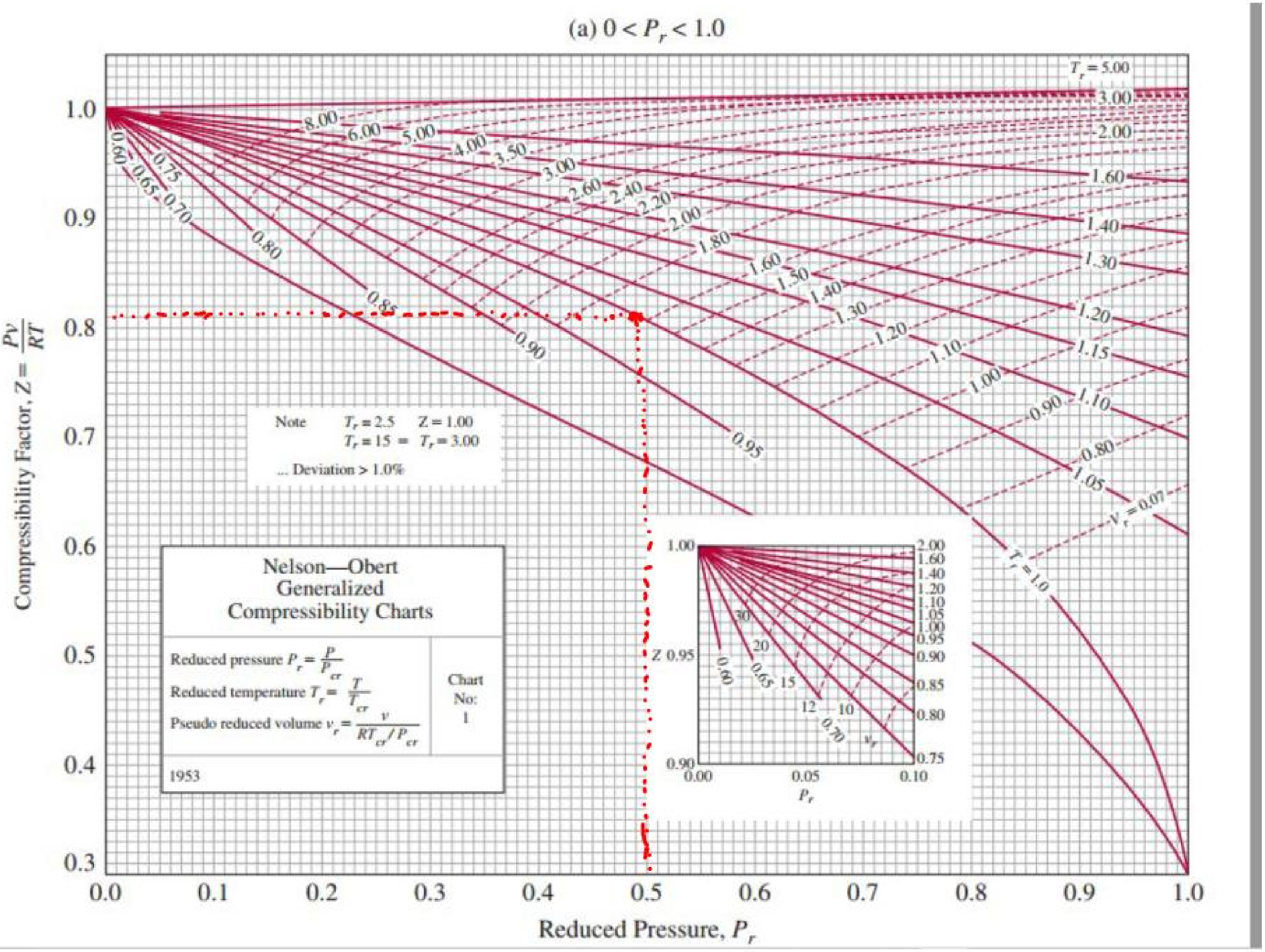
Variables reducidas

$$P_r = \frac{P_{sis}}{P_c}$$

$$T_r = \frac{T_{sis}}{T_c}$$

$$V_r = \frac{\bar{V}_{sis}}{\bar{V}_c}$$

Adimensional


(a) 0 < P_r < 1.0
Compressibility Factor, $Z = \frac{Pv}{RT}$
Reduced Pressure, P_r
Note $T_r = 2.5$ Z = 1.00
$T_r = 15$ = $T_r = 3.00$
... Deviation > 1.0%
Nelson—Obert
Generalized
Compressibility Charts
Reduced pressure $P_r = \frac{P}{P_{cr}}$
Reduced temperature $T_r = \frac{T}{T_{cr}}$
Pseudo reduced volume $v_r = \frac{v}{RT_{cr}/P_{cr}}$
Chart No: 1
1953
$T_r = 5.00$
$T_r = 1.0$
$v_r = 0.07$

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

$$Z = \frac{\bar{V}}{RT}\left[\frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2}\right] = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}RT}$$

$$\frac{\bar{V}}{\bar{V}-b} = \frac{1}{1-\frac{b}{\bar{V}}} = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 \cdots$$

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

$$Z = 1 + \frac{b}{\bar{V}} - \frac{a}{\bar{V}RT} \cdots\cdots$$

$$Z = 1 + \frac{1}{\bar{V}}\left[b - \frac{a}{RT}\right] + \frac{b^2}{\bar{V}^2} + \cdots\cdots$$

$$\frac{1}{\bar{V}} = \frac{P}{RTZ} \qquad Z = \frac{P\bar{V}}{RT}$$

$$Z = 1 + \frac{1}{RTZ}\left[b - \frac{a}{RT}\right]P + \left[\frac{b^2}{R^2T^2Z^2}\right]P^2$$

$$Z \rightarrow 1 \quad (\text{ideal})$$

$$Z = 1 + \frac{1}{RT}\left[b - \frac{a}{RT}\right]P$$

$$Z = f(T, P)$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{1}{RT}\left[b - \frac{a}{RT}\right]$$

$$b - \frac{a}{RT} = 0 \qquad T_B = \text{Temp. Boyle}$$

$$\boxed{T_B = \frac{a}{bR}}$$

$$Z = \frac{p\bar{V}}{RT} = 1 + \frac{1}{\bar{V}}\left[b - \frac{a}{RT}\right]$$

$$p\bar{V} = RT\left\{1 + \frac{1}{\bar{V}}\left[b - \frac{a}{RT}\right]\right\}$$

$$a = \frac{27}{64}\frac{R^2 T_c^2}{p_c}$$

$$b = \frac{1}{8}\frac{R T_c}{p_c}$$

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

$$= \frac{27/64\ R^2 T_c^2/p_c}{\frac{R T_c}{p_c 8}\ R}$$

$$T_B = \frac{27}{8} T_c$$

$$Z = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \frac{D(T)}{\bar{V}^3},$$

Kammerligh - Onnes

$B(T) = B$ como función de T

$B = L/mol \quad C = \frac{L^2}{mol^2} \quad D = \frac{L^3}{mol^3}$

$$Z = 1 + B'(T)p + C'(T)p^2 + D'(T)p^3 \ldots$$

$B' = atm^{-1} \quad C' = atm^{-2} \quad D' = atm^{-3}$

$$B' = \frac{B}{RT} = \frac{L/mol}{\frac{atm\,L}{mol\,K}\,K} = atm^{-1}$$

$$C' = \frac{C - B^2}{R^2 T^2} = atm^{-2}$$

interacciones moleculares

$$= \frac{(L/mol)^2 - (L/mol)^2}{\left(\frac{atm\,L}{mol\,K}\right)^2 K^2}$$

$$D' = \frac{D - 3BC - 2B^3}{R^3 T^3}$$

Calcular a y b a 0°C 1atm

si $T_B = 107\,K$ $\quad Z = 1.00054$

$$Z = 1 + \frac{1}{RT}\left[b - \frac{a}{RT}\right]P$$

$$T_B = \frac{a}{bR} \qquad a = T_B b R$$

$$Z = 1 + \frac{1}{RT}\left[b - \frac{T_B b \cancel{R}}{\cancel{R} T}\right]P$$

$$Z = 1 + \frac{1}{RT}\left[b - \frac{T_B b \cancel{R}}{\cancel{R} T}\right] P$$

$$1.00054 = 1 + \frac{1}{\left(\frac{0.082\ \cancel{atm}\ L}{\cancel{mol}\ \cancel{K}}\right)(273.15\ \cancel{K})}\left[b - \frac{107\ \cancel{K}\ b}{273.15\ \cancel{K}}\right] 1\ \cancel{atm}$$

$$b = L/mol = 0.01988\ L/mol$$

$$a = T_B b R = (107\ \cancel{K})\left(0.01988\ \frac{L}{mol}\right)\left(0.082\ \frac{atm\ L}{mol\ \cancel{K}}\right)$$

$$= 0.1744\ \frac{atm\ L^2}{mol^2}$$

Propiedades Fisicoquímicas de sustancias

Nombre	neón	
Masa Molar	20.183	g/mol
Temperatura Crítica	44.400	K
Presion Crítica	27.200	atm
Volumen Crítico	0.0417	L/mol
Punto ebullición	27.000	K
Punto de fusión	24.500	K
Cp (cal/mol K)	0.000e+0	a
$Cp=a+bT+cT^2+dT^3$	0.000e+0	b
(300-2500)K	0.000e+0	c
	0.000e+0	d
Constantes de Antonio	14.0099	A
LN(p)=A-(B/(T+C))	180.4700	B
T=K	-2.6100	C
p=mmHg		

Dr. Juan Carlos Vázquez Lira 2020
Con apoyo del programa UNAM-DGAPA-PAPIME
PE-200419

iedades | Obtención de a y b

Obtención de a y b de Van der Waals

Modelo

$$p=\frac{RT}{(\overline{V}-b)}-\left[\frac{a}{\overline{V}^2}\right]$$

R (atmL/molK): 0.082

Modelo

$$a = 3pc\overline{Vc}^2 \qquad b = \frac{\overline{Vc}}{3}$$

a	$atmL^2/mol^2$	0.14189
b	L/mol	0.01390

Independiente de volumen crítico

Modelo

$$a = \frac{27R^2Tc^2}{64pc} \qquad b = \frac{RTc}{8pc}$$

a	$atmL^2/mol^2$	0.20559
b	L/mol	0.01673

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PE-200419

T (K)	Z
53	0.9953
107	1.0000
273.15	1.00054
546.3	1.00038

Fugacidad (f)

- f (presión) real.
- $f = \Phi p$
- Φ = coef. de Fugacidad
- $\Phi = \frac{f}{p}$ = adimensional.

energía libre de Gibbs

$$d\bar{G} = \bar{V}dp - \bar{S}dT$$

$d\bar{G} = \frac{dG}{n} = d\mu$ = potencial químico

T = isotérmico   T = cte

$$d\bar{G} = \bar{V}\,dp \qquad \bar{V} = \frac{RT}{P}$$

$$\int_1^2 d\bar{G} = \frac{RT}{P}\int_{p_1}^{p_2} dp = \Delta\bar{G} = RT\ln\frac{p_2}{p_1}$$

$$p_1 = 1\,\text{atm}$$

$$\Delta\bar{G} = RT\ln p \quad \text{ideal.}$$

$$\Delta\bar{G} = RT\ln f \quad \text{real.}$$

$\Delta \bar{G} = RT \ln \bar{\Phi} p$ real.

Modelo Real

$\mu = RT \ln f$

Modelo ideal.

$\mu = \bar{V} dp$

$\mu = d\bar{G}$