

Clase 60 2 diciembre 2020

Título de la nota

02/12/2020

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$P + \frac{an^2}{V^2} = \frac{nRT}{V-nb}$$

$$\left(P + \frac{an^2}{V^2} \right) (V-nb) = nRT$$

$$PV - Pnb + \frac{an^2}{V} - \frac{an^3b}{V^2} = nRT$$

$$pV - pnb + \frac{an^2}{V} - \frac{an^3b}{V^2} = nRT$$

$$pV - pnb + \frac{an^2}{V} - \frac{an^3b}{V^2} - nRT = 0$$

$$pV - n(RT + pb) + \frac{an^2}{V} - \frac{an^3b}{V^2} = 0$$

$$-\frac{an^3b}{V^2} + \frac{an^2}{V} - n(RT + pb) + pV = 0$$

$$n = \frac{m}{M}$$

$$-\frac{an^3b}{V^2} + \frac{an^2}{V} - n(RT + pb) + pV = 0$$

$$-\frac{a\left(\frac{m}{M}\right)^3b}{V^2} + \frac{a\left(\frac{m}{M}\right)^2}{V} - \frac{m}{M}(RT + pb) + pV = 0$$

$$\left[-\frac{am^3b}{M^3V^2} + \frac{am^2}{VM^2} - \frac{m}{M}(RT + pb) + pV = 0 \right] M^3$$

$$-\frac{am^3b}{V^2} + \frac{am^2M}{V} - mM^2(RT + pb) + M^3pV = 0$$

$$pVM^3 - M^2m(RT + pb) + M\frac{am^2}{V} - \frac{am^3b}{V^2} = 0$$

$$pV = nRT \quad h = \frac{m}{M}$$

$$pV = \frac{m}{M} RT$$

$$M = \frac{mRT}{pV}$$

Propiedades Obtención de a y b

Propiedades Físicoquímicas de sustancias		
Nombre	acetona	
Masa Molar	58.080	g/mol
Temperatura Crítica	508.100	K
Presión Crítica	46.400	atm
Volumen Crítico	0.2090	L/mol
Punto ebullición	329.400	K
Punto de fusión	178.200	K
Cp (cal/mol K)	1.505e+0	a
Cp=a+bT+cT²+dT³	6.224e-2	b
(300-2500)K	-2.992e-5	c
	4.867e-9	d
Constantes de Antonio	16.6513	A
LN(p)=A-(B/(T+C))	2940.4600	B
T=K	-35.9300	C
p=mmHg		



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PE-200419

Obtención de a y b de Van der Waals

Modelo

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

R (atmL/molK)

0.082

Modelo

$$a = 3pc\bar{V}_c^2 \quad b = \frac{\bar{V}_c}{3}$$

a	atmL ² /mol ²	6.08040
b	L/mol	0.06967



Independiente de volumen crítico

Modelo

$$a = \frac{27R^2T_c^2}{64pc} \quad b = \frac{RT_c}{8pc}$$

a	atmL ² /mol ²	15.78309
b	L/mol	0.11224

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Masa molar real

Mezclado

Masa molar real Ind Vc

Masa molar real Dep Vc

Obtención de ecuación cúbica de la masa molar (M) tipo Van der Waals

Introducir los valores en las celdas de color amarillo

T (K)	360.15
m (g)	0.3475
p (atm)	0.7700
a (atmL ² /mol ²)	15.7831
b (L/mol)	0.11224
R (atmL/molK)	0.0820
V (L)	0.2530



M ³	M ²	M	Cte
0.19481	-10.29251	7.53323	-1.16135

$$pVM^3 - mM^2(RT+pb) + M\left(\frac{am^2}{V}\right) - \frac{abm^3}{V^2} = 0$$

M ideal (g/mol) 52.6794

Resolución de M cúbico tipo $AM^3+BM^2+CM+D=0$

A=	0.194810	
B=	-10.292507	
C=	7.533233	
D=	-1.161351	
Expresión	2	decimales

	Real	Imaginaria	
M ₁ =	52.093449		+52.09
M ₂ =	0.220040	0	+0.22
M ₃ =	0.520076	0	+0.52

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Relaciones Maxwell.

$$\Delta U = q - w$$

$$du = \delta q - \delta w \quad w = p dv$$

$$\frac{\delta q}{T} = ds$$

$$d\bar{u} = T d\bar{s} - p d\bar{v}$$

$$du = T ds - p dv \quad v = \text{cte}$$

$$du = T ds = \text{calor a } v = \text{cte}$$

$$d(u + pV) = Tds - p dv + p dv + v dp$$

$$dH = Tds + v dp$$

$$d\bar{H} = T d\bar{s} + \bar{v} dp \quad p = \text{cte}$$

$$d\bar{H} = T d\bar{s} = \text{calor a } p = \text{cte}$$

$$d(\bar{H} - T\bar{s}) = \cancel{T d\bar{s}} + \bar{v} dp - \cancel{T d\bar{s}} - \bar{s} dT$$

$$d\bar{G} = -\bar{s} dT + \bar{v} dp$$

$$d\bar{G} = -\bar{s}dT + \bar{v}dp$$

$$T = \text{cte} \quad p = \text{cte}$$

$$d\bar{G} = 0 \quad \text{equilibrio}$$

Cambio de fase

$$d(\bar{u} - T\bar{s}) = \cancel{T}d\bar{s} - p d\bar{v} - \cancel{T}d\bar{s} - \bar{s}dT$$

Helmholtz

$$d\bar{A} = -\bar{s}dT - p d\bar{v}$$

$$T = \text{cte}$$

$$V = \text{cte}$$

$$d\bar{A} = 0$$

equilibrio

Isotérmico Real Van der Waals

$$d\bar{u} = T d\bar{s} - p d\bar{v}$$

$$\bar{u} = f(\bar{s}, \bar{v})$$

$$d\bar{u} = \left(\frac{\partial \bar{u}}{\partial \bar{s}} \right)_{\bar{v}} d\bar{s} + \left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_{\bar{s}} d\bar{v}$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{s}} \right)_{\bar{v}} = T \quad \left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_{\bar{s}} = -p$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{s}}\right)_{\bar{v}} = T \quad \left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_{\bar{s}} = -P$$

$$d\bar{u} = T d\bar{s} - P d\bar{v}$$

$$dA = -P d\bar{v} - \bar{s} dT$$

$$\left(\frac{\partial \bar{s}}{\partial \bar{v}}\right)_{\bar{T}} = \left(\frac{\partial P}{\partial T}\right)_{\bar{v}}$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_{\bar{T}} = T \left(\frac{\partial \bar{s}}{\partial \bar{v}}\right)_{\bar{T}} - P \left(\frac{\partial \bar{v}}{\partial \bar{v}}\right)_{\bar{T}}$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_T = \left(\frac{\partial p}{\partial T} \right)_{\bar{v}} - p$$

$$p = \frac{RT}{\bar{v}}$$

$$\left(\frac{\partial p}{\partial T} \right)_{\bar{v}} = \frac{R}{\bar{v}}$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_T = T \left(\frac{R}{\bar{v}} \right) - \frac{RT}{\bar{v}} = 0$$

ideal

real.

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

$$\left(\frac{\partial P}{\partial T} \right)_{\bar{v}} = \frac{R}{\bar{v} - b}$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_{\bar{v}} - \left[\frac{RT}{\bar{v} - b} - \frac{a}{\bar{v}^2} \right]$$

$$d\bar{u} = \frac{a}{\bar{v}^2} d\bar{v}$$

$$\int_1^2 \cancel{d\bar{U}} = a \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{U}}{\bar{V}^2}$$

$$\Delta \bar{U} = a \left[- \left(\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}_1} \right) \right]$$

$$\Delta \bar{U} = a \left[\frac{1}{\bar{V}_1} - \frac{1}{\bar{V}_2} \right]$$

$$\frac{\text{atmL}^2}{\text{mol}^2} \cdot \frac{1}{\cancel{\text{L}}} = \frac{\text{atmL}}{\text{mol}}$$

$$\left(\frac{\cancel{\text{atm}}}{\text{mol}} \right) \left(\frac{1.01325 \times 10^5 \text{ N/m}^2}{\cancel{\text{atm}}} \right) \left(\frac{\cancel{\text{m}^3}}{10^3 \cancel{\text{L}}} \right)$$

$$= \frac{\text{J}}{\text{mol.}} = \Delta U$$

ideal. isot.

$$W = nRT \ln \frac{V_2}{V_1}$$

$$\bar{W} = RT \ln \frac{\bar{V}_2}{\bar{V}_1}$$

$$\bar{w} = p d\bar{v} \quad p = \frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2}$$

$$\bar{w}_R = \left(\frac{RT}{\bar{v}-b} - \frac{a}{\bar{v}^2} \right) d\bar{v}$$

$$= RT \int_{\bar{v}_1}^{\bar{v}_2} \frac{d\bar{v}}{(\bar{v}-b)} - a \int_{\bar{v}_1}^{\bar{v}_2} \frac{d\bar{v}}{\bar{v}^2}$$

$$= RT \int_{\bar{v}_1}^{\bar{v}_2} \frac{d\bar{v}}{\bar{v}} - a \int_{\bar{v}_1}^{\bar{v}_2} \frac{d\bar{v}}{\bar{v}^2}$$

$$u = \bar{v} - b$$

$$du = d\bar{v}$$

$$\bar{W} = RT \ln \left(\frac{\bar{v}_2 - b}{\bar{v}_1 - b} \right) + a \left(\frac{1}{\bar{v}_2} - \frac{1}{\bar{v}_1} \right)$$

$$\left(\frac{\text{J}}{\text{mol} \cancel{\text{K}}} \right) (\cancel{\text{K}})$$

$$\frac{\text{J}}{\text{mol}} + \left(\frac{\text{atmL}^2}{\text{mol}^2} \frac{1}{\cancel{\text{L/mol}}} \right) \left(\frac{1.01325 \times 10^5 \text{N/m}^2}{\text{atm}} \right) \left(\frac{\text{m}^3}{\text{L}^3} \right)$$

$$\frac{\text{J}}{\text{mol}} + \frac{\text{J}}{\text{mol}} = \frac{\text{J}}{\text{mol}} = \bar{W}_R$$

$$\bar{W}_R = RT \ln \left(\frac{\bar{v}_2}{\bar{v}_1} \right) \text{ ideal.}$$

$$W_{IR} = p_2 (\bar{v}_2 - \bar{v}_1) \text{ ideal}$$

Real.

$$\bar{W}_{IR} = \left(\frac{RT}{\bar{v}_2 - b} - \frac{a}{\bar{v}_2^2} \right) (\bar{v}_2 - \bar{v}_1)$$

$$R = \frac{\text{atmL}}{\text{molK}}$$

$$\bar{W}_{12} = \left(\frac{\text{atm L}}{\text{mol}} \right) \left(\frac{1.01325 \times 10^5 \text{ N/m}^2}{\text{atm}} \right) \left(\frac{\text{m}^3}{10^3 \text{ L}} \right)$$

$$\bar{W}_{12} = \frac{\text{J}}{\text{mol}}$$

$\overline{\Delta s}_R$ ideal

$$\overline{\Delta s}_R = R \ln \frac{v_2}{v_1}$$

real.

$$\left(\frac{\partial \overline{s}}{\partial \overline{v}} \right)_T = \left(\frac{\partial \overline{p}}{\partial T} \right)_{\overline{v}}$$

$$\left(\frac{\partial \overline{p}}{\partial T} \right)_{\overline{v}} = \frac{R}{\overline{v} - b}$$

$$\overline{p} = \frac{RT}{\overline{v} - b} - \frac{a}{\overline{v}^2}$$

$$\left(\frac{\partial \bar{s}}{\partial \bar{v}} \right)_T = \frac{R}{\bar{v} - b}$$

$$\int_1^2 d\bar{s}_R = \frac{R}{\bar{v} - b} \int_{\bar{v}_1}^{\bar{v}_2} d\bar{v}$$

$$\Delta U = q - w$$

$$\Delta \bar{s}_R = R \ln \left(\frac{\bar{v}_2 - b}{\bar{v}_1 - b} \right) \quad R = \frac{J}{\text{molK}}$$


$$\bar{q}_R = \Delta \bar{U}_R + \bar{w}_R$$

$$\frac{\bar{q}_{IR}}{T} = \bar{\Delta S}_{IR}$$

$$\bar{\Delta U}_{IR} = \bar{\Delta U}_R$$

$$\bar{q}_{IR} = \bar{\Delta U}_{IR} + \bar{w}_{IR}$$

$$\bar{\Delta S}_{IR} = \frac{\bar{q}_{IR}}{T}$$

Expansión ó compresión de un gas real con comportamiento tipo Van der Waals			
Introducir los valores en las celdas de color amarillo			
V_1 (L)	50.0000		a y b Independiente de $V_{\text{crítico}}$
V_2 (L)	100.0000		
Temperatura (K)	298.15		
p_1 (atm)	4.0000		
R (atmL/molK)	0.0820		
T_c (K)	154.60		
p_c (atm)	49.8000		
a (atmL ² /mol ²)	1.3614		
b (L/mol)	0.0318		
n (mol)	8.1805		
Ideal			
w_R (J)	14046.63	p_2 (atm)	2.0000
w_{IR} (J)	10132.50	ΔU_R (J)	0
q_R (J)	14046.63	ΔU_{IR} (J)	0
q_{IR} (J)	10132.50	ΔH_R (J)	0
ΔS_R (J/K)	47.11	ΔH_{IR} (J)	0
ΔS_{IR} (J/K)	33.98	ΔG_R (J)	-14046.63
		ΔG_{IR} (J)	-10132.50
Real			
w_R (J)	14007.27	p_2 (atm)	1.9961
w_{IR} (J)	10112.79	ΔU_R (J)	92.32
q_R (J)	14099.59	ΔU_{IR} (J)	92.32
q_{IR} (J)	10205.10	ΔH_R (J)	52.89
ΔS_R (J/K)	47.29	ΔH_{IR} (J)	52.89
ΔS_{IR} (J/K)	34.23	ΔG_R (J)	-14046.70
		ΔG_{IR} (J)	-10152.21
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$$p_2 = \frac{RT}{\bar{V}_2 - b} - \frac{a}{\bar{V}_2^2}$$

$$\bar{V}_2 = \frac{V_2}{n}$$

$$\Delta \bar{G}_R = \Delta \bar{H}_R - T \Delta \bar{S}_R$$

$$\Delta \bar{G}_{IR} = \Delta \bar{H}_{IR} - T \Delta \bar{S}_{IR}$$

ideal
o
real.

$$P_2 = \frac{nRT}{(V_2 - nb)} - \frac{an^2}{V_2^2}$$