Clase 61 2 Diciembre 2020

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Proceso Isotérmico Real.

$$d\bar{U} = T\,d\bar{S} - P\,d\bar{V}$$

$$\bar{U} = f(\bar{S}, \bar{V})$$

$$d\bar{U} = \boxed{\left(\frac{\partial \bar{U}}{\partial \bar{S}}\right)_{\bar{V}}} d\bar{S} + \boxed{\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_{\bar{S}}} d\bar{V}$$

$$\left(\frac{\partial \bar{U}}{\partial \bar{S}}\right)_{\bar{V}} = T \qquad \left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_{\bar{S}} = -P$$

$$d\bar{A} = -p\,d\bar{V} - \bar{S}\,dT$$

$$d\bar{A} = \left(\frac{\partial \bar{A}}{\partial \bar{V}}\right)_T d\bar{V} + \left(\frac{\partial \bar{A}}{\partial T}\right)_{\bar{V}} dT$$

$$\bar{A} = f(\bar{V}, T)$$

$$d\bar{U} = T\,d\bar{S} - p\,d\bar{V}$$

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\boxed{\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T} - p\cancel{\left(\frac{\partial \bar{V}}{\partial \bar{V}}\right)}_T$$

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T - P$$

$$d\bar{A} = -P\,d\bar{V} - \bar{S}\,dT$$

$$\boxed{\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T} = \boxed{\left(\frac{\partial P}{\partial T}\right)_{\bar{V}}}$$

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P$$

ideal. $P = \frac{RT}{\bar{V}}$

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\boxed{\left(\frac{\partial P}{\partial T}\right)}_{\bar{V}} - P$$

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

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\left(\frac{R}{\bar{V}}\right) - \frac{RT}{\bar{V}}$$

$$= 0 \quad \text{ideal}$$

modelo real.

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P$$

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

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

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = \cancel{T\left(\frac{R}{\bar{V}-b}\right)} - \left[\cancel{\frac{RT}{\bar{V}-b}} - \frac{a}{\bar{V}^2}\right]$$

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T = \frac{a}{\bar{V}^2}$$

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

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

o

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

$$\Delta\bar{U} = \frac{atm\,\cancel{L^2}}{\cancel{mol^2}}\left[\frac{1}{\cancel{L}/\cancel{mol}}\right]$$

$$= \left(\frac{\cancel{atm}\,\cancel{L}}{mol}\right)\left(\frac{1.01325\times10^5\,N/\cancel{m^2}}{\cancel{atm}}\right)\left(\frac{1\,\cancel{m^3}}{10^3\,\cancel{L}}\right)$$

$$\Delta\bar{U} = \frac{J}{mol}$$

ideal. Isotermico

$$W_R = nRT\ln\frac{V_2}{V_1} \qquad \bar{W}_R = RT\ln\left(\frac{\bar{V}_2}{\bar{V}_1}\right)$$

$$R = J/mol\,K$$

$$\bar{W}_{IR} = p_2(\bar{V}_2 - \bar{V}_1)$$

$$\left(\frac{\cancel{atm}\,\cancel{L}}{mol}\right)\left(\frac{1.01325\times10^5\,N/\cancel{m^2}}{1\,\cancel{atm}}\right)\left(\frac{1\,\cancel{m^3}}{10^3\,\cancel{L}}\right)$$

$$= \frac{J}{mol}.$$

Real.

$$\bar{W} = p\,d\bar{V}$$

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

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

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

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

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

$$\bar{W}_R = RT\ln\left(\frac{\bar{v}_2 - b}{\bar{v}_1 - b}\right) - a\left[-\left(\frac{1}{v_2} - \frac{1}{v_1}\right)\right]$$

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

$$R = atm\,L/mol\,K$$

$$\left(\frac{atm\,L}{mol\,\cancel{K}}\right)(\cancel{K}) + \frac{atm\,L^2}{mol^2}\left(\frac{1}{L/mol}\right)$$

$$\left(\frac{a\cancel{tm}\,\cancel{L}}{mol}\right)\left(\frac{1.01325\times10^5\,N/\cancel{m^2}}{a\cancel{tm}}\right)\left(\frac{1\,\cancel{m^3}}{10^3\,\cancel{L}}\right)$$

$$= \frac{J}{mol}$$

Real.

$$\bar{W}_{IR} = p_2(\bar{V}_2 - \bar{V}_1) = \frac{RT}{\bar{V}_2 - b} - \frac{a}{\bar{V}_2^2}(\bar{V}_2 - \bar{V}_1)$$

$$\bar{W}_{IR} = p_2(\bar{V}_2-\bar{V}_1) = \frac{RT}{\bar{V}_2-b} - \frac{a}{\bar{V}_2^2}(\bar{V}_2-\bar{V}_1)$$

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

$$\left(\frac{atm\,L}{mol}-\frac{atm\,L}{mol}\right)\left(\frac{1.01325\times10^5\,N/m^2}{atm}\right)\left(\frac{1\,m^3}{10^3\,L}\right)$$

$$=\frac{J}{mol}$$

$$\overline{\Delta U} = \bar{q} - \bar{w}$$

$$\boxed{\bar{q}_R = \overline{\Delta U}_R + \overline{W}_R}$$

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

$$\boxed{\bar{q}_{IR} = \overline{\Delta U}_{IR} + \overline{W}_{IR}}$$

$$\overline{\Delta S}_R = \frac{\bar{q}_R}{T}$$

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

ideal.

$$\overline{\Delta S}_R = R \ln \frac{\bar{V}_2}{\bar{V}_1}$$

Real.

$$\overline{\Delta S_R}$$

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

$$\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T$$

$$\left(\frac{\partial \bar{S}_R}{\partial \bar{V}}\right)_T = \frac{R}{\bar{V}-b}$$

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

$$\overline{\Delta S}_R = R \ln\left(\frac{\bar{V}_2 - b}{\bar{V}_1 - b}\right)$$

$$\boxed{\overline{\Delta S}_R \text{ ideal} < \overline{\Delta S}_R \text{ Real.}}$$

$$\Delta G = \Delta H - T\Delta S$$

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

$$\overline{\Delta G}_{IR} = \overline{\Delta H}_{IR} - T\Delta S_{IR}$$

ideal y real.

$$\Delta H = \Delta U + \Delta pV$$

$$\Delta \overline{H} = \Delta \overline{U} + \boxed{\left(p_2\overline{V}_2 - p_1\overline{V}_1\right)}$$

isotérmico $p_2V_2 = p_1V_1$

iedades | Obtención de a y b

Propiedades Fisicoquímicas de sustancias

Nombre	nitrógeno	
Masa Molar	28.013	g/mol
Temperatura Crítica	126.260	K
Presion Crítica	33.540	atm
Volumen Crítico	0.0901	L/mol
Punto ebullición	77.400	K
Punto de fusión	63.300	K
Cp (cal/mol K)	7.440e+0	a
$Cp=a+bT+cT^2+dT^3$	-3.240e-3	b
(300-2500)K	6.400e-6	c
	-2.790e-9	d
Constantes de Antonio	14.9342	A
LN(p)=A-(B/(T+C))	588.7200	B
T=K	-6.6000	C
p=mmHg		

FES ZARAGOZA

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

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

a	atmL^2/mol^2	0.81629
b	L/mol	0.03002

Independiente de volumen crítico

Modelo

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

a	atmL^2/mol^2	1.34828
b	L/mol	0.03859

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Predicciones
ideal.

$- = \overline{w}_R < \overline{w}_{IR}$ $\overline{\Delta S}_R < \overline{\Delta S}_{IR} = -$

$- = \overline{q}_R < \overline{q}_{IR}$ $\Delta G_R < \Delta G_{IR} = +$

$\Delta H \; \Delta U = 0$

$\Delta H, \Delta U$ Real $\neq 0$

$\Delta S_{Real} > \Delta S_{ideal}$ $\overline{\Delta G}_{Real} > \overline{\Delta G}_{ideal}$