Clase 73 6 Enero 2021

Título de la nota 06/01/2021

Fugacidad (F, f)

- Desviación idealidad
- F (atm) $F \propto P$
- $F = \Phi P$
- Φ = coef. de Fugacidad

- $\Phi \to 1$ ideal.
- $\Phi > 1$ $\Phi < 1$

potencial químico $\boxed{d\bar{G} = \bar{V}dp - \bar{S}dT} = d\mu$

Isotérmico

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

$$\int_1^2 d\mu = \int_1^2 d\bar{G} = \frac{RT}{P}\int_{P_1}^{P_2} dP$$

$$P_1 = 1\,\text{atm}$$

$$\mu = \Delta\bar{G} = RT\ln\frac{P_2}{P_1}$$

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

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

$$\Delta\bar{G} = RT\ln \Phi P \quad \text{real}$$

$$\mu = RT \ln f \qquad \mu = \bar{v}\, dp$$

Real ideal.

$$RT \ln f = \bar{v}\, dp \qquad \frac{RT}{P}$$

$$RT \ln f = \left(\bar{v} + \frac{RT}{P} - \frac{RT}{P}\right) dp$$

$$RT \ln f = \left(\bar{v} - \frac{RT}{P}\right) dp + \frac{RT}{P} \int_{P_1}^{P_2} dp$$

$$RT \ln f = \left(\bar{v} - \frac{RT}{P}\right) dp + RT \ln p$$

$$RT\ln f = \left(\bar{v} - \frac{RT}{p}\right)dp + RT\ln p$$

$$RT\ln f - RT\ln p = \left(\bar{v} - \frac{RT}{p}\right)dp$$

$$RT\ln\left(\frac{f}{p}\right) = \left(\bar{v} - \frac{RT}{p}\right)dp \qquad \Phi = \frac{f}{p}$$

$$RT\ln\Phi = \left(\frac{ZRT}{p} - \frac{RT}{p}\right)dp \qquad Z = \frac{p\bar{v}}{RT}$$

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

$$\cancel{R}T\ln\Phi = \cancel{R}T\left(\frac{Z-1}{p}\right)dp$$

$$\ln \Phi = \int_{P_1}^{P_2} \left(\frac{Z-1}{P} \right) dP$$

$$e \qquad e^{\left[\left(\frac{Z-1}{P} \right) \int_{P_1}^{P_2} dP \right]}$$

$$\Phi = e \qquad Z = 1$$

$$\Phi = e^0 = 1 \quad \text{ideal.}$$

$$Z = f(P)$$

$$\Phi = f(P) \quad \text{3 gráficas}$$

$$f = f(P)$$

Un gas a 100°C se ha determinado su ecuación virial hasta el tercer coeficiente en un intervalo de presiones de 1 a 60 atm. Se obtienen los términos $B = -242.5\ cm^3/mol$, $C = 25{,}200\ cm^6/mol^2$. Calcular $\overline{W}$ de expansión cuando la presión cambia de 50 a 10 atm.

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

$$\boxed{Z = 1 + B'(T)p + C'(T)p^2}$$

1) obtener B' y C'

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

$$B' = \frac{\left(-242.5\ \cancel{cm^3}/\cancel{mol}\right)\left(\frac{1\cancel{L}}{10^3\ \cancel{cm^3}}\right)}{\left(\frac{0.082\ atm\cancel{L}}{\cancel{mol}\ \cancel{K}}\right)\left(373.15\cancel{K}\right)} = atm^{-1}$$

$$= -7.9252 \times 10^{-3}\ atm^{-1}$$

$$C' = \frac{\left[\left(25{,}200\ \cancel{cm^6}/\cancel{mol}^2\right) - \left(-242.5\ \frac{\cancel{cm^3}}{\cancel{mol}}\right)^2\right]\left(\frac{1L^2}{10^6\ \cancel{cm^6}}\right)}{\left(\frac{0.082\ atmL}{\cancel{mol}\ \cancel{K}}\right)^2\left(373.15\cancel{K}\right)^2}$$

$$c' = -3.5894 \times 10^{-5}\ atm^{-2}$$

$$\boxed{Z = 1 - 7.9252 \times 10^{-3}\ atm^{-1}\, P - 3.5894 \times 10^{-5}\ atm^{-2}\, P^2}$$

$$\bar{W}expansión = + \qquad \bar{W} = p\, d\bar{V}$$

$$Z = \frac{p\bar{V}}{RT}$$

$$\frac{p\bar{V}}{RT} = 1 - 7.92\ 2 \times 10^{-3} P - 3.5894 \times 10^{-5} P^2$$

$$\bar{V} = \left(\frac{1 - 7.9252 \times 10^{-3} P - 3.5894 \times 10^{-5} P^2}{P}\right) RT$$

$$\boxed{\bar{v} = \left(\frac{1}{p} - 7.9252\times10^{-3} - 3.5894\times10^{-5}\,p\right)RT}$$

$$\bar{w} = p\,d\bar{v}$$

$$\boxed{\left(\frac{\partial \bar{v}}{\partial p}\right)_T} dp = d\bar{v}$$

$$\left(\frac{\partial \bar{v}}{\partial p}\right)_T = -\frac{1}{p^2} - 3.5894\times10^{-5}$$

$$d\bar{v} = \left[\boxed{-\frac{1}{p^2} - 3.5894\times10^{-5}}\right]RT\,dp$$

$$\bar{w} = p\, d\bar{v}$$

$$\bar{w} = p\left[-\frac{1}{p^2} - 3.5894\times10^{-5}\right] RT\, dp$$

$$\bar{w} = \left[-\frac{1}{p} - 3.5894\times10^{-5}\, p\right] RT\, dp$$

$$\bar{w} = \left[-\frac{1}{p}\int_{p_1}^{p_2} dp - 3.5894\times10^{-5}\int_{p_1}^{p_2} p\, dp\right] RT$$

$$\bar{w} = RT\left[-\ln\frac{p_2}{p_1} - \frac{3.5894\times10^{-5}}{2}\left(p_2^2 - p_1^2\right)\right]$$

$$\overline{W} = RT\left[-\ln\frac{P_2}{P_1} - \frac{3.5894\times10^{-5}}{2}\left(P_2^2 - P_1^2\right)\right]$$

$$= \frac{J}{mol\,\cancel{K}}\,\cancel{K}\left[\ln\frac{\cancel{atm}}{\cancel{atm}} - \cancel{atm}^{-2}\left(\cancel{atm}^2\right)\right]$$

$$J/mol = \overline{W}$$

$$\overline{W} = \left(\frac{8.314\,J}{mol\,\cancel{K}}\right)\left(373.15\,\cancel{K}\right)\left[-\ln\frac{10\,\cancel{atm}}{50\,\cancel{atm}} - \frac{3.5894\times10^{-5}}{2\,\cancel{atm}^2}\left(10^2 - 50^2\ \cancel{atm}^2\right)\right]$$

$$\overline{W} = 5126.6981\ J/mol$$

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

$$= RT \ln \frac{P_1}{P_2}$$

$$= -RT \ln \frac{P_2}{P_1}$$

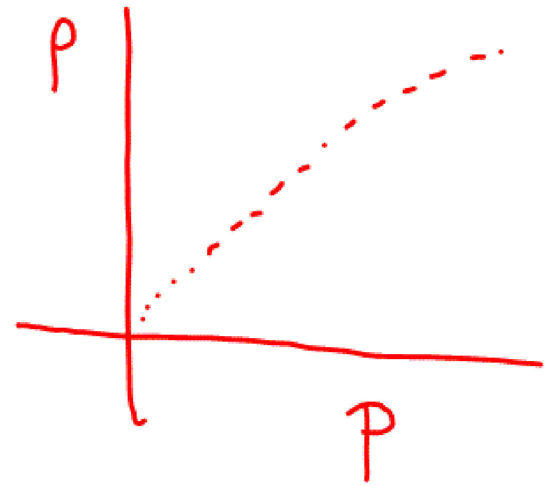
$$\boxed{\bar{W}_{ideal} =} \left(\frac{8.314\ J}{mol\ K}\right)(373.15\ K) \ln \frac{50}{10}$$

$$\boxed{= 4993.0704\ J/mol}$$

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

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

ρ (g/L)	p (atm)
1.82	1
3.667	2
7.58	4
11.501	6
15.668	8
20.061	10



$$\boxed{Z = 1 + B'p}$$ Línea recta

$$Z = \frac{pV}{nRT} \qquad Z = f(p)$$

$$pV = ZnRT \qquad n = \frac{m}{M}$$

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

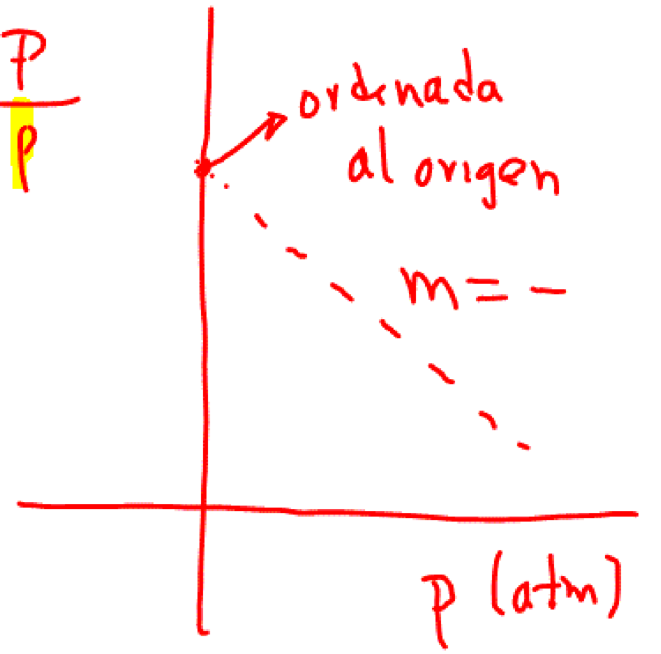
$$Z = \frac{pV}{\frac{m}{M}RT} \qquad Z = 1 + B'p$$

$$\frac{pV}{\frac{m}{M}RT} = 1 + B'p \qquad \rho = \frac{m}{V}$$

$$\frac{PV}{m} = \frac{RT}{M}\left(1 + B'p\right) \qquad \frac{P}{\rho}$$

$$\frac{P}{\rho} = \frac{RT}{M}\left(1 + B'p\right)$$

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



$\frac{P}{\rho}$ (atm L/g)	p (atm)
0.5494	1
0.5439	2
0.5277	4
0.5216	6
0.5105	8
0.4984	10

$r = -0.9945$

$a = 0.5539\ \frac{atm\,L}{g}$

$b = -0.005539\ \frac{L}{g}$

$$\frac{P}{\rho} = a + bP$$

$$\frac{P}{\rho} = \frac{RT}{M} + \frac{RT}{M} B' P$$

$$\frac{RT}{M} = a$$

$$M = \frac{RT}{a} = \frac{\left(\frac{0.082 \cancel{atm} \cancel{L}}{mol \cancel{K}}\right)(298.15 \cancel{K})}{0.5539 \frac{\cancel{atm} \cancel{L}}{g}}$$

$$\boxed{g/mol = 44.138\ g/mol}$$

$$\boxed{CO_2}$$ ó $CH_3CH_2CH_3$ ó C_3H_8

$$\frac{RT}{M} B' = b$$

$$a B' = b$$

$$B' = \frac{b}{a}$$

$$B' = \frac{-0.005539\ L/g}{0.5539\ atm L/g}$$

$$B' = -0.01\ \text{atm}^{-1}$$

$$\boxed{Z = 1 - 0.01\ \text{atm}^{-1}\, p}$$

Introducir en las celdas de color amarillo, los datos correspondientes

p (atm)	ρ (g/L)
1	1.82
2	3.677
4	7.58
6	11.501
8	15.668
10	20.061

Temperatura (K)	298.15
R (atmL/molK)	0.082

p/ρ (atmL/g)	p (atm)
0.54945	1
0.54392	2
0.52770	4
0.52169	6
0.51059	8
0.49848	10

Modelo lineal hasta el segundo coeficiente de la ecuación virial

$$Z=1+B'p$$

$$Z=\frac{pV}{nRT}$$

$$Z=\frac{pV}{\frac{mRT}{M}}=1+B'p$$

$$\frac{p}{\rho}=\frac{RT}{M}[1+B'p]$$

$$Z=\frac{pV}{nRT}=1+B'p$$

$$\frac{pV}{m}=\frac{RT}{M}[1+B'p]$$

$$\frac{p}{\rho}=\frac{RT}{M}+\frac{RT}{M}B'p$$

Regresión lineal para obtener ordenada al origen y pendiente

ordenada al origen (atmL/g)	0.55390	pendiente (L/g)	-0.00553
coef de correlación	-0.9945		

Masa Molar

M (g(mol) 44.138

Ecuación virial

$Z=1+B'p$ Z=1-0.01 p

Dr. Juan Carlos Vázquez Lira UNAM FES Zaragoza 2021 V2

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a Molar | Z y Fugacidad

Obtención de Factor de compresibilidad, a partir de una ecuación virial

Introducir en las celdas de color amarillo, los datos correspondientes

p (atm)	Z (atm)	Conclusión de Z
1	0.99001	Atracción
2	0.98002	Atracción
4	0.96003	Atracción
6	0.94005	Atracción
8	0.92006	Atracción
10	0.90008	Atracción

Obtención del coefiente de fugacidad (F) y fugacidad (Φ) a partir de una ecuación virial

Introducir en las celdas de color amarillo, los datos correspondientes

p (atm)	Φ	F (atm)	Conclusión de F
1	1.00000	1.000	Ideal
2	0.99006	1.980	Atracción
4	0.97047	3.882	Atracción
6	0.95127	5.708	Atracción
8	0.93244	7.460	Atracción
10	0.91399	9.140	Atracción

Modelo del coeficiente de fugacidad

$$\ln\Phi = \int_{p_1}^{p_2} \left(\frac{Z-1}{p}\right) dp$$

Dr. Juan Carlos Vázquez Lira UNAM FES Zaragoza 2021 V2