Clase 35 30 Septiembre - 1 octubre 2014

Título de la nota 9/30/2014

Obtención de M_μ de una mezcla tipo Berthelot

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

si se modifica dependiendo de n

$$p = \frac{nRT}{V - nb} - \frac{a}{V^2 T}$$

Despejar n

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

$$\frac{pV^2T + an^2}{V^2T} = \frac{nRT}{V-nb} = (pV^2T + an^2)(V-nb) = nRV^2T^2$$

$$\left(pV^3T - pnbV^2T + an^2V - an^3b = nRV^2T^2\right) - 1$$

reacomodando

$$-pv^3T + pnbv^2T - an^2v + nRv^2T^2 + an^3b = 0$$

$$n^3(ab) - n^2(av) + n(pbv^2T + Rv^2T^2) - pv^3T = 0$$

Checar unidades

$$\cancel{mol^3}\left(\frac{atm\,L^2\,K}{\cancel{mol^2}}\right)\left(\frac{L}{\cancel{mol}}\right) - \cancel{mol^2}\left[\left(\frac{atm\,L^2\,K}{\cancel{mol^2}}\right)(L)\right] + \cancel{mol}\left[atm\left(\frac{L}{\cancel{mol}}\right)(L)^2(K) + \left(\frac{atm\,L}{\cancel{mol}\,\cancel{K}}\right)(L^2)(K^{\cancel{2}})\right]$$

$$-(atm)(L)^3K = 0$$

$$atm\,L^3K - atm\,L^3K + atm\,L^3K - atm\,L^3K = 0$$ unidades correctas

Determinar M_M con los siguientes datos

Mezcla N_2 y O_2 (3 y 2 mol)   149 g de muestra

$T = 263.15 K$

$p = 20 atm$

$a_m = 184.002 \frac{atm L^2}{mol^2} K$

$b_m = 0.03433 \frac{L}{mol}$

$T_{cM} = 137.55 K$

$V = 5.46 L$

$p_{cM} = 40 atm$

$\bar{V}_{cM} = 0.1069 L/mol$

Sustituyendo en la ecuación

$$n^3(ab) - n^2(av) + n(pbv^2T + Rv^2T^2) - pv^3T = 0$$

$$n^3(a_mb_m) - n^2(a_mV) + n(pb_mv^2T + Rv^2T^2) - pv^3T = 0$$

$$n^3\left[(184.002)(0.1069)\right] - n^2\left[(184.002)(5.46)\right] + n\left[(20)(0.03433)(5.46)^2(263.15)\right]$$

$$+ n\left[(0.082)(5.46)^2(263.15K)^2\right] - \left[(20)(5.46)^3(263.15)\right] = 0$$

se obtiene la ecuación

$$19.6698\,n^3 - 1004.65092\,n^2 + 174666.4184\,n - 856665.5413 = 0$$

Resolviendo

$n_1 = 5.0360$

$n_2 = 23.019 + 90.10\,i$

$n_3 = 23.019 - 90.10\,i$

149 g de muestra

$n = 5.0360$

$M_M = \frac{149\,g}{5.0360\,mol} = 29.5869\ g/mol$

Si se compara con el M_M ideal

3 mol N_2 2 mol O_2

$M_M = \sum_{i=1}^{n} y_i M_i = \left[\frac{3}{5}(28\ g/mol) + \frac{2}{5}(32\ g/mol)\right]$

$= 29.6\ g/mol$

existe poca diferencia con el valor ideal.

Proceso Isotérmico tipo Van der Waals

Cálculo de ΔU, ΔS, Q

de acuerdo a la ecuación fundamental.

$$dU = \delta Q - \delta W$$

$$dU = T\,dS - p\,dV$$

Si se maneja molar

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

reacomodando isotérmicamente

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

si $p = \dfrac{RT}{\bar{V}-b} - \dfrac{a}{\bar{V}^2}$

si $\left(\dfrac{\partial S}{\partial \bar{V}}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$ de $d\bar{A} = -\bar{S}dT - p d\bar{V}$

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

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

reacomodando

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

$$\left(\frac{\partial \bar{U}}{\partial \bar{v}}\right)_T = \frac{a}{\bar{v}^2}$$ despejando e integrando

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

$$\overline{\Delta U} = -a\left[\frac{1}{\bar{V}_2} - \frac{1}{\bar{V}_1}\right] = \frac{-\text{atm}\,L^2}{\text{mol}^2}\left[\frac{1}{L/\text{mol}}\right] = \frac{\text{atm}\,L}{\text{mol}}$$

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

en relación a $\overline{\Delta S}$

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

reacomodando

$$\int_{\bar{S}_1}^{\bar{S}_2} d\bar{S} = R\int_{\bar{V}_1}^{\bar{V}_2}\frac{d\bar{V}}{\bar{V}-b} = R\ln\left(\frac{\bar{V}_2-b}{\bar{V}_1-b}\right) = J/\text{mol}\,K\ \ln\left[\frac{L/\text{mol}-L/\text{mol}}{L/\text{mol}-L/\text{mol}}\right]$$

$$= J/\text{mol}\,K$$

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = T\left(\frac{-\partial \bar{V}}{\partial T}\right)_P + \bar{V}$$

igualando

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

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

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

de la ecuación cúbica

$$p\bar{v}^3 - \bar{v}^2(pb + RT) + a\bar{v} - ab = 0$$

en forma diferencial

$$(3\bar{v}^2 p - 2\bar{v}pb - 2\bar{v}RT + a)\,d\bar{v} + (\bar{v}^3 - b\bar{v}^2)\,dp$$

$$(-Rv^2)\,dT = 0$$

por lo tanto

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = T\left(\frac{-\partial \bar{V}}{\partial T}\right)_P + \bar{V}$$

igualando

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

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

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

de la ecuación cúbica

$$p\bar{v}^3 - \bar{v}^2(pb + RT) + a\bar{v} - ab = 0$$

en forma diferencial

$$\left(3\bar{v}^2 p - 2\bar{v}pb - 2\bar{v}RT + a\right)d\bar{v} + \left(\bar{v}^3 - b\bar{v}^2\right)dp$$

$$(-Rv^2)\,dT = 0$$

por lo tanto

$$\left(\frac{\partial \bar{v}}{\partial T}\right)_p = \frac{-R\bar{v}^2}{(3\bar{v}^2 p - 2pb\bar{v} - 2RT\bar{v} + a)}$$

$$\left(\frac{\partial \bar{v}}{\partial p}\right)_T = \frac{b\bar{v}^2 - \bar{v}^3}{3\bar{v}^2 p - 2pb\bar{v} - 2RT\bar{v} + a}$$

de esta forma

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

$$\left(\frac{\partial \bar{H}}{\partial p}\right)_T = -T\,\frac{-R\bar{v}^2}{3\bar{v}^2 p - 2pb\bar{v} - 2RT\bar{v} + a}$$

Reacomodando

$$\int_{\bar{H}_1}^{\bar{H}_2} d\bar{H} = T\left[R\bar{v}^2 \int_{p_1}^{p_2} \left(\frac{dp}{3\bar{v}^2 p - 2pb\bar{v} - 2RT\bar{v} + a}\right)\right]$$

Resolver con cambio de Variable

$$u = 3\bar{v}^2 p - 2pb\bar{v} - 2RT\bar{v} + a$$

$$du = (3\bar{v}^2 - 2b\bar{v})\,dp$$

$$dp = \frac{du}{3\bar{v}^2 - 2b\bar{v}}$$

Sustituyendo

$$\Delta H = TR\bar{v}^2 \left[\int_{p_1}^{p_2} \frac{du}{u\,(3\bar{v}^2 - 2b\bar{v})} \right] = -TR\bar{v}^2 \left[\frac{\ln u}{(3\bar{v}^2 - 2b\bar{v})} \right] \Bigg|_{p_1}^{p_2}$$

$$\overline{\Delta H} = \frac{-TR\bar{v}^2}{3\bar{v}^2 - 2b\bar{v}} \left[\ln \frac{3\bar{v}^2 p_2 - 2p_2\bar{v}b - 2RTv + a}{3\bar{v}^2 p_1 - 2p_1\bar{v}b - 2RTv + a} \right]$$

Unidades

$$\overline{\Delta H} = \frac{-(K)(J/molK)\left(\frac{L}{mol}\right)^2}{\left(\frac{L}{mol}\right)^2 - \left(\frac{L}{mol}\right)\left(\frac{L}{mol}\right)} = J/mol$$

✓

Unidades correctas

para el caso de mezclas cambiar b por bm y a por am

Ecuación de Dieterici

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

unidades de a

$$e^{-a/RT\bar{v}} = \frac{atm\,L^2/mol^2}{\frac{atm\,L}{mol\,K}(K)\frac{L}{mol}}$$

$$a = \frac{atm\,L^2}{mol^2} = 2RT_c\bar{V}_c^2$$

$$b = L/mol = \frac{\bar{V}_c}{2}$$

Calcular ΔU de la ecuación de Dieterici

$$dU = \delta Q - \delta W$$

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

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

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

si $\quad p = \dfrac{RT e^{-a/RT\bar{v}}}{\bar{v}-b}$ $\quad$ producto

$$\left(\frac{\partial p}{\partial T}\right)_{\bar{v}} = \frac{R}{\bar{v}-b}\left[e^{-a/RT\bar{v}} + e^{-a/RT\bar{v}}\frac{a}{RT^2\bar{v}}\right]$$

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

$$\left(\frac{\partial \bar{U}}{\partial \bar{v}}\right)_T = T\left\{\left[\frac{R}{\bar{v}-b}\left(e^{-a/RT\bar{v}} + T e^{-a/RT\bar{v}}\frac{a}{RT^2\bar{v}}\right)\right] - \frac{RTe^{-a/RT\bar{v}}}{\bar{v}-b}\right.$$

Simplificando

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_T = \left[\cancel{\frac{RT}{\bar{v}-b}\, e^{-a/RT\bar{v}}} + \frac{\cancel{T^2}\,\cancel{R}\, e^{-a/RT\bar{v}}\, a}{\cancel{R}\,\cancel{T^2}\,\bar{v}\,(\bar{v}-b)} - \cancel{\frac{RT e^{-a/RT\bar{v}}}{\bar{v}-b}}\right]$$

$$\left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_T = \frac{a\, e^{-a/RT\bar{v}}}{(\bar{v}-b)\,\bar{v}} = \frac{a\, e^{-a/RT\bar{v}}}{\bar{v}^2-\bar{v}b}$$

$$\int_{\bar{u}_1}^{\bar{u}_2} d\bar{u} = a\left[\int_{\bar{v}_1}^{\bar{v}_2} \frac{e^{-a/RT\bar{v}}}{\bar{v}^2-\bar{v}b}\right] d\bar{v}$$

Resolver

$$\Delta \bar{U} = a\, e^{-a/RT} \int_{\bar{V}_1}^{\bar{V}_2} \frac{e^{-1/\bar{V}}}{\bar{V}\,(\bar{V}-b)}\, d\bar{V}$$

otra alternativa

$$\Delta \bar{U} = \frac{a}{e^{a/RT}} \int_{\bar{V}_1}^{\bar{V}_2} \frac{d\bar{V}}{e^{1/\bar{V}}(\bar{V}^2 - \bar{V}b)}$$

Tarea:

Calcular ΔU, ΔH, ΔS, Q y W en un proceso de compresión Isotérmica reversible de comportamiento Van der Waals para ello se emplearon 5 y 10 moles de (Metano y Etano respectivamente) cuando la $T = -20°C$ y la presión inicial es de 2 atm; la compresión se lleva a cabo a la mitad de su volumen inicial ($V_1 = 155.68725\ L$)