Clase 30 22 Septiembre 2014

Título de la nota 22/09/2014

Mezcla de gases composición del aire de acuerdo a los siguientes datos; calcular PF_M, $\overline{Cp}_M$ y $\overline{Cv}_M$ (de las clases anteriores)

esto esta en % p/p

$N_2 = 78.084\%$ $CO = 0.001\%$

$O_2 = 20.015\%$

$Ar = 0.934\%$

$H_2O = 0.930\%$

$CO_2 = 0.035\%$

Calcular n_i y n_{total}

$$n_{N_2} = \frac{78.084\,g}{28\,g/mol} = 2.7887$$

$$n_{CO} = \frac{0.001\,g}{28\,g/mol} = 3.57\times10^{-5}$$

$$n_{O_2} = \frac{20.015\,g}{32\,g/mol} = 0.6254$$

$$n_{CO_2} = \frac{0.035\,g}{44\,g/mol} = 7.95\times10^{-4}$$

$$n_{H_2O} = \frac{0.930\,g}{18\,g/mol} = 5.166\times10^{-2}$$

$$n_{Ar} = \frac{0.934\,g}{40\,g/mol} = 2.33\times10^{-2}$$

$$n_T = 3.4899$$

$\overline{C_p}$ = cal/mol K

	n_i	y_i	C_{pi}
N_2	2.7887	0.7990	$7.440 - 0.324\times10^{-2}T + 6.4\times10^{-6}T^2 - 2.79\times10^{-9}T^3$
O_2	0.6254	0.1792	$6.713 - 0.879\times10^{-6}T + 4.17\times10^{-6}T^2 - 2.544\times10^{-9}T^3$
H_2O	5.166×10^{-2}	1.47×10^{-2}	$7.701 + 4.595\times10^{-4}T + 2.321\times10^{-6}T^2 - 0.859\times10^{-9}T^3$
CO	3.57×10^{-5}	1.02×10^{-5}	$7.373 - 0.307\times10^{-2}T + 6.552\times10^{-6}T^2 - 3.037\times10^{-9}T^3$
CO_2	7.95×10^{-4}	2.27×10^{-4}	$4.788 + 1.754\times10^{-2}T - 5.338\times10^{-5}T^2 + 4.097\times10^{-9}T^3$
Ar	2.33×10^{-2}	6.67×10^{-3}	$4.969 - 0.767\times10^{-5}T + 1.234\times10^{-8}T^2$
	$n_T = 3.4899$	~ 1	

$$\overline{C}_{pM} = \sum_{i=1}^{n} y_i \overline{C}_{p\,i}$$

$$= 7.28 - 0.018T + 5.9797 \times 10^{-6} T^2 - 2.6906 \times 10^{-9} T^3$$

$$\overline{C}_{vM} = \overline{C}_{pM} - R \qquad R = 1.9889 \text{ cal/mol K}$$

$$\overline{C}_{vM} = 5.2911 - 1.8 \times 10^{-2} T + 5.9797 \times 10^{-6} T^2 - 2.6906 \times 10^{-9} T^3$$

$$\overline{C}_{vM} = \sum_{i=1}^{n} y_i \overline{C}_{vi}$$

$$\rho_{FM} = \sum_{i=1}^{n} y_i \rho_{Fi}$$

$$= 28.67 \text{ g/mol}$$

Continuando con la obtención de a y b a partir de la parcial

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_{p.c.} = 0 \qquad \left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_{p.c.} = 0$$

Obtención de a y b de Van der Waals (en el punto crítico)

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}$$

Sabiendo que en el punto crítico:

$$\left(\frac{\partial P_c}{\partial \bar{V}_c}\right)_{p.c.} = 0 \qquad \left(\frac{\partial^2 P_c}{\partial \bar{V}_c^2}\right)_{p.c.} = 0 \quad \checkmark$$

$$P_c = \frac{RT_c}{(\bar{V}_c - b)} - \frac{a}{\bar{V}_c^2} \quad \cdots\cdots \quad ①$$

$$\left(\frac{\partial P_c}{\partial \bar{V}_c}\right)_{p.c.} = \frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2\bar{V}_c a}{(\bar{V}_c)^4}$$

$$= \frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{(\bar{V}_c)^3} = 0 \quad \cdots \quad ②$$

$$\left(\frac{\partial^2 P_c}{\partial \bar{V}_c^2}\right)_{p.c.} = \frac{2(\bar{V}_c - b)RT_c}{(\bar{V}_c - b)^4} - \frac{6a\bar{V}_c^2}{(\bar{V}_c)^6} = \frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

③

Primero se obtiene b de 2 y 3

$$\left[\frac{-RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{(\bar{V}_c)^3} = 0 \right] \frac{3}{\bar{V}_c}$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

$$-\frac{3RT_c}{(\bar{V}_c - b)^2 \bar{V}_c} + \frac{6a}{(\bar{V}_c)^4} = 0$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{(\bar{V}_c)^4} = 0$$

arreglando

$$-\frac{3RT_c}{(\bar{V}_c-b)^2\bar{V}_c}+\frac{2RT_c}{(\bar{V}_c-b)^3}=0$$

$$-\frac{3\cancel{RT_c}}{\cancel{(\bar{V}_c-b)^2}\,\bar{V}_c}=-\frac{2\cancel{RT_c}}{(\bar{V}_c-b)^{\cancel{3}}}$$

$$3(\bar{V}_c-b)=2\bar{V}_c$$

$$3\bar{V}_c-3b=2\bar{V}_c$$

$$\bar{V}_c=3b$$

$$\boxed{b=\frac{1}{3}\bar{V}_c}=\boxed{\frac{L}{mol}}$$

para obtener a se utiliza un sistema de 3 ecuaciones ① → ③

$$\left[P_c - \frac{RT_c}{(\bar{V}_c - b)} + \frac{a}{\bar{V}_c^2} = 0 \right] \frac{3}{(\bar{V}_c - b)^2}$$

$$\left[- \frac{RT_c}{(\bar{V}_c - b)^2} + \frac{2a}{\bar{V}_c^3} = 0 \right] - \frac{1}{(\bar{V}_c - b)}$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

obteniendose

$$\frac{3P_c}{(\bar{V}_c - b)^2} - \frac{3RT_c}{(\bar{V}_c - b)^3} + \frac{3a}{\bar{V}_c^2(\bar{V}_c - b)^2} = 0$$

$$\frac{RT_c}{(\bar{V}_c - b)^3} - \frac{2a}{\bar{V}_c^3(\bar{V}_c - b)} = 0$$

$$\frac{2RT_c}{(\bar{V}_c - b)^3} - \frac{6a}{\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c - b)^2} + \frac{3a}{\bar{V}_c^2(\bar{V}_c - b)^2} - \frac{2a}{\bar{V}_c^3(\bar{V}_c - b)} - \frac{6a}{\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c - b)^2} + \boxed{\frac{3a}{\bar{V}_c^2(\bar{V}_c - b)^2} - \frac{2a}{\bar{V}_c^3(\bar{V}_c - b)} - \frac{6a}{\bar{V}_c^4}} = 0$$

Tomando solo esta parte y si $b = \frac{1}{3}\bar{V}_c$

$$\frac{3a}{(\bar{V}_c - \frac{1}{3}\bar{V}_c)^2 \bar{V}_c^2} - \frac{2a}{(\bar{V}_c - \frac{1}{3}\bar{V}_c)\bar{V}_c^3} - \frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{(\frac{2}{3}\bar{V}_c)^2 \bar{V}_c^2} - \frac{2a}{(\frac{2}{3}\bar{V}_c)(\bar{V}_c^3)} - \frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{\frac{4}{9}\bar{V}_c^4} - \frac{2a}{\frac{2}{3}\bar{V}_c^4} - \frac{6a}{\bar{V}_c^4}$$

$$\frac{3a}{4/9\sqrt{c^4}} - \frac{2a}{2/3\sqrt{c^4}} - \frac{6a}{\sqrt{c^4}}$$

$$\frac{3a}{4/9\sqrt{c^4}} - \frac{2a}{6/9\sqrt{c^4}} - \frac{6a}{9/9\sqrt{c^4}}$$

$$\frac{27a}{4\sqrt{c^4}} - \frac{18a}{6\sqrt{c^4}} - \frac{54a}{9\sqrt{c^4}} =$$

$$= \frac{9(27)a - 6(18)a - 4(54)a}{36\sqrt{c^4}} = -\frac{81a}{36\sqrt{c^4}} = \boxed{-\frac{9}{4\sqrt{c^4}}a}$$

por lo tanto retomando

$$\frac{3P_c}{(\bar{V}_c - b)^2} - \frac{9a}{4\bar{V}_c^4} = 0$$

$$\frac{3P_c}{(\bar{V}_c - 1/3\bar{V}_c)^2} = \frac{9a}{4\bar{V}_c^4}$$

$$\frac{3P_c}{(2/3\bar{V}_c)^2} = \frac{9a}{4\bar{V}_c^4}$$

$$\frac{3P_c}{\cancel{4/9}\,\cancel{\bar{V}_c^2}} = \frac{\cancel{9}a}{\cancel{4}\,\bar{V}_c^{4\,2}} \longrightarrow 3P_c = \frac{a}{\bar{V}_c^2}$$

$$\boxed{a = 3P_c\bar{V}_c^2 = \frac{atm\,L^2}{mol^2}}$$

✓

En relación a la ecuación de Van der Waals las constantes a, b, R

Se obtienen con otras ecuaciones comparadas a las obtenidas

obtenidas

$$a = 3P_c\bar{V}_c^2$$

$$b = \frac{1}{3}\bar{V}_c^2$$

Independientes de R

$$R = \frac{8}{3}\frac{P_c\bar{V}_c}{T_c}$$

otras ecuaciones

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} = \left(\frac{atm\,L}{mol\,\cancel{K}}\right)^{\cancel{2}}\frac{(\cancel{K})^{\cancel{2}}}{(at\cancel{m})} = \frac{atm\,L^2}{mol^2}$$

$$b = \frac{R\,T_c}{8\,P_c} = \left(\frac{a\cancel{tm}\,L}{mol\,\cancel{K}}\right)\left(\frac{\cancel{K}}{a\cancel{tm}}\right) = \frac{L}{mol}$$

Independientes de $\bar{V}_c$

$$R = 0.082\ \frac{atm\,L}{mol\,K}$$

Obtención de b

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2}$$

$$a = 3P_c(V_c)^2$$

$$\bar{V}_c = 3b$$

$$P_c = \frac{RT_c}{3b - b} - \frac{3P_c(\bar{V}_c)^2}{\bar{V}_c^2}$$

$$p_c = \frac{RT_c}{2b} - 3P_c$$

$$4P_c = \frac{RT_c}{2b}$$

$$\boxed{b = \frac{RT_c}{8P_c}} = \frac{(\cancel{atm}\,L/mol\,\cancel{K})(\cancel{K})}{8\ (\cancel{atm})} = \frac{L}{mol}$$

✓

obtención de a

$$P_c = \frac{RT_c}{\bar{V}_c - b} - \frac{a}{\bar{V}_c^2} \qquad P_c = \frac{RT_c}{3b - b} - \frac{a}{(3b)^2}$$

$$P_c = \frac{RT_c}{2b} - \frac{a}{(3b)^2} = \frac{9b^2 RT_c - 2ab}{18b^3}$$

$$18b^3 P_c = 9b^2 RT_c - 2ab$$

$$\frac{-18b^3 P_c + 9b^2 RT_c}{2b} = a \qquad -9b^2 P_c + \frac{9}{2} b RT_c = a$$

$$-9\left(\frac{RT_c}{8P_c}\right)^2 P_c + \frac{9}{2}\left(\frac{RT_c}{8P_c}\right) RT_c = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2\,\cancel{P_c}}{P_c^{\cancel{2}}} + \frac{9}{16}\,\frac{R^2T_c^2}{P_c} = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2}{P_c} + \frac{9}{16}\,\frac{R^2T_c^2}{P_c} = a$$

$$-\frac{9}{64}\,\frac{R^2T_c^2}{P_c} + \frac{36}{64}\,\frac{R^2T_c^2}{P_c} = a$$

$$\frac{27}{64}\,\frac{R^2T_c^2}{P_c} = a \qquad \frac{27}{64}\,\frac{(atm\,L/mol\,\cancel{K})^{\cancel{2}}\,(\cancel{K})^2}{a\cancel{t}m} = \frac{atm\,L^2}{mol^2}$$

Forma alterna de obtener a

$$p_c = \frac{RT_c}{\bar{v}_c - b} - \frac{a}{\bar{v}_c^2} \qquad p_c = \frac{RT_c}{2b} - \frac{a}{(3b)^2}$$

$$p_c = \frac{RT_c}{2b} - \frac{a}{9b^2} \qquad p_c + \frac{a}{9b^2} = \frac{RT_c}{2b}$$

$$\frac{p_c 9b^2 + a}{9b^2} = \frac{RT_c}{2b} \qquad p_c 9b^2 + a = \frac{9b^2 RT_c}{2b}$$

$$p_c 9b^2 + a = \frac{9b\, RT_c}{2} \qquad a = \frac{9bRT_c}{2} - 9b^2 p_c$$

Sustituyendo $b = \frac{1}{8}\frac{RTc}{Pc}$

$$a = \frac{9\left(\frac{1}{8}\frac{RTc}{Pc}\right)RTc}{2} - 9\left(\frac{1}{8}\frac{RTc}{Pc}\right)^2 Pc$$

$$a = \frac{9}{16}\frac{R^2Tc^2}{Pc} - \frac{9}{64}\frac{R^2Tc^2}{Pc}$$

$$a = \frac{36}{64}\frac{R^2Tc^2}{Pc} - \frac{9}{64}\frac{R^2Tc^2}{Pc}$$

$$a = \frac{27\,R^2Tc^2}{64\,Pc}$$

Resulltado semejante

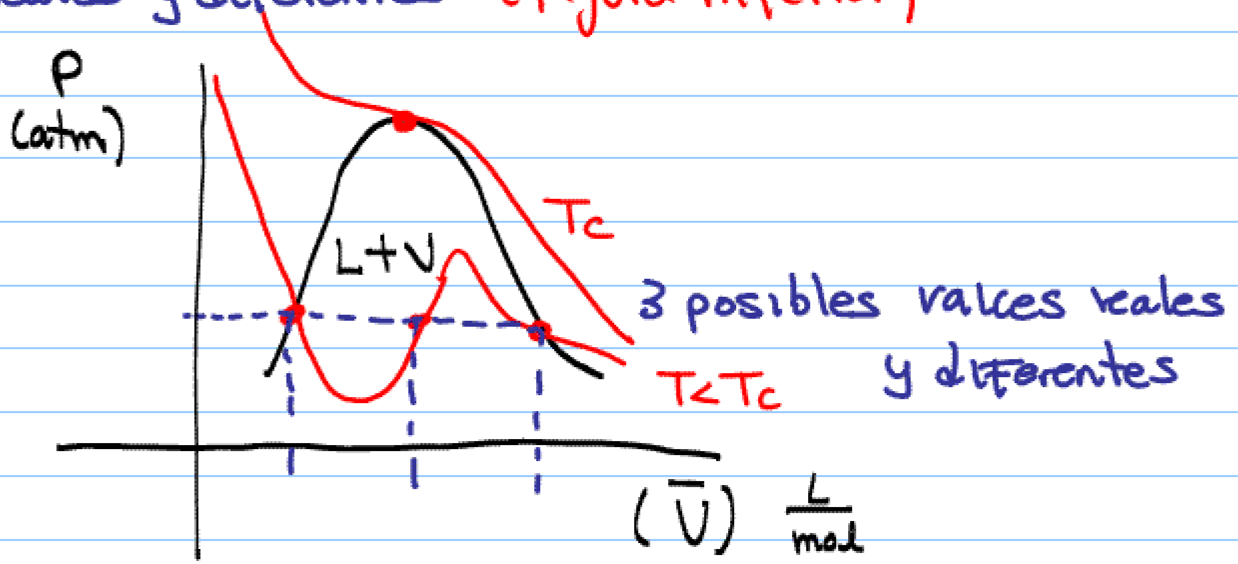
Por lo tanto es necesario obtener la relación de $\bar{V}$ de Van der Waals

Se tienen los posibles casos para obtener el volumen

a) Una raiz real y dos imaginarias

b) Tres raices reales e iguales (punto crítico)

c) Tres raices reales y diferentes (Figura inferior)



por lo tanto de la ecuación de Van der Waals

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

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

$$(P\bar{v}^2 + a)(\bar{v}-b) = \bar{v}^2 RT$$

$$P\bar{v}^3 + a\bar{v} - ab - bP\bar{v}^2 = \bar{v}^2 RT$$ arreglando

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

dividiendo entre p

$$\bar{V}^3 - \bar{V}^2\left(b + \frac{RT}{p}\right) + \bar{V}\,\frac{a}{p} - \frac{ab}{p} = 0$$

$$\left(\frac{L}{mol}\right)^3 - \frac{L^2}{mol^2}\left[\frac{L}{mol} + \frac{(atm\,L/mol\,K)(K)}{atm}\right] + \frac{L}{mol}\,\frac{atm\,L^2}{mol^2}\,\frac{1}{atm} - \frac{atm\,L^2/mol^2\,\frac{L}{mol}}{atm}$$

$$\frac{L^3}{mol^3} - \frac{L^3}{mol^3} + \frac{L^3}{mol^3} - \frac{L^3}{mol^3} = 0$$ correcto

Tarea:

El CO_2 de comportamiento real tiene las sig. propiedades

$\delta c = 0.46 \ g/cm^3$

$pc = 78 \ atm$

$Tc = 30.98 \ °C$

Calcular a y b por las 2 alternativas y obtener $\overline{V}$ cuando 1mol de gas se encuentra a 0°C y 60 atm; suponiendo comportamiento Van der Waals