

## Clase 38 6-7 octubre 2014

Título de la nota

07/10/2014

Continuando con el ejercicio de la clase anterior

$n_T = 10 \text{ mol}$  propano y n-butano

$$P_{\text{ideal}} = \frac{nRT}{V} = \frac{(10 \text{ mol})(0.082 \text{ atm L/mol K})(298.15 \text{ K})}{100 \text{ L}} = 2.4448 \text{ atm}$$

Comportamiento tipo Van der Waals

$$\text{Propano } a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} = \frac{27}{64} \frac{(0.082 \text{ atm L/mol K})^2 (369.85 \text{ K})^2}{(41.922 \text{ atm})} = 9.25594 \frac{\text{atm}^2}{\text{mol}^2}$$
$$b = \frac{T_c R}{P_c 8} = \frac{(369.85)(0.082)}{(41.922) 8} = 0.090924 \text{ mol}$$

$$n\text{-Butano } a = 14.273 \text{ atmL}^2/\text{mol}^2$$

$$b = 0.1213 \text{ L/mol}$$

$$a_m = \left[ \sum_{i=1}^n y_i a_i^{1/2} \right]^2 = \left[ 0.5 (9.2559)^{1/2} + 0.5 (14.273)^{1/2} \right]^2$$
$$= 11.62919 \frac{\text{atmL}^2}{\text{mol}^2}$$

$$b_m = \sum_{i=1}^n y_i b_i = \left[ 0.5 (0.09042 \text{ L/mol}) + 0.5 (0.1213 \text{ L/mol}) \right]$$
$$= 0.10586 \text{ L/mol}$$

$$P_{\text{Vander Waals}} = \frac{RT}{\bar{V} - b_m} - \frac{a_m}{\bar{V}^2}$$

$$\bar{V} = \frac{100\text{L}}{10\text{mol}} = 10\text{L/mol}$$

$$= \frac{\frac{0.082\text{ atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} (298.15\text{K})}{(10\text{L/mol}) - (0.10586\text{L/mol})} - \frac{11.62919\text{ atm}\cdot\text{L}^2/\text{mol}^2}{(10\text{L/mol})^2}$$

$$= 2.3547\text{ atm}$$

## Compartimiento tipo Berthelot

propano  $a = \frac{27}{64} \frac{R^2 T_c^3}{P_c} = (a_{\text{vanderWaals}}) T_c = 3423.309409 \frac{\text{atm L}^2 \text{ K}}{\text{mol}^2}$

$b = b_{\text{vanderWaals}} = 0.09092 \text{ L/mol}$

n-Butano  $a = 6068.30868 \frac{\text{atm L}^2 \text{ K}}{\text{mol}^2}$

$b = 0.1213 \text{ L/mol}$

$a_m = 4651.813154 \frac{\text{atm L}^2 \text{ K}}{\text{mol}^2}$

$b_m = 0.10586 \text{ L/mol}$

$$P_{\text{Berthelot}} = \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2 T}$$

$$= \frac{(0.082 \text{ atm L/mol K})(298.15 \text{ K})}{104 \text{ L/mol} - 105864 \text{ L/mol}} - \frac{4651.813154 \text{ atm L}^2/\text{mol}^2 \text{ K}}{(104 \text{ L/mol})^2 (298.15 \text{ K})}$$

$$= 2.3156 \text{ atm}$$

Compartimiento tipo Dieterici

$$\text{propeno} \quad a = 2RT_c \bar{V}_c = 2(0.082 \text{ atm L/mol K})(369.85 \text{ K})(0.20304 \text{ mol})$$
$$= 12.31304 \frac{\text{atm L}^2}{\text{mol}^2}$$

$$b = \frac{\bar{V}_c}{2} = \frac{0.2030 \text{ L/mol}}{2} = 0.1015 \text{ L/mol}$$

n-Butano

$$a = 18.338 \text{ atm L}^2/\text{mol}^2$$

$$b = 0.1315 \text{ L/mol}$$

$$a_m = \left[ \sum_{i=1}^n y_i a_i^{1/2} \right]^2 = \left[ 0.5 (12.31304)^{1/2} + 0.5 (18.338)^{1/2} \right]^2$$
$$= 15.170023 \text{ atm L}^2/\text{mol}^2$$

$$b_m = \sum_{i=1}^n y_i b_i = \left[ 0.5 (0.1015 \text{ L/mol}) + 0.5 (0.1315 \text{ L/mol}) \right] = 0.1165 \text{ L/mol}$$

$$P_{\text{Dieterici}} = \frac{RT e^{-a_m/\bar{V}RT}}{\bar{V} - b_m} = \frac{0.082 \text{ atm L} / (\text{mol K}) (298.15 \text{ K})}{10 \text{ L/mol} - 0.1165 \text{ L/mol}} e^{-\frac{15.1760 \text{ atm L}^2/\text{mol}^2}{(10 \text{ L/mol})(298.15 \text{ K})(0.082 \text{ atm L} / \text{mol K})}}$$

$$= 2.3248 \text{ atm}$$

Presión con la gráfica de  $\bar{z}$  generalizada

$$\text{Calcular } T_{CH} = [0.5 (369.85 \text{ K}) + 0.5 (425.16 \text{ K})] = 397.505 \text{ K}$$

$$\bar{V}_{CH} = [0.5 (0.2030 \text{ L/mol}) + 0.5 (0.2630 \text{ L/mol})] = 0.233 \text{ L/mol}$$

$$P_{CH} = [0.5 (41.922 \text{ atm}) + 0.5 (35.92 \text{ atm})] = 38.923 \text{ atm}$$

## Cálculo de parámetros reducidos

$$T_r = \frac{T_{\text{sis.}}}{T_{cH}} = \frac{298.15K}{397.505K} = 0.75$$

$$V_r = \frac{\bar{V}_{\text{sis}}}{\bar{V}_{cH}} = \frac{10.2 \text{ l/mol}}{0.2334 \text{ l/mol}} = 42.9184$$

Localizando  $Z$  en la gráfica

$$Z \approx 1$$

$$p = \frac{RTZ}{\bar{V}} = 2.4483 \text{ atm}$$



## Conclusiones

el comportamiento del sistema tiende a la idealidad ✓

Si  $V_r$  es muy grande  $Z \approx 1$  (ideal) ✓

Si  $Tr \rightarrow 0$   $Z \approx 1$  (ideal) ✓

## Factor de compresibilidad $Z$

- evolución ecuación de Von der Waals
- gráfica generalizada con parámetros reducidos
- $\frac{\bar{V}_{real}}{\bar{V}_{ideal}} = 1$  (ideal)  $> 1$  repulsión  $< 1$  atracción
- relaciona la ecuación virial y el coeficiente de Fugacidad  $\Phi$

por lo tanto

$$Z = \frac{\bar{P}\bar{V}}{RT} \quad \text{si relacionamos Von der Waals}$$

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

$$Z = \frac{\bar{V}}{RT} \left[ \frac{RT}{\bar{V}-b} - \frac{a}{\bar{V}^2} \right] = \frac{\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}RT} \quad \frac{\bar{V}}{\bar{V}-b} = \frac{1}{1-\frac{b}{\bar{V}}}$$

si se simplifica

$$Z = \frac{1}{1-\frac{b}{\bar{V}}} - \frac{a}{\bar{V}RT}$$

Resolviendo  $\frac{1}{1-\frac{b}{\bar{V}}} = 1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \left(\frac{b}{\bar{V}}\right)^3 \dots$

$$Z = 1 + \frac{b}{\bar{v}} + \left(\frac{b}{\bar{v}}\right)^2 + \dots \left[ -\frac{a}{\bar{v}RT} \right] = 1 + \frac{1}{\bar{v}} \left[ b - \frac{a}{RT} \right] + \frac{b^2}{\bar{v}^2} + \dots$$

por lo tanto si

$$\frac{1}{\bar{v}} = \frac{P}{RTZ}$$

$$Z = 1 + \frac{1}{RTZ} \left[ b - \frac{a}{RT} \right] P + \left[ \frac{b^2}{R^2 T^2 Z^2} \right] P^2 + \dots$$

a presiones bajas  $Z \rightarrow 1$  (ideal) y se simplifica

$$Z = 1 + \frac{1}{RT} \left[ b - \frac{a}{RT} \right] P + \dots$$

por lo tanto  $Z = f(T, P)$

sí

$$\left( \frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left[ b - \frac{a}{RT} \right]$$

Segundo coeficiente virial

Implicaciones  $b - \frac{a}{RT} = 0$  para originar la  $T_B$  (Temp. de Boyle)

$$b - \frac{a}{RT_B} = 0 \therefore T_B = \frac{a}{bR}$$

de esta forma se obtiene  $(z = \frac{P\bar{V}}{RT})$

$$P\bar{V} = RT \left[ 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \frac{D(T)}{\bar{V}^3} \dots \right]$$

Ecuación de  
Kammerligh - Onnes

$$z = \left[ 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \frac{D(T)}{\bar{V}^3} \dots \right]$$

ecuación  
Función

se transforma

de Temperatura

$$\frac{1}{\bar{V}} = \frac{P}{RTz} \quad z = 1 \text{ (ideal)}$$

$$Z = 1 + B'P + C'P^2 + D'P^3$$

$$B' = \frac{B}{RT} \quad C' = \frac{(C-B)^2}{R^2 T^2} \quad D' = \frac{D - 3BC - 2B^3}{R^3 T^3}$$

Interacciones  
moleculares

checondo unidades

$$B = \text{L/mol} \quad C = (\text{L/mol})^2 \quad D = (\text{L/mol})^3$$

$$B' = \text{atm}^{-1} \quad C' = \text{atm}^{-2} \quad D' = \text{atm}^{-3}$$

## Checando unidades

$$B' = \frac{B}{RT} = \frac{\cancel{\text{L/mol}}}{\frac{\text{atm L}}{\cancel{\text{mol K}}}} = \text{atm}^{-1} \checkmark$$

$$C' = \frac{C - B^2}{R^2 T^2} = \frac{(\cancel{\text{L/mol}})^2 - (\cancel{\text{L/mol}})^2}{\left(\frac{\text{atm L}}{\cancel{\text{mol K}}}\right)^2 \cancel{\text{K}^2}} = \text{atm}^{-2} \checkmark$$

$$D' = \frac{D - 3BC - 2B^3}{R^3 T^3} = \frac{(\cancel{\text{L/mol}})^3 - 3(\cancel{\text{L/mol}})(\cancel{\text{L/mol}})^2 - 2(\cancel{\text{L/mol}})^3}{\left(\frac{\text{atm L}}{\cancel{\text{mol K}}}\right)^3 (\cancel{\text{K}})^3} = \text{atm}^{-3} \checkmark$$



de esta forma

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{1}{\bar{V}} \left[ b - \frac{a}{RT} \right] \dots \dots$$

La  $T_B$  será cuando el segundo coeficiente virial sea 0

$$P\bar{V} = RT \left\{ 1 + \frac{1}{\bar{V}} \left[ b - \frac{a}{RT} \right] \right\}$$

$$T_B = \frac{a}{bR} = \frac{27 T_c}{8}$$

$$T_B = \frac{\frac{27}{64} \frac{R^2 T_c^2}{P_c}}{\frac{RT_c}{8 P_c} R} = \frac{27}{64} 8 T_c$$

por lo tanto con la  $T_B$  es posible calcular  $a$  y  $b$  de Van der Waals.

Ejercicio

Calcular  $a$  y  $b$  de un gas real a  $0^\circ\text{C}$  y  $1\text{atm}$  si la  $T_B = 107\text{K}$ , bajo estas

condiciones  $Z = 1.00054$

Respuesta : utilizar

$$Z = 1 + \frac{1}{RT} \left[ b - \frac{a}{RT} \right] p$$

$$T_B = \frac{a}{bR}$$

$$a = T_B b R$$

$$a = (107\text{K}) \left( \frac{0.082 \text{ atm L}}{\text{mol K}} \right) (b)$$

$$a = 8.774 \frac{\text{atm L}}{\text{mol}} b$$

Substituer

$$1.00054 = 1 + \frac{1}{\left( \frac{0.082 \text{ atm L}}{\text{mol K}} \right) (273.15\text{K})} \left[ b - \frac{8.774 \frac{\text{atm L}}{\text{mol}} b}{\left( \frac{0.082 \text{ atm L}}{\text{mol K}} \right) (273.15\text{K})} \right] \text{ atm}$$

despejando  $b$  y realizando análisis dimensional (2 adimensional)

$$1.00054 = 1 + \left\{ \frac{1}{\left(\frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}\right) \cancel{(\text{K})}} \left[ \frac{\cancel{\text{L}}}{\cancel{\text{mol}}} - \frac{\cancel{\text{atm}} \cdot \cancel{\text{L}}^2}{\cancel{\text{mol}} \cdot \cancel{\text{K}}^2} \right] \cancel{\text{atm}} \right\}$$
$$\left\{ \frac{\text{atm} \cdot \text{mol} \cdot \text{L}}{\text{atm} \cdot \text{L} \cdot \text{mol}} - \frac{\text{atm}^2 \cdot \text{K}^2 \cdot \text{L}}{\text{atm}^2 \cdot \text{K}^2 \cdot \text{L}} \right\} \text{OK}$$

adimensional

Resolviendo

$$b = 0.01988 \text{ L/mol}$$

por lo tanto  $a = T b R$

$$a = (107 \text{ K})(0.01988 \text{ L/mol})\left(0.082 \frac{\text{atm L}}{\text{mol K}}\right)$$

$$a = 0.1714 \frac{\text{atm L}^2}{\text{mol}^2}$$

Se pueden evaluar otras temperaturas para determinar como cambia  $Z$

$T(K)$	$Z$
53	0.995388
107	1.0000
190	1.00055
273.15	1.00054
546	1.00038

La  $T_c$  del gas debe ser  $< T_B$  ✓

Se observa que a  $T < T_B$   
el gas posiblemente  
comienza a condensar ✓

El gas a medida que aumenta  $T$   
tiene un valor máximo alrededor de  
190 K ✓

