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ALGEBRAIC RELATIONS FOR PROPERTY-COMPOSITION CURVES OF BINARY MIXTURE

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Application of the Dimension Principle to an appropriate equation of state gives these relations by a purely formal method. Using the equation of van der Waals: (1)

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \quad (1)$$

one gets thus for V of vapor (2) or liquid phase (3):

$$\text{Dim }[V] = b \qquad \overline{V} = \overline{v}_1 y^2 + ky(1-y) + \overline{v}_2(1-y)^2 \quad (2) \quad y\text{: molefraction}$$

$$V = v_1x^2 + Kx(1-x) + v_2(1-x)^2 \quad (3) \quad x\text{: " "}$$

(at const. T)

of first component and $\overline{v}_1$ $\overline{v}_2$ or v_1 v_2 volumes of pure components. For a binary mixture the volume is a function of second degree in y or x. The constants k and K must be found with help of Thermodynamics or Statistics. For P one gets:

$$\text{Dim }[P] = \frac{a}{b^2} \text{ and thus: } P = \frac{a_1 x^2 + A_p x(1-x) + a_2(1-x)^2}{[b_1x^2 + Bx(1-x) + b_2(1-x)^2]^2} \quad (4)$$

(at const. T)

$$\text{For } x=1 \therefore P = P_1 \therefore a_1 = b_1^2P_1$$

$$\text{" } x=0 \therefore P = P_2 \therefore a_2 = b_2^2P_2$$

where P_1 and P_2 are the vaporpressures and b_1 and b_2 the values for the components, calculated by the additivity rules of van Laar (Zustandsgleichung, 1931) from the b values of the elements. B is found from:

$$B = 2\, b_{12} \text{ and } 2\sqrt[3]{b_{12}} = \sqrt[3]{b_1} + \sqrt[3]{b_2}\ .$$

A_p can be found from thermodynamics, as shown below. For T one has:

$$\text{Dim }[T] = \frac{a}{b} \quad \text{and thus: } T = \frac{\overline{a}_1 x^2 + A_t x(1-x) + \overline{a}_2(1-x)^2}{b_1x^2 + Bx(1-x) + b_2(1-x)^2} \quad (5)$$

(at const. P)

$$\left.\begin{aligned}\text{For } x=1 \therefore T = T_1 \therefore \overline{a}_1 = b_1T_1\\ \text{" } x=0 \therefore T = T_2 \therefore \overline{a}_2 = b_2T_2\end{aligned}\right\}$$

where T_1 and T_2 are the boiling points for the components.

A_p can be found - at low pressure and temperature - from the Gibbs-Duhem relation:

$$x\, p_2\, p_1' + (1-x)\, p_1\, p_2' = 0 \qquad \text{where } p_2 = \text{Partial Pressure of components.}$$

Writing for these:

$$p_1 = \frac{a_1 x^2 + A_1 x(1-x)}{[b_1x^2 + Bx(1-x) + b_2(1-x)^2]^2} \qquad p_2 = \frac{a_2(1-x)^2 + A_2 x(1-x)}{[b_1x^2 + Bx(1-x) + b_2(1-x)^2]^2}$$

where $P = p_1 + p_2$ and $A_p = A_1 + A_2$.

and using the fact, that one has for many mixtures:

$$p_1 = p_2 \quad \text{for} \quad \bar{x} = \frac{P_2}{P_1 + P_2}$$, the Gibbs-Duhem

relation gives:

$$\bar{x}\, p_1' + (1-\bar{x})\, p_2' = 0 \qquad \text{and}$$

$$a_1 \bar{x}^2 + A_1 \bar{x}(1-\bar{x}) = a_2 (1-\bar{x})^2 + A_2 \bar{x}(1-\bar{x})$$

so that:

$$\left.\begin{array}{l} \bar{x}[1-2\bar{x} - m\bar{x}(1-\bar{x})]\, A_1 = a_2(1-\bar{x})^2 - a_1\bar{x}^2(1-m\bar{x}) \\ (1-\bar{x})\,[1-2\bar{x} - m\bar{x}(1-\bar{x})]\, A_2 = a_2(1-\bar{x})^2(1+m\bar{x}) - a_1\bar{x}^2 \end{array}\right\} \bar{x} = \frac{P_2}{P_1+P_2}$$

where $m[b_1\bar{x}^2 + B\bar{x}(1-\bar{x}) + b_2(1-\bar{x})^2] = 4b_1\bar{x} + 2B(1-2\bar{x}) - 4b_2(1-\bar{x})$.

Thus $A_p = A_1+A_2$ is found for the P-x curve. From

$$p_1 = yP \quad \text{one gets then:} \quad y = \frac{a_1 x^2 + A_1 x(1-x)}{a_1 x^2 + A_p x(1-x) + a_2(1-x)^2}$$

and thus $y = f(x)$ is found at const. T.

In order to find A_t for the T-x curve (P const.), one starts from the P-x curve, which is applied at:

$$2\tilde{T} = T_1 + T_2 \quad \text{and} \quad \tilde{P} = 1 \text{ atm.}$$

As $A_{\tilde{p}}$ at this $\tilde{T}$ and $\tilde{P}$ can be calculated, one finds the value of $\tilde{x}$ belonging to this $\tilde{T}$ and introduction of this $\tilde{x}$ into (5) gives then A_t.

These functions can then be applied to other thermodynamic relations. For the Heat of Evaporation, L, one has:

$$L = RT^2 \frac{\partial(\text{luP})}{\partial T}$$

and this becomes:

$$L = RT^2 \frac{a_1' x^2 + A_p' x(1-x) + a_2'(1-x)^2}{a_1 x^2 + A_p x(1-x) + a_2(1-x)^2}$$

where:

$$A_p' = \frac{\partial A_p}{\partial T} \quad \text{and} \quad a_n' = \frac{\partial a_n}{\partial T}$$

The Dimension Principle can also be applied to other properties, like Heatextension, Viscosity, etc.

For 1 Butene, n Butane -- for which Sage and Lacey gave experimental P-x and y-x values [Ind. Eng. Chem. 40, 1299 (1948)], one finds with:

$b_1 = 0.00512 \qquad b_2 = 0.0054 \qquad B = 0.010496 \qquad \bar{x} = 0.4518$

$A_1 = 0.09501 \qquad A = 0.1654$

so that

at 100^oF: $$P_{(min)} = \frac{-0.00297x^2+0.01006x+0.07767}{[0.000024x^2-0.000304x+0.0054]^2} \qquad y = \frac{-0.01025x^2+0.09501x}{-0.00297x^2+0.01006x+0.7767}$$

1 - Butene:	P exp.	P calc.	y exp.	y calc.
x	lb/sq.in.			
0	51.5			
0.3	55	55.1	0.337	0.34
0.5	57.4	57.3	0.537	0.58
0.7	59.6	59.6	0.728	0.74
1	62.5			