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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)

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

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

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

$$V = v_1 x^2 + Kx(1-x) + v_2(1-x)^2 \quad (3) \quad x: \quad " \quad "$$

(at const. T)

of first component and \bar{v}_1 , \bar{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:

$$\text{Dim } [P] = \frac{a}{b^2} \quad \text{and thus: } P = \frac{a_1 x^2 + A_p x(1-x) + a_2(1-x)^2}{[b_1 x^2 + Bx(1-x) + b_2(1-x)^2]^2} \quad (4)$$

(at const. T)

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

$$" \quad x=0 \therefore P = P_2 \therefore a_2 = b_2^2 P_2$$

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:

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

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

$$\text{Dim } [T] = \frac{a}{b} \quad \text{and thus: } T = \frac{\bar{a}_1 x^2 + A_t x(1-x) + \bar{a}_2(1-x)^2}{b_1 x^2 + Bx(1-x) + b_2(1-x)^2} \quad (5)$$

(at const. P)

$$\text{For } x=1 \therefore T = T_1 \therefore \bar{a}_1 = b_1 T_1$$

$$" \quad x=0 \therefore T = T_2 \therefore \bar{a}_2 = b_2 T_2$$

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:

$$x p_2 p'_1 + (1-x) p_1 p'_2 = 0 \quad \text{where } p_2 = \text{Partial Pressure of components.}$$

Writing for these:

$$p_1 = \frac{a_1 x^2 + A_1 x(1-x)}{[b_1 x^2 + Bx(1-x) + b_2(1-x)^2]^2} \quad p_2 = \frac{a_2(1-x)^2 + A_2 x(1-x)}{[b_1 x^2 + Bx(1-x) + b_2(1-x)^2]^2}$$

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

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

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

relation gives:

$$\bar{x} p'_1 + (1-\bar{x}) p'_2 = 0 \quad \text{and}$$

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

so that:

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

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

$$P_1 = y^P \quad \text{one gets then:} \quad y = \frac{a_1 x^2 + A_1 x (1-x)}{a_1 x^2 + A_p x (1-x) + a_2 (1-x)^2}$$

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_p at this \tilde{T} and \tilde{P} can be calculated, one finds the value of \tilde{x} belonging to this 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:

$$L = RT^2 \frac{\partial(\ln P)}{\partial T}$$

and this becomes:

$$L = \frac{RT^2 a'_1 x^2 + A'_p x (1-x) + a'_2 (1-x)^2}{a_1 x^2 + A_p x (1-x) + a_2 (1-x)^2}$$

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 Heat extension, 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:

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

$$A_1 = 0.09501 \quad A = 0.1654$$

so that

$$\text{at } 100^\circ\text{F:} \quad P = \frac{-0.00297x^2 + 0.01006x + 0.07767}{[0.000024x^2 - 0.00304x + 0.0054]^2} \quad y = \frac{-0.01025x^2 + 0.09501x}{-0.00297x^2 + 0.01006x + 0.07767}$$

<u>1 - Butene:</u> <u>x</u>	<u>P exp.</u>	<u>P calc.</u>	<u>y exp.</u>	<u>y calc.</u>
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			