Studies on the P-V-T Relations of Fluids at High Pressure III

The factor ξ is given by :

$$\xi = 1 + (1/4) [\alpha_n \mu_p^{*2} / (r_o)_n^3] (\varepsilon_p / \varepsilon_n)^{1/2}, \tag{5}$$

in which α_n is the polarizability of the non-polar molecule ($\alpha_n = 1.76$ Å³ for nitrogen and 0 Å³ for argon) and $\mu_p^* = \mu_p / [\varepsilon_p(r_o)_p^3]^{1/2}$.

The numerical tables of the reduced second virial coefficient B^* had been given in the literature⁶⁾ for each potential function by :

 $B(T)=b_{\circ} B^{*}(T^{*})$, for the Lennard-Jones (12-6) potential;

 $B(T) = b_{\circ}B^{*}(T^{*}, t^{*})$, for the Stockmayer potential;

where $T^* = kT/\varepsilon$ and $t^* = 8^{1/2} \mu_p^{*2}$.

The theoretical values of the second virial coefficients for each pure gas were obtained by the use of the above values of the force constants and the tables of B^* . For the mixtures, they were obtained by the use of the following relation:

$$B_{mix} = x_n^2 B_n + 2x_n x_p B_{np} + x_p^2 B_p \tag{6}$$

where B_{mix} is the second virial coefficient for the mixture, B_n and B_p are the second virial coefficients calculated for each pure component of non-polar or polar molecule, B_{np} is the second virial coefficient in regard to the interaction between non-polar and polar molecules, and x_n and x_p are the mole fractions of non-polar and polar components in the mixture, respectively.

The results for the comparison are shown in Table 5 and graphically in Fig. 1. There exist the differences between the experimental and the values calculated theoretically for these binary systems from 0.05 to 9.9 cc/mol. However, it was estimated that these values of B_{exp} for the gradients of the isotherms at zero pressure had some uncertainties of which the quantities would be the same order as the above differences. From this viewpoint, it can be said that both the experimental and the calulated values of the second virial coefficients were in agreement with each other for these binary systems.

| | B, cc/mol | | Difference |
|--|---------------------------|-----------------------|---|
| Composition, mol% | Experimental $B_{ m epx}$ | Calculated B_{calc} | $B_{\rm exp} - B_{\rm calc},$ cc/mol |
| 100% Ar | - 11.24 | - 11.19 | 0.05 |
| 100% N2 | - 0.37 | - 0.27 | 0.10 |
| 100% NH ₃ | - 217.2 | - 207.3 | 9.9 |
| 91.8% Ar — 8.2% NH ₃ | - 17.48 | - 16.13 | 1.35 |
| 83.9% Ar - 16.1% NH ₃ | - 22.96 | - 22.33 | 0.63 |
| 63.5% Ar – 36.5% NH ₃ | - 43.97 | - 47.67 | - 3.70 |
| 87.3% N ₂ - 12.7% NH ₃ | - 8.20 | - 11.48 | - 3.28 |
| 77.0% N ₂ — 23.0% NH ₃ | - 21.9 | - 23.79 | - 1.9 |
| 62.3% N ₂ - 37.7% NH ₃ | - 47.9 | - 46.35 | 1.5 |

| Table 5 | Comparison of second virial | coefficient for | argon-ammonia | and nitrogen-ammonia |
|---------|-----------------------------|-----------------|---------------|----------------------|
| | mixture systems at 50°C | | | |

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