Notes

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THE RELATION BETWEEN THE VOLUME VIRIAL COEFFICIENTS AND THE PRESSURE VIRIAL COEFFICIENTS

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A simple method is presented for obtaining the relations between the volume virial coefficients and the pressure virial coefficients. The first six volume (pressure) coefficients as a function of pressure (volume) coefficients are given.

The virial equation of state in powers of the density is written in the form:

$$Z=\frac{Pv}{RT} = 1 + \sum_{j=1} A_j v^{-j} \tag{1}$$

where $v=\frac{V}{n}$

is the molecular volume. An entirely anologous to (1) expression in which the pressure is substituted for the density is as follows:

$$Z=\frac{Pv}{RT} = 1 + \sum_{k=1} B_k P^k \tag{2}$$

The coefficients A_1, A_2,... and B_1, B_2,... are functions of the temperature only, and the forms of these functions depend on the types of intermolecular forces in the gas. The series (2) is mathematically equivalent to the series (1) and the coefficients of the two series are uniquely related to each other.

Several procedures[1-6] have been proposed to derive the relations between the coefficients of (2) and those of (1). Despite the simplicity of a recently proposed method,[6] it is still quite tedious for one to obtain relations between the higher terms of (1) and (2). It is the purpose of this note to present a very simple and straightforward method for obtaining these relations.

Eq. (1) can be solved with respect to P:

$$P=\frac{RT}{v} \left(1 + \sum_{j=1} A_j v^{-j}\right) \tag{3}$$

By equating the right-hand sides of Equations (1) and (2) we obtain:

$$\sum_{j=1} A_j v^{-j} = \sum_{k=1} B_k P^k \tag{4}$$

Substituting equation (3) into (4), the last is transformed as follows:

$$\sum_{j} A_j v^{-j} = \sum_{k} B_k (RTv^{-1})^k (1 + \sum_{j} A_j v^{-j})^k \tag{5}$$

By grouping the terms of the same power in v on the right hand side of equation (5) and equating them with the corresponding terms on the left hand side of equation (5) we can obtain the relation we are looking for. The term $(1 + \sum_{J} A_j v^{-j})^k$

of equation (5) can be expanded using the well known formula of polynomial expansion:

$$(\beta_1 + \beta_2 + \ldots + \beta_m)^\lambda = \sum \frac{\lambda!}{\lambda_1! \, \lambda_2! \ldots \lambda_m!} \beta^{\lambda}{}_1 \beta^{\lambda}{}_2 \ldots \beta^{\lambda}{}_m \tag{6}$$

where the summation includes all different combinations of $\lambda_1, \lambda_2, \ldots \lambda_m$ with $\sum_{i=1} \lambda_i = \lambda$

and λ_i and λ are all integrals.

As an example we apply equation (5) in combination with formula (6) for $j = k = 6$:

$$\frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots = B_1 \frac{RT}{v} \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right) +$$

$$+ B_2 \left(\frac{RT}{v}\right)^2 \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right)^2 + \ldots \tag{7}$$

$$+ B^6 \left(\frac{RT}{v}\right)^6 \left(1 + \frac{A_1}{v} + \frac{A_2}{v^2} + \ldots + \frac{A_6}{v^6} + \ldots\right)^6 + \ldots$$

From equation (7) we obtain:

$$B_1 = \frac{A_1}{RT}$$

$$B_2 = \frac{A_2 - A^2{}_1}{(RT)^2} \tag{8}$$

$$B_3 = \frac{A_3 - 3A_1A_2 + 2A^3{}_1}{(RT)^3}$$

$$B_4 = \frac{A_4 - 4A_1A_3 + 10A^2{}_1A_2 - 5A^4{}_1 - 2A^2{}_2}{(RT)^4}$$

$$B_5 = \frac{A_5 - 5A_1A_4 - 5A_2A_3 + 15A_1A^2{}_2 + 15A^2{}_1A_3 - 35A^3{}_1A_2 + 14A^5{}_1}{(RT)^5}$$

$$B_6 = \frac{\dfrac{A_6 - 6A_1A_5 - 6A_2A_4 + 42A_1A_2A_3 + 21A^2{}_1A_4 - 84A^2{}_1A^2{}_2 - 56A^3{}_1A_3 + }{126A^4{}_1A_2 - 42A^6{}_1 + 7A^3{}_2 - 3A^2{}_3}}{(RT)^6} \qquad (8)$$

An interesting observation concerning the numerical coefficients of the numerators in the expressions (8), is that their algebraic sum in each term (with the obvious exception of the first term, B_1) is zero.

The relations (8) can be inverted to give:

$$A_1 = RTB_1$$
$$A_2 = (RT)^2 (B_2 + B^2{}_1)$$
$$A_3 = (RT)^3 (B_3 + 3B_1B_2 + B^3{}_1)$$
$$A_4 = (RT)^4 (B_4 + 4B_1B_3 + 6B^2{}_1B_2 + B^4{}_1 + 2B^2{}_2)$$
$$A_5 = (RT)^5 (B_5 + 5B_1B_4 + 5B_2B_3 + 10B_1B^2{}_2 + 10B^2{}_1B_3 + 10B^3{}_1B_2 + B^5{}_1)$$
$$A_6 = (RT)^6 (B_6 + 6B_1B_5 + 6B_2B_4 + 30B_1B_2B_3 + 20B^3{}_1B_3 + 15B^2{}_1B_4 + 30B^2{}_1B^2{}_2 + 15B^4{}_1B_2 + B^6{}_1 + 5B^3{}_2 + 3B^2{}_3)$$

The first four terms given in Eqs. (8) are in exact agreement with the results given by L. Epstein,[2,3] W. Putman — E. Kilpatrick[4] and S. Vassiliadou-Athanassiou — Th. Yannakopoulos.[6]

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Περίληψις

Ἡ σχέσις μεταξὺ τῶν συντελεστῶν virial ὄγκου καὶ συντελεστῶν virial πιέσεως.

Παρουσιάζεται μέθοδος συσχετίσεως τῶν συντελεστῶν virial ὄγκου καὶ τῶν συντελεστῶν virial πιέσεως. Ἂν καὶ ἡ μέθοδος στερεῖται μαθηματικῆς κομψότητος καὶ δὲν δίδονται γενικοὶ ὅροι, ἐν τούτοις εἶναι ἁπλουστέρα τῶν ἤδη ὑπαρχουσῶν μεθόδων καὶ ἔχει πρακτικὴν σημασίαν. Ὡς παράδειγμα ἐφαρμογῆς παράγονται οἱ πρῶτοι ἕξ (συμβατικῶς ἑπτὰ) συντελεσταὶ virial ὄγκου ὡς συνάρτησις τῶν συντελεστῶν virial πιέσεως.

References and Notes

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