THE VIRIAL COEFFICIENTS OF A GAS MIXTURE

By J. S. Rowlinson, F. H. Sumner and J. R. Sutton

Dept. of Chemistry, University of Manchester

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A simple expression is proposed for calculating the virial coefficients of a gas mixture from those of the pure components. A third virial coefficient is computed numerically and compared with this and with two other approximations which, on the whole, are not as satisfactory. Approximate values of this third virial coefficient, which were used earlier in interpreting the solubility of a solid in a compressed gas, are very close to values computed directly and so need no revision.

1. INTRODUCTION

The thermodynamic properties of a mixture of imperfect gases can be expressed by the coefficients of the virial equation of state,[1]

$$pV/RT = 1 + B/V + C/V^2 + \ldots, \tag{1.1}$$

$$B = \sum_i \sum_j x_i x_j B_{ij},$$

$$C = \sum_i \sum_j \sum_k x_i x_j x_k C_{ijk}, \tag{1.2}$$

where x_i is the mole fraction of the ith species. For convenience we denote B by A_2, C by A_3, B_{ij} by A_2^{ij}, etc. The usual object of theories of solutions is the expression of the excess thermodynamic properties in terms of properties of the pure components, and parameters characterizing the various intermolecular energies. For a gas mixture, this problem becomes that of expressing A_n^{ijk--} in terms of A_n^{ii--} (or A_n^{jj--}, etc.) and the parameters of the ii, ij, etc. interactions. A partial solution of this problem is obtained here for gas mixtures whose inter-molecular energies may all be written

$$u_{ij} = a_{ij}\epsilon \, g(b_{ij}\sigma/r_{ij}), \tag{1.3}$$

where a_{ij} and b_{ij} are pure numbers, where g denotes a function common to all interactions, and where ϵ and σ are parameters of energy and distance characteristic of one interaction for which $a_{11} = b_{11} = 1$. Species 1 will be taken as a reference species.

2. THE FIRST APPROXIMATIONS

An exact solution for the second virial coefficient can be written thus,[2]

$$B_{ij}[T] = b_{ij}^3 B_{11}[T/a_{ij}]. \tag{2.1}$$

Although there is no corresponding expression for the higher coefficients, a solution may be obtained if all the a_{ij} and b_{ij} are close to unity. Longuet-Higgins[3] has calculated the free energy of such a mixture from which the equation of state is readily obtained,

$$\frac{pV}{RT} = 1 + \sum_{n=2} \frac{A_n^{11--}}{V^{n-1}} \left\{ 1 + \sum_i \sum_j x_i x_j \left[3(n-1)(b_{ij}-1) - \frac{d \ln A_n^{11--}}{d \ln T}(a_{ij}-1) \right] \right\}. \tag{2.2}$$

This is equivalent to putting

$$A_n^{ij--} = A_n^{11--} + \frac{2}{n(n-1)} \left[3(n-1)A_n^{11--} \sum (b_{pq}-1) - \frac{dA_n^{11--}}{d \ln T} \sum (a_{pq}-1) \right], \tag{2.3}$$

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where pq are all possible combinations in pairs of the interactions i, j, etc., represented in this coefficient. The number of pair combinations in any A_n^{ij--} is $n(n-1)/2$. The dimensions of this coefficient are $3(n-1)$, the factor which multiplies the parameters $(b_{pq}-1)$. There are $[(N+n-1)!/n!\,(N-1)!]$ coefficients of order n in a mixture of N components. This is the first approximation to A_n^{ij--} that is, it is correct to the first derivatives in Taylor's expansion

$$A_n^{ij--} = A_n^{11--} + \sum \left\{ \left(\frac{\partial A_n^{ij--}}{\partial a_{pq}}\right)_0 (a_{pq}-1) + \left(\frac{\partial A_n^{ij--}}{\partial b_{pq}}\right)_0 (b_{pq}-1) \right\} + \ldots, \quad (2.4)$$

where the subscript 0 is used to show that the derivatives are to be taken where all $a_{pq}=b_{pq}=1$. Eqn. (2.3) will be called approximation (a).

However, this is not an ideal solution to the problem. This approximation is difficult to use practically, as it expresses the coefficient not only as a function of A_n^{11--}, but also of its temperature derivative. Moreover it does not give exactly the simple result,

$$A_n^{ij--}[T] = (b_{jj})^{3(n-1)} A_n^{11--}[T/a_{jj}]. \quad (2.5)$$

This equation, a consequence of the principle of corresponding states, holds for all values of a_{jj} and b_{jj}. A better approximation might therefore be one which gives correctly the first-order terms of (2.4) and yet satisfies (2.5) exactly. Such an approximation is

$$A_n^{ij--}[T] = (\Pi b_{pq})^{6/n} A_n^{11--}[T/(\Pi a_{pq})^{2/n(n-1)}]. \quad (2.6)$$

This is called approximation (b). It is obvious that it satisfies (2.5). We now show that it gives the correct derivatives in (2.4).

Each virial coefficient is a sum of one or more irreducible cluster integrals of the type

$$\beta_m^{ij--} = V^{-1} \int \ldots \int \Pi f_{pq} \mathrm{d}\mathbf{r}_i \mathrm{d}\mathbf{r}_j \ldots, \quad (2.7)$$

$$f_{pq} = \exp(-u_{ij}/kT) - 1, \quad (2.8)$$

where there are m terms in the product and m lies in the range $n \leqslant m \leqslant n(n-1)/2$, except for $n=2$ when $m=1$ only. The derivatives of the cluster integral with respect to any two of the parameters occurring in it are

$$\left(\frac{\partial \beta_m}{\partial a_{st}}\right)_0 = V^{-1} \int \ldots \int \left(\frac{u_{st}^\circ}{kT}\right) \exp\left(\frac{-u_{st}^\circ}{kT}\right) \Pi' f_{pq} \mathrm{d}\mathbf{r}_i \, \mathrm{d}\mathbf{r}_j \ldots, \quad (2.9)$$

$$\left(\frac{\partial \beta_m}{\partial b_{st}}\right)_0 = V^{-1} \int \ldots \int \left(\frac{\epsilon\sigma}{kTr_{st}}\right) g'\left(\frac{\sigma}{r_{st}}\right) \exp\left(\frac{-u_{st}^\circ}{kT}\right) \Pi' f_{pq} \mathrm{d}\mathbf{r}_i \, \mathrm{d}\mathbf{r}_j \ldots, \quad (2.10)$$

where the suffix $^\circ$ shows that all parameters within the integral sign are to be put equal to unity, and where g' denotes differentiation with respect to σ/r. The term f_{st} is omitted from the products. These derivatives are independent of the choice of s and t. If now the first approximation to β_m is defined by

$$\beta_m^{ij--}[T] = (\Pi b_{pq})^{1/m} \beta_m^{11--}[T/(\Pi a_{pq})^{1/m}], \quad (2.11)$$

then its derivatives are given correctly by (2.9) and (2.10). All coefficients above the third are composed of more than one cluster integral. As it is not convenient to apply (2.11) to each one separately, according to its value of m, it is fortunate that the numbers of each type in any coefficient are such [4] that the correct result is also obtained by applying (2.6) to the whole virial coefficient. (There is reason to believe that the simplification introduced by this last step is only valid for the first derivatives of Taylor's expansion. If the higher terms are needed it will probably be necessary to consider each cluster integral separately.)

3. THE DIRECT CALCULATION OF C_{112}

Approximations (a) and (b) are tested by calculating a third virial coefficient, by numerical integration, for the potential

$$u_{ij} = 4a_{ij}\epsilon[(b_{ij}\sigma/r_{ij})^{12} - (b_{ij}\sigma/r_{ij})^6], \quad kT/\epsilon = \tau. \tag{3.1}$$

The coefficient is given by

$$C_{ijk} = \frac{8\pi^2 N^2}{3} \int \int \int f_{ij}f_{jk}f_{ki}r_{ij}r_{jk}r_{ki}\mathrm{d}r_{ij}\mathrm{d}r_{jk}\mathrm{d}r_{ki}, \tag{3.2}$$

where the integration is taken over all r_{ij}, etc., which form a triangle. Kihara [5, 6] has shown that, for a pure gas, such an integral can be expressed as a power series in $\tau^{-\frac{1}{2}}$. The range of integration in (3.2) may be divided into three parts, in each of which one of the distances r_{ij} is equal or larger than the other two. Kihara's expansion may be used for each part separately, and the three series added to give

$$C_{ijk} = v_0^2 \sum_{n=0} c_n \tau^{-(n+1)/2}, \tag{3.3}$$

$$v_0 = (2/3)\pi N\sigma^3, \tag{3.4}$$

$$c_n = -\frac{2^{n-1}}{n!} \Gamma\left(\frac{n-1}{2}\right) \int_0^{3/4} \int_{1-(1-y^2)^{\frac{1}{2}}}^{(1-y^2)^{\frac{1}{2}}} \sum_{ijk} G_n{}^i \mathrm{d}x\,\mathrm{d}y^2, \tag{3.5}$$

$$G_n{}^i = \begin{bmatrix} \left(\sum_{stu} \lambda_s\right)^{(1-n)/2} \left(\sum_{stu} \mu_s\right)^n \\ -\sum_{stu} (\lambda_s + \lambda_t)^{(1-n)/2} (\mu_s + \mu_t)^n \\ +\sum_{stu} \lambda_s^{(1-n)/2} \mu_s^n \end{bmatrix} \tag{3.6}$$

$$\lambda_s = a_{st}(b_{st}X_{iu})^{12}, \tag{3.7}$$
$$\mu_s = a_{st}(b_{st}X_{iu})^6,$$

where, for clarity, the subscript i has been suppressed in λ and μ,

$$X_{ii} = X_{jj} = X_{kk} = 1, \tag{3.8}$$
$$X_{ij} = X_{jk} = X_{ki} = [x^2 + y^2]^{-\frac{1}{2}}, \tag{3.9}$$
$$X_{ji} = X_{kj} = X_{ik} = [(1-x)^2 + y^2]^{-\frac{1}{2}}. \tag{3.10}$$

The dummy subscripts s, t and u are to be replaced by i, j and k, taken in cyclic order. A check on the algebra is provided by differentiating c_n when

$$\left(\frac{\partial c_n}{\partial a_{ij}}\right)_0 = \left(\frac{n+1}{6}\right)(c_n)_0, \tag{3.11}$$

$$\left(\frac{\partial c_n}{\partial b_{ij}}\right)_0 = \frac{1}{3}(c_n)_0, \tag{3.12}$$

as required by (2.3). The term c_1 needs special consideration [5] as (3.5) is indeterminate for that value.

The coefficient C_{112} was calculated from (3.3)-(3.10), when $a_{11} = b_{11} = 1$ and $a_{12} \geqslant 1$, $b_{12} \geqslant 1$. That is we calculated the coefficient for the interaction of a large molecule with two smaller ones. This particular coefficient occurs in

the expression for the solubility of a pure solid in a compressed gas.[7] The seven pairs of parameters chosen were, dropping the subscripts from a_{12} and b_{12}: $a = b^3 = 1$; $a = 3/2, b^3 = 1$; $a = 2, b^3 = 1$; $a = 1, b^3 = 3/2$; $a = 1, b^3 = 2$; $a = b^3 = 3/2$; and $a = b^3 = 2$. The temperature derivative $\tau(dC_{111}/d\tau)$ was calculated by differentiating (3.3). The summation was taken to $n = 20$. The integration over x and y^2 was carried out on the Manchester University electronic

TABLE 1.—THE COEFFICIENTS c_n

n	0	1	2	3	4
c_n (this work)	$+ 1{\cdot}7293$	$- 3{\cdot}1944$	$+ 1{\cdot}5139$	$+ 0{\cdot}9490$	$+ 0{\cdot}4210$
c_n (Kihara)	$+ 1{\cdot}729$	$- 3{\cdot}203$	$+ 1{\cdot}519$	$+ 0{\cdot}958$	$+ 0{\cdot}429$
c_n (Bergeon)	$+ 1{\cdot}7288$	$- 3{\cdot}1910$	$+ 1{\cdot}4881$	$+ 0{\cdot}9478$	$+ 0{\cdot}5791$

5	6	7	8	9	10
$+ 0{\cdot}05053$	$- 0{\cdot}1490$	$- 0{\cdot}2189$	$- 0{\cdot}2124$	$- 0{\cdot}1723$	$- 0{\cdot}1253$
$+ 0{\cdot}059$	$- 0{\cdot}140$	$- 0{\cdot}210$	$- 0{\cdot}205$	$- 0{\cdot}168$	$- 0{\cdot}123$
$+ 0{\cdot}03101$	—	—	—	—	—

11	12	13	14	15	16
$- 0{\cdot}0842$	$- 0{\cdot}0553$	$- 0{\cdot}0313$	$- 0{\cdot}0185$	$- 0{\cdot}0103$	$- 0{\cdot}00556$
$- 0{\cdot}084$	$- 0{\cdot}059$	$- 0{\cdot}035$	$- 0{\cdot}020$	$- 0{\cdot}011$	$- 0{\cdot}006$
—	—	—	—	—	—

17	18	19	20
$- 0{\cdot}00291$	$- 0{\cdot}00148$	$- 0{\cdot}000738$	$- 0{\cdot}000359$
$- 0{\cdot}004$	—	—	—

computer, with Gauss' method of integration and the same points as were used in computing C for a polar gas.[8] The value of C_{111} may be checked in two ways. First, the values of c_n may be compared with the revised values of Kihara [6] and those of Bergeon.[9] Secondly, the complete coefficient may be compared with that calculated by Bird, Spotz and Hirschfelder.[10] The first comparison is shown in table 1. Coefficients 0-3 lie between those of Kihara and those of Bergeon.
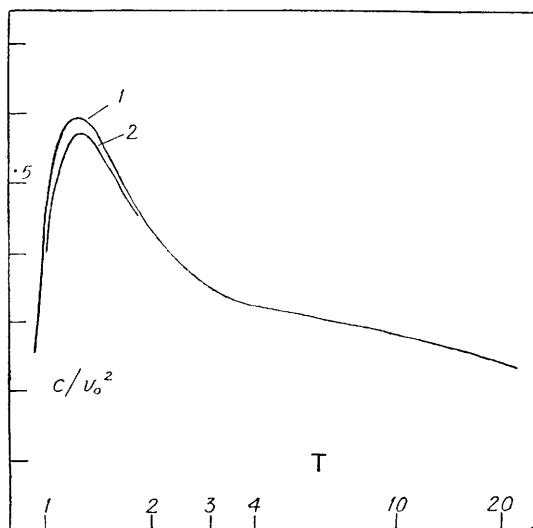

FIG. 1.—Comparison of the third virial coefficient C_{111}/v_0^2 computed by Bird, Spotz and Hirschfelder (curve 1) with that computed in this paper (2). The temperature scale is logarithmic.

We suspect an error in c_4 of Bergeon. His coefficients are calculated quite differently, so the agreement for c_0-c_3 is satisfactory. As Kihara's coefficients above c_{11} are calculated by yet another method, it is unlikely that there is any serious systematic error in our higher coefficients. The comparison of the complete

virial coefficient with values [10] found without making the expansion in powers of $\tau^{-\frac{1}{2}}$ is shown in fig. 1. The disagreement at the maximum of C_{111} is less than 4 %, above $\tau = 3$, it is less than $\frac{1}{2}$ % and from $\tau = 6$ to $\tau = 400$ it is less than 0·1 %. Our values of the temperature derivative of the third virial coefficient are equally close.

4. DISCUSSION

Values of C_{112} calculated directly are compared in fig. 2-7 with those calculated from approximations (a) and (b) of 2. This comparison is a severe test as the range of parameters for the 1-2 interactions is greater than is warranted by the neglect of the higher terms of (2.4). Nevertheless, both approximations
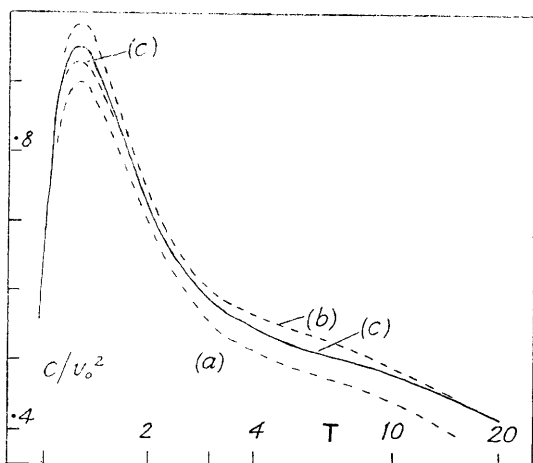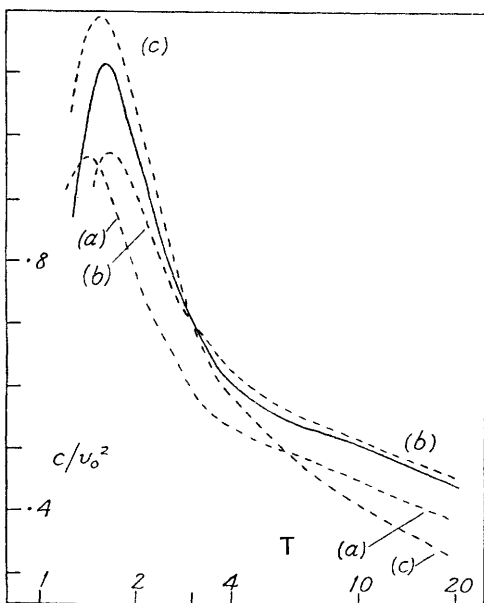

FIG. 2.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.
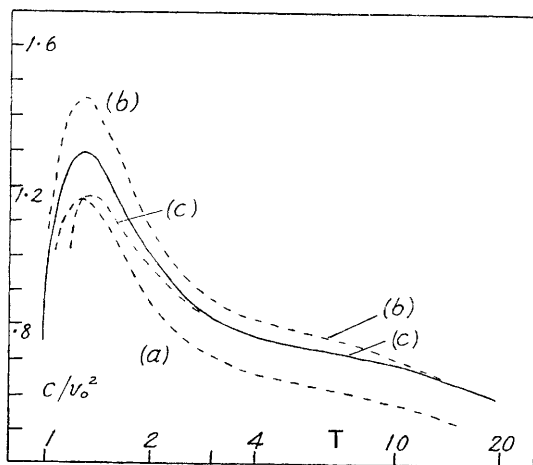
$$C_{112} = \tfrac{3}{2}, \ b^3{}_{12} = 1$$
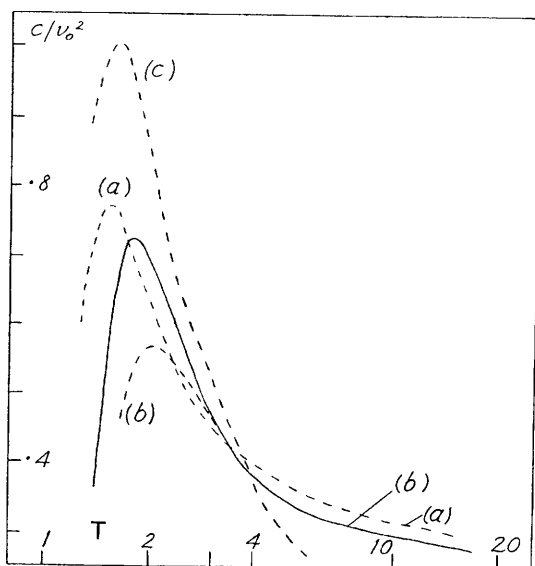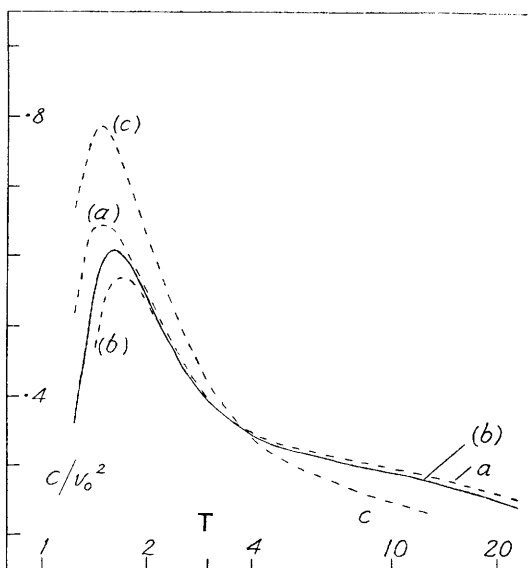
FIG. 3.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.

$$C_{112} = 2, \ b^3{}_{12} = 1$$

FIG. 4.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.

$$C_{112} = 1, \quad b^3{}_{12} = \tfrac{3}{2}$$

FIG. 5.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.

$$C_{112} = 1, \quad b^3{}_{12} = 2$$

FIG. 6.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.

$$C_{112} = \tfrac{3}{2}, \quad b^3{}_{12} = \tfrac{3}{2}$$

give quite acceptable values in all cases but the last where $a = b^3 = 2$. Approximation (b) always becomes the more accurate at high temperatures and, as it is the easier to use practically, we recommend it for actual calculations of " mixed " coefficients.

FIG. 7.—The exact and approximate values of C_{112}/v_0^2 for a pair of parameters of the 1-2 interactions. Curves (a)-(c) are the approximations of § 2 and § 4.

$$C_{112} = 2, \quad b^3_{12} = 2$$
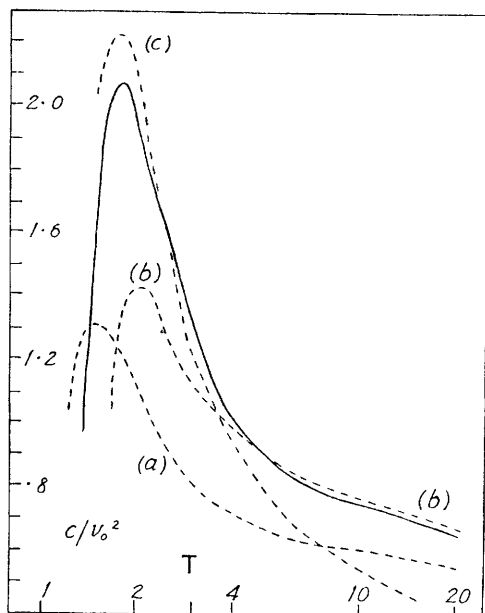
Curve (c) is an empirical approximation suggested by Bird, Spotz and Hirschfelder [10] based upon a comparison of the virial coefficient for (3.1) and that for a square-well potential, for which C_{ijk} can be calculated exactly. This approximation is cumbersome to use and, in general, not as accurate as either of the other two.
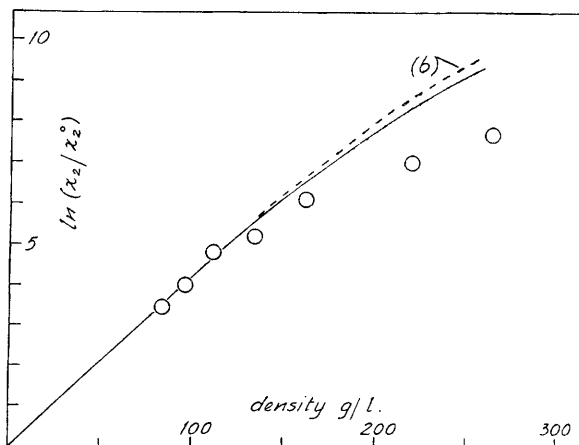

FIG. 8.—Calculated curves for the solubility of naphthalene in ethylene at 35° C, using virial coefficients up to the third. Curve (b) is calculated from approximation (b) and the full curve from " exact " values. The notation and source of experimental results are those of ref. (7).

When the coefficients B_{12} and C_{112} were used to interpret the solubility of solids in compressed gases,[7] the latter was calculated by a method which is virtually the same as approximation (b). The more exact values computed here improve a little the agreement between theory and experiment, but the change is very small. Fig. 8 shows a typical case, the solubility of naphthalene in ethylene at $35°$ C. The remaining disagreement between theory and experiment is due apparently to the neglect of coefficients higher than the third, rather than to any error in approximation (b).

[1] see, e.g., Beattie and Stockmayer, in Taylor and Glasstone, *Treatise on Physical Chemistry* (van Nostrand, New York, 3rd ed., 1951), p. 247.

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