

The Virial Coefficients of Pure Gases and Mixtures

A Critical Compilation

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and

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TO
OUR MENTOR

Joel H. Hildebrand

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PREFACE

Tables of the virial coefficients of pure gases in substantially the present form were prepared by Professor M. L. McGlashan in 1955. In 1964 these tables were revised and extended to almost double the original length at the Physical Chemistry Laboratory, Oxford University. Both these sets of tables were produced in very limited quantities and privately circulated. As it proved impossible to satisfy the demand by this method it was decided in 1969 to publish a new and enlarged edition in co-operation with Oxford University Press. The latest version is again much enlarged; it is some three times longer than the 1969 edition and includes a comprehensive collection of material published up to early 1979 not only for pure substances but for the virial coefficient data on binary mixtures.

Again we would acknowledge the numerous scientists who have communicated with us and provided their data often prior to publication. The previous compilation was remarkably free of errors but as the present work is three times as long the problem of eliminating errors has become increasingly difficult. We would be most grateful if errors and omissions could be brought to our attention.

We would also appreciate it if those workers engaged in the study of gas imperfection would send reprints of their work to J. H. D. at the Department of Chemistry, University of Glasgow or E. B. S. at the Physical Chemistry Laboratory, South Parks Road, Oxford to ensure their inclusion in any subsequent editions.

J. H. D.
E. B. S.

INTRODUCTION

THE imperfection of real gases is a subject that has concerned physicists and chemists for over a century. Some of this interest has arisen from the importance of the study of gas imperfections in the elucidation of the forces between molecules. But many of those involved with the behaviour of real gases have been concerned with the resolution of practical problems that occur in many diverse aspects of thermodynamics.

Gas Imperfections

The perfect gas is characterized by the equation of state

$$Z = \frac{P \bar{V}}{RT} = 1,$$

where P is the pressure, \bar{V} the molar volume, T the absolute temperature, and R the gas constant. Real gases may show significant deviations from this equation of state, even at low pressure. At low temperatures and pressures the compressibility factor Z is usually less than unity, whereas at high temperatures and pressures the converse is true. Typical behaviour of Z is illustrated in Fig. 1 for a series of temperatures such that $T_3 > T_2 > T_1$. The temperature T_3 , at which the density dependence of Z as

$\frac{1}{\bar{V}} \rightarrow 0$ is zero, is termed the Boyle temperature.

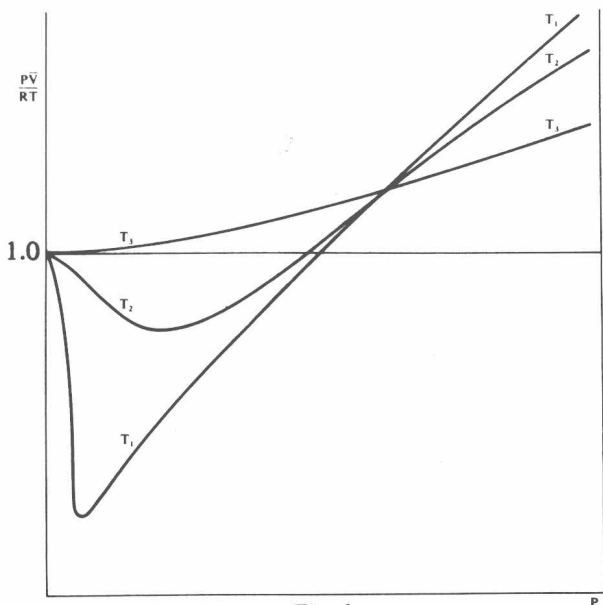


Fig. 1

The equation of state of real gases is best represented, at all but the highest pressures, by the series

$$\frac{P\bar{V}}{RT} = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \frac{D(T)}{\bar{V}^3} + \dots,$$

where $B(T)$, $C(T)$, and $D(T)$ are respectively termed the second, third, and fourth virial coefficients. $B(T)$ is defined as follows:

$$B(T) = \lim_{1/\bar{V} \rightarrow 0} \left(\frac{P\bar{V}}{RT} - 1 \right) \bar{V} \equiv \lim_{1/\bar{V} \rightarrow 0} \mathcal{A}$$

and $B(T)$ is zero at the Boyle temperature. The general manner of the variation of $B(T)$ with temperature is indicated in Fig. 2. At low temperatures $B(T)$ is large and negative, whereas at high temperatures it has small positive values.

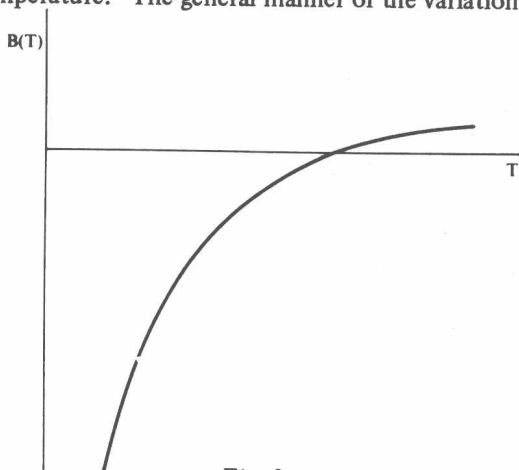


Fig. 2

The third virial coefficient is equal to the slope of \mathcal{A} at zero pressure.

$$C(T) = \lim_{1/\bar{V} \rightarrow 0} (\mathcal{A} - B) \bar{V}.$$

However, values for this coefficient are usually determined experimentally from gas-compressibility data by fitting the results at a given temperature by a polynomial in reciprocal volume. The coefficients of this polynomial are then identified with the coefficients of the infinite virial series. Values for the virial coefficients obtained in this way depend on the degree of polynomial used and on the density range of the compressibility data. The resulting uncertainties in

the second virial coefficient are small (usually less than 1 per cent) but are much larger for the third virial coefficient.¹ The general dependence of $C(T)$ on temperature is illustrated in Fig 3.

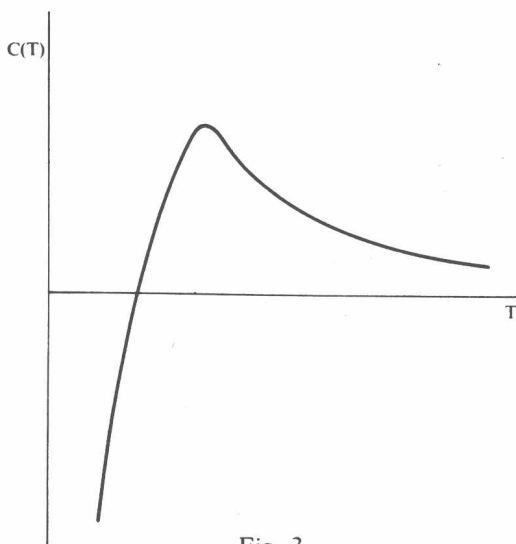


Fig. 3

Virial Coefficients and Intermolecular Energy

Besides providing a convenient method of describing gas imperfection, the virial form of the equation of state is important because the coefficients are related in a fairly simple manner to the intermolecular potential energy function, $U(R)$, of the molecules concerned.² Thus it can be shown that, for molecules with a spherically symmetric potential energy function, such as that illustrated in Fig. 4,

$$B(T) = -2\pi N \int_0^{\infty} (e^{-U(R)/kT} - 1) \cdot R^2 \cdot dR.$$

In principle it is not possible to determine the potential energy function $U(R)$ uniquely from second virial coefficient data alone, (except for a purely monotonic repulsion function). This can be seen when the second virial coefficient is expressed.³

$$B(T) = \frac{2\pi N}{3kT} e^{\epsilon/kT} \int_0^{\infty} \Delta \exp\left[-\frac{\phi}{kT}\right] d\phi$$

where $\Delta = r_L^3 - r_R^3$, ϵ is the maximum depth of the potential energy well, and $\phi = U + \epsilon$ is the potential energy measured from the bottom of the well. r_L and r_R are the inner and outer coordinates of the potential energy function at ϕ . In the repulsive region $\Delta = r_L^3$. A formal inversion of this expression should be

possible as

$$B(T)T / \frac{2}{3} \pi N e^{\epsilon/kT}$$

is the Laplace transform of Δ . The inversion of B can, in principle, give the repulsive branch of $U(R)$ and the well width as a function of the depth. This has only proved useful in the case of helium at high reduced temperatures.

Despite the formal limitations, inversion methods have been devised which enable the pair potential energy function, $U(R)$ to be determined from high accuracy second virial coefficient data.⁴ In brief, the methods define a characteristic length, \tilde{r} , defined by

$$\tilde{r} = \left\{ \frac{B + T (dB/dT)}{2/3 \pi N} \right\}^{1/3}.$$

The intermolecular potential energy at this separation $U(\tilde{r})$, can be related to kT where T is the temperature at which B was determined by

$$U(\tilde{r}) = \mathcal{G}(T) kT.$$

The function $\mathcal{G}(T)$ is called the inversion function. It is comparatively insensitive to the detailed form of $U(R)$ and can be calculated using a very crude model potential such as the Lennard-Jones (12-6) function. Thus $U(R)$ can be directly determined from $B(T)$. With data of very high quality, this approach can be made the basis of an iterative procedure.

The third virial coefficient can also be related to $U(R)$ if the intermolecular energies are considered pair-wise additive. However, this assumption introduces considerable error.

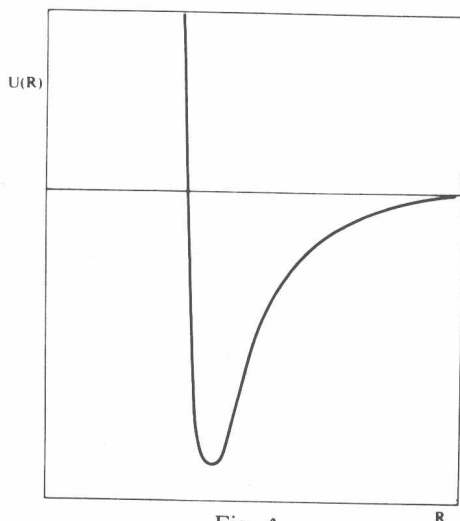


Fig. 4

Properties of Gases in terms of virial coefficients

The thermodynamic properties of gases may readily be deduced from a knowledge of the virial coefficients and their dependence on temperature.⁵ For calculations at pressures not much greater than 1 atm, a knowledge of the second virial coefficient is usually sufficient. At high pressures, the contribution of the third virial coefficient may become significant.

In the following paragraphs, expressions for the thermodynamic properties are given, generally, in terms of the equation of state and, specifically, in terms of virial coefficients ($\bar{}$ indicates a quantity per mol and 0 refers to the perfect gas state).

(i) Fugacity, f

Fugacity may be defined in terms of the chemical potential, μ , by the relation

$$\partial \ln f = \partial \mu / RT.$$

From this the following expression may be derived:

$$RT \ln \frac{f}{P} = - \int_0^P \left(\frac{RT}{P} - \bar{V} \right) dP.$$

Expressing \bar{V} , the molar volume of the real gas, in terms of the virial coefficients leads to the equation:

$$\ln \frac{f}{P} = \frac{B}{\bar{V}} + \frac{C + B^2}{2(\bar{V})^2} + \dots$$

(ii) Internal Energy, U

The departure of the molar internal energy from the perfect gas value may be written

$$\bar{U} - \bar{U}^0 = - \int_{\bar{V}}^{\infty} \left(T \left(\frac{\partial P}{\partial T} \right)_{\bar{V}} - P \right) d\bar{V}.$$

Using the virial equation of state, this becomes

$$\bar{U} - \bar{U}^0 = -RT \left(\frac{B_1}{\bar{V}} + \frac{C_1}{2(\bar{V})^2} + \dots \right),$$

where

$$B_1 = T \left(\frac{dB}{dT} \right); \quad C_1 = T \left(\frac{dC}{dT} \right).$$

(iii) *Enthalpy, H*

The difference between the enthalpy of a real gas and that of a perfect gas under the same conditions is simply related to the corresponding difference in internal energy

$$\bar{H} - \bar{H}^0 = \bar{U} - \bar{U}^0 + P\bar{V} - RT.$$

Thus, using the virial equation of state,

$$\bar{H} - \bar{H}^0 = RT \left(\frac{B - B_1}{\bar{V}} + \frac{2C - C_1}{2(\bar{V})^2} + \dots \right).$$

(iv) *Heat capacity at constant volume, C_v*

This function for a real gas is given in terms of the standard state value by the expression

$$\bar{C}_v - \bar{C}_v^0 = -T \int_{\bar{V}}^{\infty} \left(\frac{\partial^2 P}{\partial T^2} \right)_{\bar{V}} d\bar{V},$$

which, in terms of the virial equation of state, becomes

$$\bar{C}_v - \bar{C}_v^0 = -R \left(\frac{2B_1 + B_2}{\bar{V}} + \frac{2C_1 + C_2}{2(\bar{V})^2} + \dots \right),$$

where

$$B_2 = T^2 \left(\frac{d^2 B}{dT^2} \right); \quad C_2 = T^2 \left(\frac{d^2 C}{dT^2} \right).$$

(v) *Heat capacity at constant pressure, C_p*

This function is given by the equation:

$$\bar{C}_p - \bar{C}_p^0 = -R - T \left(\frac{\partial P}{\partial T} \right)_{\bar{V}}^2 / \left(\frac{\partial P}{\partial \bar{V}} \right)_T - T \int_{\bar{V}}^{\infty} \left(\frac{\partial^2 P}{\partial T^2} \right)_{\bar{V}} d\bar{V}.$$

Substituting the virial equation of state leads to the result

$$\bar{C}_p - \bar{C}_p^0 = -R \left\{ \frac{B_2}{\bar{V}} - \frac{(B - B_1)^2 - (C - C_1) - C_2/2}{\bar{V}^2} + \dots \right\}.$$

(vi) *Entropy, S*

The departure of the entropy from the perfect gas value is given by

$$\bar{S} - \bar{S}^0 = -R \ln P + R \ln \frac{P\bar{V}}{RT} - \int_{\bar{V}}^{\infty} \left\{ \left(\frac{\partial P}{\partial T} \right)_{\bar{V}} - \frac{R}{\bar{V}} \right\} d\bar{V},$$

which leads to the following result

$$\bar{S} - \bar{S}^0 = -R \left\{ \ln P + \frac{B_1}{\bar{V}} + \frac{(B^2 - C + C_1)}{2(\bar{V})^2} + \dots \right\}.$$

(vii) *Joule–Thomson coefficient, χ .*

The Joule–Thomson coefficient is given by the relation:

$$\chi = \frac{1}{\bar{C}_p} \left(T \left(\frac{\partial \bar{V}}{\partial T} \right)_p - \bar{V} \right),$$

which takes the following form in terms of virial coefficients:

$$\chi = \frac{1}{\bar{C}_p^0} \left\{ (B_1 - B) + \frac{2B^2 - 2B_1B - 2C + C_1}{\bar{V}} + \frac{R}{\bar{C}_p^0} \left(\frac{B_2(B_1 - B)}{\bar{V}} \right) + \dots \right\},$$

where \bar{C}_p^0 is the zero pressure value of the molar heat capacity.

The virial coefficients of mixtures

The virial coefficient of a binary gas mixture may be expressed

$$B_M(T) = B_{11}(T)x_1^2 + 2B_{12}(T)x_1x_2 + B_{22}(T)x_2^2.$$

Here x_1 and x_2 are the mole fractions of species 1 and 2 in the mixture. B_{11} and B_{22} are the second virial coefficients of pure component 1 and component 2, respectively. B_{12} the so-called interaction virial coefficient is the second virial coefficient which corresponds to the potential energy function $U_{12}(R)$ which describes the interaction of molecules of species 1 with those of species 2. B_{12} is also referred to as the cross virial coefficient, the cross-term virial coefficient, and the mixed virial coefficient.

The excess virial coefficient E is given by

$$E = B_{12}(T) - 0.5 [B_{11}(T) + B_{22}(T)].$$

The third virial coefficient of a binary gas mixture may be written

$$C_M(T) = C_{111}x_1^3 + 3C_{112}x_1^2x_2 + 3C_{122}x_1x_2^2 + C_{222}x_2^3.$$

C_{111} and C_{222} are the third virial coefficients of the pure components, C_{112} is the contribution that arises from two molecules of species 1 interacting with one molecule of species 2, and C_{122} arises from the interaction of one molecule of species 1 with two of species 2.

The second virial coefficients of multicomponent mixtures may be calculated if the second virial coefficients of the pure components and the interaction virial coefficients of all pairs of molecules present in the mixture are known.

Thus for an n component mixture

$$B_M(T) = \sum_{\alpha=1}^n \sum_{\beta=1}^n B_{\alpha\beta}(T) x_{\alpha} x_{\beta}$$

which written in full for a three component mixture is

$$B_M(T) = B_{11} x_1^2 + 2B_{12} x_1 x_2 + 2B_{13} x_1 x_3 + 2B_{23} x_2 x_3 + B_{22} x_2^2 + B_{33} x_3^2 .$$

The Tables

The revised tables include material published up to early 1979. For the most part, substances are listed by the name used by the authors who reported the virial coefficients. However, when more than one set of data is available for a compound this procedure cannot always be followed. The proper entry to the tables is by way of the formula index, which is based on the system used in the *Chemical abstracts* formula index. A name index is also provided for convenience in finding data, especially for complex organic substances, but in view of the diversity of names in use for many substances, the formula index should always be checked if the compound does not appear to be present in the name index.

An attempt has been made to give some assessment of the quality of the second virial coefficients quoted. However, in view of the variety of techniques used, it has proved virtually impossible to give completely reliable independent estimates of the accuracy of the data in these tables. The following procedures have been adopted.

- (i) Where the authors make general statements about the supposed accuracy or precision of their work these are quoted.
- (ii) Where estimates of the reproducibility or precision of individual determinations are given these are reproduced.
- (iii) If information about the quality of the results is not given in the original paper the results have been classified, where possible, into one of three groups, according to the precision to be expected from the technique used.

The groups are:

Class I. Estimated precision < 2 per cent or $< 1 \text{ cm}^3 \text{ mol}^{-1}$, whichever is the greater.

Class II. Estimated precision < 10 per cent or $< 15 \text{ cm}^3 \text{ mol}^{-1}$, whichever is the greater.

Class III. Estimated precision greater than 10 per cent or $15 \text{ cm}^3 \text{ mol}^{-1}$, whichever is the greater.

Results obtained by the analysis of thermodynamics data (such as heats of vaporization) and determinations made at a single temperature have generally not been classified. All estimates of accuracy must be regarded with caution, and those for whom an assessment of this factor is of prime importance should consult the original papers.

Where sets of data for a single substance of apparently high precision are in obvious conflict, or in cases where there is a profusion of data, an attempt has been made to indicate with a few critical comments the relative value of the different sets of data. These comments appear at the head of the section dealing with that particular substance.

For certain important substances we have tabulated 'recommended' values of the second virial coefficients obtained from a graphical analysis of what we regard as the best data. These tables, which appear after the critical comments, may prove useful to those who require reasonably reliable estimates of second virial coefficients but do not wish to undertake a full analysis of all the available data. The second virial coefficients have all been converted to the units $\text{cm}^3 \text{ mol}^{-1}$, which is the unit in most common use at the present time. The S I units $\text{m}^3 \text{ k mol}^{-1}$ should attain more importance in the next few years, but the conversion is trivial. For third virial coefficients the units $\text{cm}^6 \text{ mol}^{-2}$ are used. Further details of the conversion procedures and the layout of the material are given in the notes that follow.

1. The symbol (*) indicates that experimental data from these references have been converted to values of B and C in the series:

$$P\bar{V} = RT \left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \dots \right)$$

and have been expressed in units of $\text{cm}^3 \text{ mol}^{-1}$ B and $\text{cm}^6 \text{ mol}^{-2}$ C .

2. Certain unpublished experimental results have been communicated and are denoted in the tables by (†)

3. For the calculations, the following formulae and values of RT_0 and T_0 have been used:

$$\begin{aligned} P\bar{V} &= A \left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \dots \right), \\ P\bar{V} &= A^* + B^* P + C^* P^2 + \dots, \\ P\bar{V} &= A' + \frac{B'}{\bar{V}} + \frac{C'}{\bar{V}^2} + \dots \end{aligned}$$

For conversion from one series to another: (strictly true for infinite series only)

$$A = A^* = A',$$

$$B = B^* = \frac{B'}{A'},$$

$$C = B^{*2} + A^* C^* = \frac{C'}{A'}.$$

$$R T_0 = 22\,414 \text{ cm}^3 \text{ atm. mol}^{-1}.$$

$$T_0 = 273.15 \text{ K.}$$

1 Amagat unit of volume = volume occupied by 1 mol of gas at 0°C and 1 atm

1 Berlin unit of volume = volume occupied by 1 mol of gas at 0°C and 1 m mercury.

4. Where possible the entries indicate the pressure range (or the maximum pressure) utilized. The degree of the polynomial used in analysing the data is given where this is greater than 2.

5. The conversion factors from the CGS units used in this work to S I units are:

$$B(\text{m}^3 \text{ k mol}^{-1}) = B(\text{cm}^3 \text{ mol}^{-1}) \times 10^{-3},$$

$$C(\text{m}^6 \text{ k mol}^{-2}) = C(\text{cm}^6 \text{ mol}^{-2}) \times 10^{-6}.$$

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- 1 Michels, A., Abels, J. C., Ten Seldam, C. A., and de Graaff, W. *Physica* **26** 381 (1960).
- 2 Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B. *Molecular theory of gases and liquids*, Chapter 3. Wiley, New York (1954).
- 3 Frisch, H. L. and Helfand, E. *J. chem Phys.* **32**, 269 (1960).
- 4 Crawford, F. W., Harris, E. J. R., and Smith, E. B. *Molec. Phys.* **37**, 1323 (1979).
- 5 See ref. 2. p: 230.

PERIODICALS CITED

The abbreviations used are those of the *World list of scientific periodicals*, 4th edition (1963-65).

Advances in Cryogenic Engineering

American Institute of Chemical Engineers Journal

American Journal of Science

Anales de la Real Sociedad espanola de fisica y quimica (Madrid)

Annalen der Physik

Applied Scientific Research (Section A)

Archives neerlandaises des sciences exactes et naturelles.

Australian Journal of Chemistry

Bulletin de l'Academie polonaise des sciences. Seriedes sciences chimiques.

Canadian Journal of Chemistry

Canadian Journal of Research

Chemical Engineering Progress

Chemical Engineering Progress Symposium Series.

Communications from the Kamerlingh Onnes Laboratory, University of Leiden

Compte rendue hebdomadaire des seances de l'Academie des Sciences.

Helvetica chimica acta

High Temperature (English translation of Teplofizika vysokikh temperature)

Industrial and Engineering Chemistry

Industrial and Engineering Chemistry (Fundamentals)

Journal of the American Chemical Society

Journal of Applied Chemistry (London)

Journal of Chemical and Engineering Data

Journal of Chemical Physics

Journal of the Chemical Society (London)

Journal de chimie physique

Journal of Physical Chemistry

Journal of Research of the National Bureau of Standards. Section A.

Molecular Physics

Nature

Philosophical Transactions of the Royal Society. Series A.

Physica

Physical Review

Physics of Fluids

Physikalische Zeitschrift (Leipzig)

Proceedings of the American Academy of Arts and Sciences.

Proceedings of the Physical Society. (London)

Proceedings of the Royal Irish Academy.

Proceedings of the Royal Society. (London) Series A.

Refrigerating Engineering

Russian Journal of Physical Chemistry (English translation of Zhurnal fizicheskoi khimii)

Science Reports of the Research Institutes, Tohoku University. Series A.

Teploenergetika (see also Thermal Engineering)
Teplofizika vysokikh temperature (see also High Temperature)
Thermal Engineering (English translation of Teploenergetika)
Transactions of the American Institute of Mining and Metallurgical Engineers.
Transactions of the American Society of Mechanical Engineers
Transactions of the Faraday Society
Zeitschrift für angewandte Physik
Zeitschrift für Elektrochemie
Zeitschrift für die gesamte Kalteindustrie
Zeitschrift für Physik
Zeitschrift für physikalische Chemie (Frankfurter Ausgabe)
Zeitschrift für physikalische Chemie (Leipzig)
Zhurnal fizicheskoi khimii (see also Russian Journal of Physical Chemistry)

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PURE GASES

ARGON Ar

The second virial coefficients above 130K are in good agreement except for the results of Onnes and Crommelin (1) above 200K which are less negative by up to $5 \text{ cm}^3 \text{ mol}^{-1}$, and above 700K where the values given by Lecocq (8) lie up to $3 \text{ cm}^3 \text{ mol}^{-1}$ below the results of Osborne and Saville (23). Below 130K recent results and theoretical calculations support the values reported by Fender and Halsey (11). These have been used in preference to the results of Weir, Wynn Jones, Rowlinson and Saville (14) and Byrne, Jones and Staveley (16) in obtaining the smoothed values given below.

T	B	T	B
81	-276 ± 5	250	-27.9 ± 1
85	-251 ± 3	300	-15.5 ± 0.5
90	-225 ± 3	400	-1.0 ± 0.5
95	-202.5 ± 2	500	$+7.0 \pm 0.5$
100	-183.5 ± 1	600	12.0 ± 0.5
110	-154.5 ± 1	700	15.0 ± 1
125	-123.0 ± 1	800	17.7 ± 1
150	-86.2 ± 1	900	20.0 ± 1
200	-47.4 ± 1	1000	22.0 ± 1

1. H. Kamerlingh Onnes and C.A. Crommelin, *Communs phys. Lab. Univ. Leiden* 118b (1910) (*).

6-term fit of PV data (V series; terms in V^0 , V^{-1} , V^{-2} , V^{-4} , V^{-6} , and V^{-8}). (Values above 200 K are probably high). Maximum pressure 60 atm. Class I.

T	B	C
151.94	-82.53	2 140
152.91	-82.17	2 240
153.96	-81.19	2 060
156.53	-79.01	2 240
157.29	-79.26	2 390
159.35	-75.70	2 030
163.27	-72.23	2 160