

Equation of State of Gases at Low Temperatures

Part 1.—Second Virial Coefficient of Argon and Krypton

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An apparatus of the Burnett type has been built with which to measure accurately the second virial coefficients of gases at low temperatures. The principal feature is a mercury manometer with which pressures up to 1 bar can be measured with an accuracy of 2×10^{-6} bar. The second virial coefficients B of argon (80–190°K) and of krypton (110–225°K) have been measured with absolute accuracies of from 0.001 to 0.01 m³ kmol⁻¹, and are discussed in relation to the pair potential of the intermolecular forces. The rapid fall of B at low temperatures implies, in each case, a deeper well in the potential than has been proposed heretofore.

The equation of state of gases at low densities is an important source of information on intermolecular forces, since the coefficients of the virial form of the equation of state are the physical properties that are linked most directly to the potential of these forces. However, the link is insensitive to the form of the potential, or, conversely, even precise measurements of virial coefficients often yield only crude information on the form of the potential. This situation is improved if the measurements extend over wide ranges of temperature, since the limiting forms at extreme temperatures of the virial coefficients, and of other physical properties, are often linked with the shapes of particular parts of the potential. This paper reports the first results of a programme in which the properties of some simple gases and their mixtures are to be measured accurately at temperatures down to and below the normal boiling point.

The two principal difficulties in studying the equation of state at low temperatures are the uncertainties in the absolute scale of temperature and the difficulty of measuring variable volumes at temperatures below the freezing point of mercury. Both difficulties are avoided by the method of expansion devised by Burnett.¹ In this experiment gas is confined to a fixed volume at a constant temperature and the pressure is observed, p_1 . The gas is shared with a second volume, initially evacuated and not necessarily at the same temperature, and the pressure measured again, p_2 . Let the ratio p_1/p_2 be π_1 . A tap between the two vessels is now closed and the second re-evacuated. A second expansion is now made by sharing the gas again between the vessels, after which the pressure is p_3 . Let $(p_2/p_3) = \pi_2$. Clearly, the ratios π_i are independent of p_i if the gas is perfect. The equation of state of a real gas can be found from the variation of π_i with p_i . No measurement of volume, temperature or amount of gas is needed (except for the calculation of corrections for "dead" spaces in tubes and taps) and the accuracy of the method rests solely on the constancy of the temperatures and on the accuracy of the measurement of pressure.

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EXPERIMENTAL

Fig. 1 shows the general arrangement of the apparatus, the various parts of which are described in detail below.

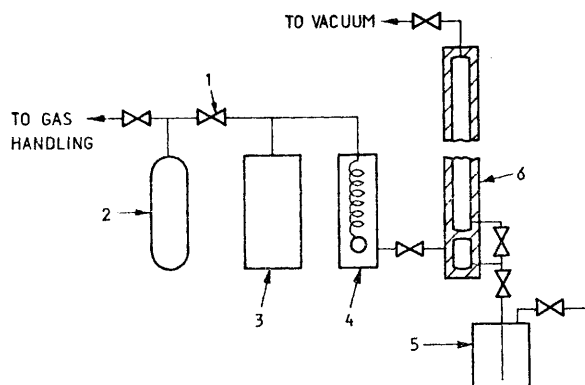


FIG. 1.—General arrangement of Burnett apparatus. 1, expansion valve; 2, ice-bath piezometer of volume V_0 and temperature T_0 ; 3, low-temperature piezometer of volume V_T and temperature T ; 4, null manometer; 5, mercury reservoir; 6, absolute manometer.

LOW TEMPERATURE PIEZOMETER (fig. 2)

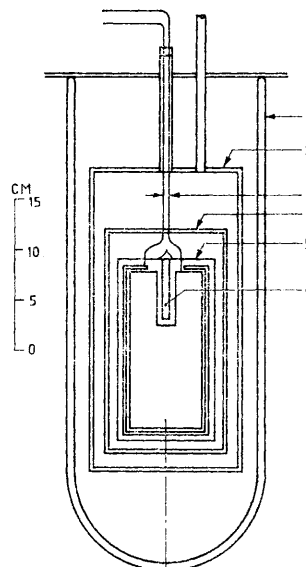


FIG. 2.—Low-temperature thermostat. 1, dewar; 2, brass vacuum jacket; 3, stainless steel gas inlet tubes; 4, copper radiation shield; 5, double walled copper piezometer; 6, platinum resistance thermometer. Electrical wiring is not shown.

The design of this was based on current practice in heat capacity determinations at low temperatures.² Thus the copper piezometer 5 was suspended by nylon threads inside a radiation shield 4 and this was in turn suspended inside an evacuated brass vessel 2. The whole was immersed in a Dewar vessel of liquid nitrogen, 1. The piezometer was of double-wall construction in order to allow measurements of B to be made with two widely different values of volume/surface area ratio and hence to determine the effect of gas adsorption on

the experimental B values. The inclusion of the outer space changed the volume by only 10 %.

The outer wall of the piezometer was of such thickness that the calculated change in volume when the piezometer was pressurized internally to 1 bar was 2 p.p.m. The inner wall was 3 mm in thickness, and to prevent too large a change in piezometer volume when only the innermost vessel was in use, pressure compensation was applied to the space between the inner and outer walls. The volume of the piezometer was 800 cm³.

Temperature control of the piezometer was effected by 10 glass encapsulated platinum resistance thermometers (Degussa type P5) in series inserted into holes in the outer wall of the piezometer. These thermometers formed one arm of a Wheatstone bridge, the unbalance signal from which was proportionally amplified and used to supply power to a heater of manganin wire wound over the whole of the outer cylindrical surface of the piezometer. The amplifier was arranged to provide its maximum power output of 2 W when the piezometer was 0.005°K below its control temperature.

To allow correct operation of the automatic controller, the radiation shield was held $0.2 \pm 0.05^\circ\text{K}$ below the temperature of the piezometer. This was done manually. The shield had three independent heaters (the top plate, the cylindrical wall, and the bottom plate) and the relative temperature of each was indicated by a copper-constantan thermocouple and galvanometer. A measuring platinum resistance thermometer 6 (Tinsley type 5187L) was used to determine the absolute temperature and also to observe the performance of the automatic controller. Its resistance was determined potentiometrically using a standard resistance and a thermoelectric-free potentiometer. Use of a photocell amplifier enabled a sensitivity of 0.0001°K to be achieved when using a thermometer current of 1 mA.

The inlet tube 3 to each part of the piezometer was of 1 mm bore stainless steel. A manganin heater was wound along the pair of tubes to prevent condensation and copper-constantan thermocouples spaced at 3 cm intervals enabled the temperature distribution along them to be obtained.

ICE-BATH PIEZOMETER

This was a thick-walled glass vessel immersed in a well-stirred bath of ice and water. The latter was constructed in the manner normally used in thermometric determinations of the ice point and had a temperature constancy and uniformity of at least 0.001°K . Statistical analysis showed that when the maximum and minimum pressures used in a Burnett series of expansions were 1 bar and 0.1 bar respectively, as used in this work, the accuracy of B depended sharply on the number of expansions. The accuracy was best when either 5 or 6 expansions were used. Thus the optimum volume of the ice bath piezometer for a given low temperature piezometer volume depends on the temperature of the latter. This meant the use of a series of ice-bath vessels to cover the temperature range of interest.

NULL MANOMETER

This was a quartz spiral manometer capsule made by Texas Instruments (Tube no. 11 for Pressure Gauge no. 140). When used as a null instrument, the internal volume of the spiral is constant and reproducible to about 0.001 cm³. The capsule had a sensitivity of 300° rotation per bar of applied pressure. Displacement of the spiral from its null position was detected by projecting a beam of light on to the plane mirror attached to the quartz spiral and thence to a pair of silicon solar cells (Ferranti MS2BE) connected in series opposition. The output from the solar cells was measured on a galvanometer (Tinsley type SR4/4500 A/10c). By using an efficient optical system, a 24 W projection bulb and a 30 cm mirror to photocell path length, a final sensitivity of 3 mm deflection per μbar was obtained. Extensive tests showed that (a) zero drift was about $5 \mu\text{bar/week}$; (b) after application of 0.2 bar pressure difference the null point changed by less than $1 \mu\text{bar}$. No trouble was experienced from vibrations, even though the gauge was insulated from the floor with a single piece of felt. However, it was necessary to screen all electrical wiring and the box containing the gauge and photocells to prevent stray electrical pickup.

ABSOLUTE MANOMETER

The two limbs of the manometer body were machined, one above the other, from a stainless steel bar, 1 m in length with a rectangular section of 5 cm × 3.5 cm. Polished plate glass, "float" glass, with faces parallel to 20 sec of arc, was used for the front and back windows and was attached with epoxy resin. Thus the mercury column was 3.5 cm square in section, two faces being of stainless steel and two of glass. The valve connecting the two limbs of the manometer and also the valve leading to the mercury reservoir was a needle valve with a P.T.F.E. seat and was completely grease-free. Vibration of the mercury surface was completely eliminated by suspending the manometer with the mercury reservoir attached from a system of springs fixed to the wall. The time period of the assembly was 0.5 sec.

The two mercury surfaces were observed using the optical system described by Marek^{3, 4} and used subsequently at the National Physical Laboratory.⁵ In this, the image of an illuminated cross-wire is projected at grazing incidence on to the mercury surface which is essentially a plane mirror at the centre of the manometer tube. A microscope with a micro-meter eyepiece was used to observe the reflected and the direct images simultaneously. The mean position between them then corresponds to the position of the mercury surface. This was compared with a steel scale graduated in mm to an accuracy of 0.001 mm suspended by the side of the manometer. By operating the manometer in a thermostatted room and passing thermostatted water through channels attached to the two sides of the manometer, a temperature control of 0.01°C was achieved and this was sufficient to obtain a reproducibility in the pressure measurements of 2 μbar. Variation in the capillary depression of the mercury was calculated to be much less than this.

MATERIALS

Argon (99.995 % purity) and krypton (99 %) were obtained from British Oxygen Co. They were distilled fractionally in a column similar to that of Clusius and Riccoboni⁶ with a head of the type described by MacGillivray.⁷

METHOD OF CALCULATION

Although it is in principle possible to correct the observed pressure measurements for gas in the dead spaces and so obtain pressure ratios corresponding with those which would be obtained in an ideal Burnett apparatus, an alternative method was used, which was more suitable for automatic computation.

During construction of the apparatus, the volume of each individual part was determined to the greatest accuracy which could be achieved conveniently. For example, the piezometer volumes were determined to an accuracy of 1 in 10⁴ by weighing full of water. All inter-connecting gas line volumes were determined by gas volumetry to 0.1 cm³. Thus, by taking the first pressure measurement (of the order of 1 bar) together with the temperatures of the various parts of the apparatus and the second virial coefficients corresponding to these temperatures, it was possible to calculate what pressures would result if a perfect experiment were carried out in an apparatus of exactly the same dimensions as those determined experimentally. This set of pressures was then compared with the actual pressures obtained in the Burnett experiment and by an iterative least-squares process the volume of the low temperature piezometer and the second virial coefficient at this low temperature were optimized to minimize the sum of the squares of the pressure differences. The virial coefficient B is that in the expansion of p in powers of the reciprocal of the molar volume v ,

$$\frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots \quad (1)$$

This method of calculation is clearly equivalent to the one used by Burnett but as the latter method produced values for volume ratio and B whereas our method gave values for V_T and B , this value of V_T should be directly proportional to V_0 and B should be independent of V_0 . (These volumes are defined in fig. 1.) This will be only approximately true due to the presence of dead space volumes. The dependence of the calculated value of B on the

volumes of the calibrated regions of the apparatus was obtained by repeating the calculation using slightly different values for the calibrated volumes and hence $(\partial B/\partial V_x)\sigma_{V_x}$ was calculated (σ_{V_x} is the standard deviation in the calibration of the volume of V_x for region x). The largest value obtained for the sum of these systematic errors was $3 \times 10^{-5} \text{ m}^3 \text{ kmol}^{-1}$ in B and in most experiments it was far less than this. This figure includes uncertainties in temperature measurement as these can be converted into corresponding volume uncertainties, and it also includes errors due to the difference between the Kelvin and platinum resistance temperature scales. Errors due to uncertainty in B in those parts of the apparatus not at the experimental temperature were negligible.

RESULTS

The second virial coefficient of argon was measured at 17 temperatures between 80.4 and 190.5°K in the 1625 cm² vessel of large surface area and at 5 temperatures between 82.5 and 107.7°K in the vessel of small surface area (500 cm²). The measurements on krypton were made at 13 temperatures between 110.6 and 224.2°K in the large vessel and at 5 temperatures from 108.2 to 119.7°K in the small vessel. The coefficients were determined as described above, with initially the neglect of third and higher virial coefficients. The results from the first sets (large area) were interpolated to the temperatures of the second, and the corrections for adsorption found by linear extrapolation of the apparent values of B to zero area. The corrections to the first sets are shown in fig. 3.

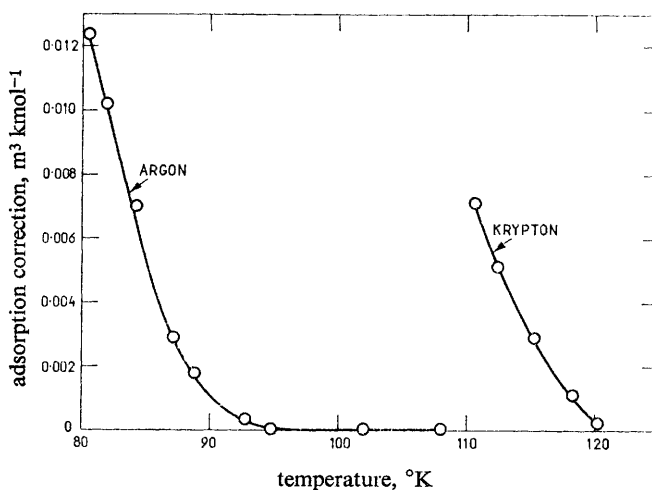


FIG. 3.—Adsorption correction to B for argon and krypton.

The values of B , reduced to zero area, were then corrected for the small effect of truncating the virial expansion at the second term. Experimental values of C could not be obtained from this apparatus but were derived from measurements at higher densities.⁸⁻¹² Extrapolation of reduced curves of C/v_c^2 as a function of T/T_c were made from our theoretical knowledge of the behaviour of these curves at low temperatures. These corrections, and the final value of B , are shown in tables 1 and 2.

It is seen that adsorption is negligible in this apparatus at temperatures above 93°K for argon and 120°K for krypton, but that the corrections rise rapidly below those temperatures. The effects of the third virial coefficients are scarcely appreciable

TABLE 1.—ARGON

- Notes (1) B , observed in vessel of large area, calculated from p by putting $C = 0$;
 (2) ΔB , corrections for adsorption ;
 (3) C , assumed values of third virial coefficient ;
 (4) ΔB , changes in apparent values of B on including C in the calculation ;
 (5) B , corrected values ;
 (6) σ_B , standard deviations of B from each set of expansions.

units $T/^{\circ}\text{K}$	$B, \text{m}^3 \text{kmol}^{-1}$		$C, \text{m}^6 \text{kmol}^{-2}$		$B(5)$	$\sigma_B(6)$
	$B(1)$	$\Delta B(2)$	$C(3)$	$\Delta B(4)$		
80.43	-0.2975	0.0124	0.0007	0	-0.2851	0.005
81.95	-0.2831	0.0102	0.0007	0	-0.2729	0.002
84.23	-0.2755	0.0070	0.0008	0	-0.2685	0.002
87.12	-0.24869	0.0029	0.0009	-0.00014	-0.2459	0.0003
88.85	-0.23751	0.0018	0.0009	-0.00015	-0.2359	0.0004
92.78	-0.21700	0.0003	0.0010	-0.00016	-0.2169	0.0004
94.75	-0.20711	0	0.0010	-0.00019	-0.20730	0.00015
97.65	-0.19465	0	0.0011	-0.00020	-0.19485	0.00028
102.08	-0.17891	0	0.0012	-0.00019	-0.17910	0.00010
105.89	-0.16764	0	0.0014	-0.00018	-0.16782	0.00015
108.07	-0.16129	0	0.0015	-0.00025	-0.16154	0.00019
120.00	-0.13400	0	0.0020	-0.00025	-0.13425	0.00016
129.56	-0.11466	0	0.0023	-0.00027	-0.11493	0.00007
144.60	-0.09288	0	0.0025	-0.00030	-0.09318	0.00013
146.05	-0.09179	0	0.0024	-0.00029	-0.09208	0.00005
157.41	-0.08010	0	0.0022	-0.00024	-0.08034	0.00016
190.52	-0.05269	0	0.0017	-0.00016	-0.05285	0.00009

TABLE 2.—KRYPTON
Conventions as in table 1

$T/^{\circ}\text{K}$	$B(1)$	$\Delta B(2)$	$C(3)$	$\Delta B(4)$	$B(5)$	$\sigma_B(6)$
110.64	-0.3776	0.0071	0.0002	0	-0.3705	0.002
112.42	-0.3595	0.0051	0.0002	0	-0.3544	0.002
115.15	-0.3370	0.0029	0.0002	0	-0.3341	0.0008
118.14	-0.3180	0.0011	0.0003	-0.00007	-0.3159	0.0004
120.24	-0.30748	0.0002	0.0004	-0.00008	-0.30740	0.0003
127.79	-0.27350	0	0.0005	-0.00010	-0.27360	0.00014
133.11	-0.25133	0	0.0006	-0.00011	-0.25144	0.00009
142.81	-0.22002	0	0.0009	-0.00005	-0.22007	0.00021
155.09	-0.18870	0	0.0013	-0.00013	-0.18873	0.00024
168.55	-0.16270	0	0.0023	-0.00018	-0.16288	0.00026
180.75	-0.14057	0	0.0030	-0.00027	-0.14284	0.00015
200.59	-0.11620	0	0.0036	-0.00036	-0.11656	0.00012
224.19	-0.09512	0	0.0032	-0.00034	-0.09546	0.00005

even at temperatures near their maxima. The standard deviations in the last column of tables 1 and 2 are measures of the accuracy with which the derived values of B reproduce the observed pressures, and are not necessarily indications of absolute accuracy.

COMPARISON WITH OTHER RESULTS

The second virial coefficient of argon in the temperature range of these experiments can be derived from the measurements of Onnes and Crommelin⁸ (1910; 143-293°K),

Holborn, Otto and Schultze ¹³ (1915-24; 173-673°K), Michels *et al.*^{9, 14} (1949, 1958; 123-423°K), Kerr ¹⁵ (1957; 100-303°K), Pool *et al.*¹⁶ (1959, 1962; 90°K), Thomaes and Steenwinkel ¹⁷ (1960, 1962; 109-295°K), Kaganer and Rogovaya ¹⁸ (1961; 90-248°K), and Fender and Halsey ¹⁹ (1962; 85-123°K). Of these, the results of Onnes and Crommelin, of Kerr, and of Kaganer and Rogovaya are not considered further since they do not match the apparent precision of the others. The measurements of Michels *et al.* at densities below 120 Am were re-analyzed to check the virial coefficients. B was found to be precise to 0.0001 m³ kmol⁻¹ above 138°K and to have an imprecision about 10 times as great at 123°K. The measurements of Holborn and Otto were re-analyzed with the corrections discussed by Cragoe.²⁰ Between 173°K and room temperature the precision is similar to that of Michels 0.0001 m³. The precision of the results of Fender and Halsey varies from 0.004 m³ at 85°K and 0.002 m³ at their higher temperatures. That of Thomaes and Steenwinkel is probably only about 0.007 m³ at their lowest temperature.

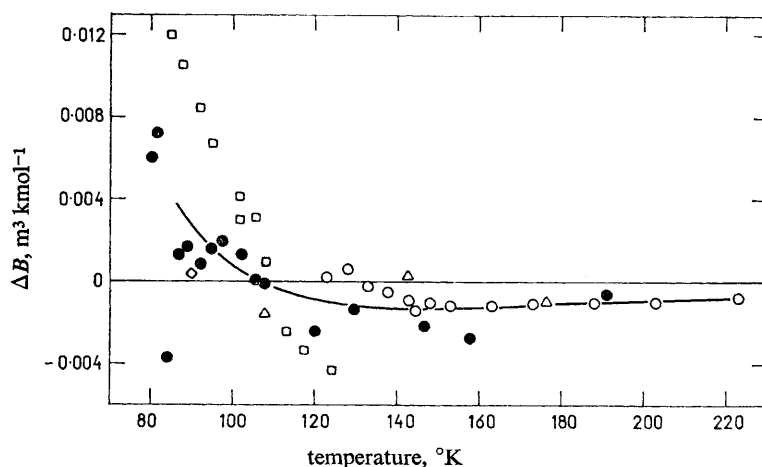


FIG. 4.— $B(\text{experimental}) - B(\text{square well})$ for argon. Symbols: open circles, Michels *et al.*^{9, 14}; squares, Fender *et al.*¹⁹; triangles, Thomaes *et al.*¹⁷; diamond, Pool *et al.*¹⁶; full circles, this work. Comparison with results for krypton suggests that the curve should show a maximum in the range 80-85°K.

The second virial coefficient of krypton at low temperatures has been measured by Thomaes and Steenwinkel ¹⁷ (110-270°K) and by Fender and Halsey ¹⁹ (108-138°K), with precisions similar to those for argon.

The comparison of these results with ours is best made by showing graphically the differences of each set from a smooth function. We use the empirical (square-well) equation of Guggenheim ²¹ for this purpose.

$$B/v_c = 0.440 + 1.40[1 - \exp(0.75T_c/T)], \quad (2)$$

with the critical constants

$$\text{argon } v_c = 0.0753 \text{ m}^3 \text{ kmol}^{-1}, T_c = 150.7^\circ\text{K},$$

$$\text{krypton } v_c = 0.0921 \text{ m}^3 \text{ kmol}^{-1}, T_c = 209.4^\circ\text{K}.$$

This simple equation is useful over the whole temperature ranges for which B has been measured, i.e., 82-1223°K for argon and 108-873°K for krypton.

The deviations of our results and those cited above from eqn. (2) are shown in fig. 4 and 5. Our results for argon agree well with those of Holborn and Otto, those

of Michels *et al.* and with the single point of Pool *et al.* However, our results disagree with the only other substantial set of results taken at low temperatures, those of Fender and Halsey. Their results cross ours at 105°K and fall more slowly as the temperature is reduced below that point. The difference reaches $0.007 \text{ m}^3 \text{ kmol}^{-1}$ at 87°K, which is about 20 times the apparent precision of our results and about 7 times our estimate of the probable absolute error (see below). We prefer our results to those of Fender and Halsey, first because of the greater apparent precision, secondly, because of the greater attention paid to the adsorption correction, thirdly, because

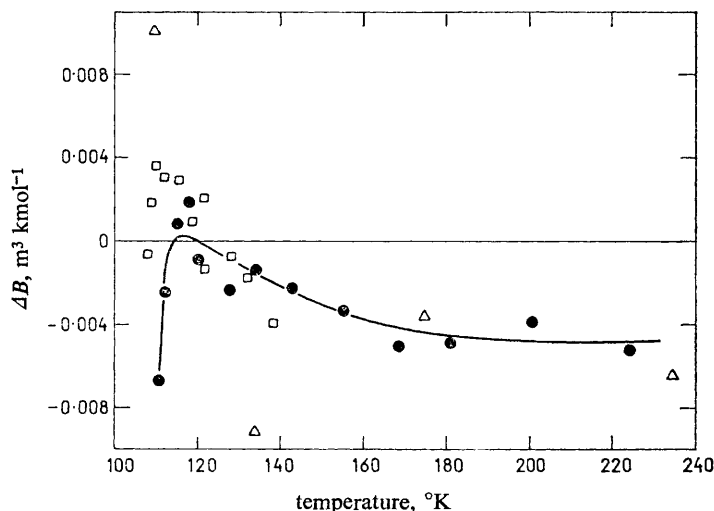


FIG. 5.— $B(\text{experimental}) - B(\text{square well})$ for krypton. Symbols: squares, Fender *et al.*¹⁹; triangles, Thomaes *et al.*¹⁷; full circles, this work.

our results join smoothly at high temperatures to the other results cited, whilst those of Fender and Halsey do not, and fourthly, because of the confirmation provided by the point of Pool *et al.*

The comparison for krypton (fig. 5) is similar, except that the discrepancy with Fender and Halsey is less, and there are fewer other results. Those of Thomaes and Steenwinkel appear to be less accurate than their measurements on argon. Our results can be joined smoothly to those of Trappeniers *et al.*¹² (1966; 273–423°K), although the gap of 50°K makes this check of little value.

For both substances we recommend as best values those calculated from eqn. (2) with the corrections shown as the full lines in fig. 4 and 5. Our estimates of the absolute accuracy of the results in tables 1 and 2, after consideration of the experimental precision and this comparison with other work, are as follows (in $\text{m}^3 \text{ kmol}^{-1}$):

<i>argon</i>	80°K	± 0.01
	82–85°K	± 0.003
	85–190°K	± 0.001
<i>krypton</i>	110–115°K	± 0.01
	115–125°K	± 0.003
	125–225°K	± 0.001

DISCUSSION

The values of B at low temperatures are best considered with the results at higher temperatures if the greatest information on the intermolecular potential is to be derived. We take the latter from the many papers on the compression of these gases at room temperature and above.⁸⁻²⁰

The relation of B to the potential is given classically by a well-known integral,²² but in practice this relation must be supplemented by the quantal corrections,²² which can be calculated only if the potential is known. They are known for the Lennard-Jones (12,6) potential and for the similar potential with a hard-core proposed by Kihara.²³ We use here our calculations for both potentials.²⁴

The best set of experimental points (100 for argon and 59 for krypton) have been fitted by iteration on a computer to various potentials. The criterion for the inclusion of a point was that its distance from the "best" line discussed above did not exceed its probable precision as estimated by those who measured it. Each point was weighted with the reciprocal of this precision, and the iteration continued, with the re-calculation of the quantal corrections, until a best fit was obtained. No quantal corrections were applied to the non-analytic potentials of McGlashan²⁵ and of Barua.²⁶

The root-mean-square residuals (in $\text{m}^3 \text{kmol}^{-1}$) for the best fit for each potential are, as follows:

<i>argon</i>	Lennard-Jones ²² (12,6)	0.0056
	Kihara ²³ (12,6)	0.0013
	McGlashan ²⁵ , set 1	0.0024
	set 2	0.0024
<i>krypton</i>	Lennard-Jones ²² (12,6)	0.0103
	Kihara ²³ (12,6)	0.0035
	Barua ²⁶ , set 1	0.0150
	set 2	0.0089

The size of the quantal corrections varies with the curvature of the potential near the minimum. Thus for argon at 80.4°K it is 0.0019 m^3 for the best Lennard-Jones potential but 0.0047 m^3 for the steeper Kihara potential. It is therefore not sufficient to use one set of corrections (e.g., Lennard-Jones) throughout the comparison of a series of potentials. The absence of any corrections for the potentials of McGlashan and Barua probably does not affect appreciably the goodness of fit but will affect the derived parameters.

The Lennard-Jones potential is inadequate for wide ranges of temperature, and this becomes more obvious when the deviations are examined graphically. The minimum depth of the best Lennard-Jones potentials are $\epsilon/k = 116 \pm 1^\circ\text{K}$ for argon and $163 \pm 1^\circ\text{K}$ for krypton, and such depths are too small to produce the rapid fall in B observed at low temperatures. The asymptotic behaviour of the classical expression for B is dominated by a factor of the form $\exp(\epsilon/kT)$. The greater success of the Kihara potentials is due to their greater depth. The deviations are much more random for these potentials. The parameters²⁷ for these potentials are, as follows:

<i>argon</i>	$\sigma = 3.15 \pm 0.00 \text{ \AA}$
	$\epsilon/k = 163.7 \pm 0.6^\circ\text{K}$
	$\gamma = 0.164$
<i>krypton</i>	$\sigma = 3.42 \pm 0.01 \text{ \AA}$
	$\epsilon/k = 213.9 \pm 1.3^\circ\text{K}$
	$\gamma = 0.126$

However, we do not stress the physical significance of any of these figures, but only put them forward as evidence that the depths of the true potentials are certainly greater than the depths associated with Lennard-Jones potentials (120°K for argon and 160°K for krypton) and probably greater even than the figure of 140-150°K for argon that represented the consensus of opinion at a recent Discussion of the Society.²⁸

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- ¹ E. S. Burnett, *J. Appl. Mech. ASME*, 1936, **58**, A136.
- ² R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde and N. Bekkendahl, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 39.
- ³ J. Marek, *Repertorium Experiment Physik.*, 1880, **16**, 585.
- ⁴ J. Marek, *Trav. Bur. Int. Pds. Mes.*, 1884, **3**, D22.
- ⁵ J. S. Clark and J. E. Sears, *Proc. Roy. Soc. A*, 1933, **139**, 130.
- ⁶ K. Clusius and L. Riccoboni, *Z. physik. Chem. B*, 1937, **38**, 81.
- ⁷ W. E. MacGillivray, *J. Chem. Soc.*, 1932, 941.
- ⁸ H. K. Onnes and C. A. Crommelin, *Comm. Leiden*, 1910, **118b**.
- ⁹ A. Michels, J. M. Levelt and W. de Graaff, *Physica*, 1958, **24**, 659.
- ¹⁰ J. A. Beattie, J. S. Brierley and R. J. Barriault, *J. Chem. Physics*, 1952, **20**, 1615.
- ¹¹ E. Whalley and W. G. Schneider, *Trans. Amer. Soc. Mech. Eng.*, 1954, **76**, 1001.
- ¹² N. J. Trappeniers, T. Wassenaar and G. J. Wolkers, *Physica*, 1966, **32**, 1503.
- ¹³ L. Holborn and H. Schultze, *Ann. Physik.*, 1915, **47**, 1089. L. Holborn and J. Otto, *Z. Physik.*, 1924, **23**, 77; 1924, **30**, 320.
- ¹⁴ A. Michels and H. Wijker, *Physica*, 1949, **15**, 627.
- ¹⁵ E. C. Kerr, *Thesis* (Ohio State Univ., 1957).
- ¹⁶ R. A. H. Pool, G. Saville, T. M. Herrington, B. D. C. Shields and L. A. K. Staveley, *Trans. Faraday Soc.*, 1962, **58**, 1692.
- ¹⁷ G. Thomaes and R. van Steenwinkel, *Rev. Sci. Instr.*, 1960, **31**, 825; *Mol. Physics*, 1962, **5**, 301; *Nature*, 1962, **192**, 160.
- ¹⁸ M. G. Kaganer and I. A. Rogovaya, *Zhur. Fiz. Kim.*, 1961, **35**, 2135.
- ¹⁹ B. E. Fender and G. D. Halsey, *J. Chem. Physics*, 1962, **36**, 1881.
- ²⁰ C. S. Cragoe, *J. Res. Nat. Bur. Stand.*, 1941, **26**, 496.
- ²¹ E. A. Guggenheim, *Applications of Statistical Mechanics*, 1966, (Clarendon Press, Oxford) chap. 3.
- ²² J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954) chap. 3.
- ²³ T. Kihara, *Rev. Mod. Physics*, 1953, **25**, 831.
- ²⁴ R. D. Weir, *Mol. Physics*, 1966, **11**, 97.
- ²⁵ M. L. McGlashan, *Disc. Faraday Soc.*, 1965, **40**, 59.
- ²⁶ A. K. Barua and P. K. Chakraborti, *Physica*, 1961, **27**, 753.
- ²⁷ J. S. Rowlinson, *Mol. Physics*, 1965, **9**, 197.
- ²⁸ *Disc. Faraday Soc.*, 1965, **40**, 19-34, 53, 59-68, 97-108, 119-134.