ABSTRACT

The most widely used experimental method for studying the forces between pairs of molecules is the determination of the second compressibility virial coefficient, B, defined by:

$$z = \frac{PV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots$$

For non-polar gases at temperatures well removed from the normal boiling point, it is relatively easy to measure values of B with adequate accuracy for assessing the merits of various model intermolecular potential energy functions. However, at temperatures little above the normal boiling point, especially for the more polar gases, adsorption effects can prove troublesome.

The density balance method can, in principle, give values of the second compressibility virial coefficient free from adsorption errors. In practice, there remain other drawbacks to such an approach, particularly the notorious instability of the density balance zero point, and the need for the molecular weight of the gas to be very precisely known, or at least constant within very small limits. The recent extensive development of vacuum micro- and ultramicro-balances suggests that the difficulty of instability should now be superable. A

simple theoretical consideration of the treatment of data from such a balance shows that adsorption effects which are not compensated in the balance design may be corrected for, to a first order, and second virial coefficients obtained which are accurate to about ±5 $cm^3 mole^{-1}$.

Accordingly, an electromagnetically operated density balance has been designed and built, incorporating the best features of balances reported in the literature. A number of unforeseen problems were encountered when setting up the balance and these were satisfactorily overcome, with the single exception of a pressure dependent effect, at least partly arising from the contraction of the buoyancy bulb. Calibration to correct for this effect had to be made <u>in situ</u>, and this has reduced the potential accuracy by a factor of about two. The final values of the second compressibility virial coefficient are believed to be accurate to about ± 10 or 15 $cm^3 mole^{-1}$.

Measurements were made for fluoroform, chlorodifluoromethane, chlorotrifluoromethane, dichlorodifluoromethane, 1,1-difluoroethylene and dimethyl ether at temperatures of 25°, 40° and 55°C. Agreement with other reported measurements is generally well within the combined estimated errors. Values of the second dielectric virial coefficient, $\mathcal{B}$, defined by:

$$ {}_{T}P = \frac{\varepsilon - 1}{\varepsilon + 2}V_m = \mathcal{A} + \mathcal{B}/V_m + \mathcal{C}/V_m^2 + \ldots\ldots $$

have been measured by A.N.M.Barnes (D.Phil. Thesis, Oxford, 1968) for these gases, and he has interpreted his results in conjunction with those obtained here in terms of the applicability of the various proposed intermolecular potential functions. The Stockmayer potential, which is based on spherical molecules with a mutual potential function of Lennard-Jones form, with point dipoles at their centres, can, with the addition of polarisability terms, reproduce the observed values of both dielectric and compressibility virial coefficients for the gases with slightly polar and nearly spherical molecules, i.e. chlorotrifluoromethane and dichlorodifluoromethane. For the other gases, it is necessary to include both a shape dependence factor for the repulsive forces and displacement of the point dipole from the origin appropriate for describing the non-polar forces in order to obtain consistency between the two second virial coefficients.

Measurements of B were also made for bromomethane and chloroethane at 25° and 40°C and for trimethylamine at 25°C. Using the values so obtained, which are in reasonable agreement with other reported measurements, and values of $(\mathcal{B} - \mathcal{A}B)$ reported by D.J.Turner (D.Phil.

Thesis, Oxford, 1966), the second dielectric virial coefficients for these gases may be obtained. Their magnitude is very much more realistic than those obtained originally by Turner, using less accurate values for B.

A detailed consideration of the likely sources of error in the apparatus as set up leads to suggestions for various improvements which could be made fairly readily, and which would be expected to reduce the error in the second compressibility virial coefficients obtained to ± 1 or 2 $cm^3 mole^{-1}$. Some considerations is also given to the directions in which the apparatus might most usefully be developed. These include (1) the evaluation of virial coefficients at low temperatures, (2) the measurement of interaction virial coefficients in two component mixtures of gases which may be adsorbed to a large extent, (3) the use of a density balance for precise and possibly automatic pressure measurements, in place of the mercury manometer which the author and almost all other workers in this field have hitherto used.

AN INVESTIGATION OF
VIRIAL COEFFICIENTS OF GASES

A THESIS

SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

W.S.HAWORTH

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CONTENTS

CHAPTER I

INTRODUCTION

The understanding of the nature of the forces between molecules in their normal energy state is of fundamental importance to many areas of chemistry. The later chapters describe an experimental investigation of one particular technique which may be used to study these forces, but it is worthwhile considering briefly here some of the presently available knowledge. Qualitatively, the types of force that exist are well established, and there is also a large amount of quantitative information.[1] There are three main types:

1. At separations of molecules which are small compared with molecular dimensions the dominating force is repulsive. This arises as a result of interpenetration of the electron clouds of the molecules, the promotions necessary in electronic energy levels as a result of the Pauli exclusion principle producing a high energy barrier to such overlapping. Theoretically[2,3] and experimentally[4,5,6] these forces have been shown to fall off relatively steeply and exponentially with increasing separation, and for the interaction of helium atoms, theory and experiment are in close agreement. For reasons which are partly historical and partly computational,

an inverse power dependence on molecular separation, often R^{-13}, has been frequently used,[1,7,8] and seems to be an adequate approximation in many cases. Other inverse powers are also used.[9,10] For simple molecules the repulsive force is spherically symmetrical. Refinements to the representation of this force have included a dependence on molecular shape[11] and the displacement of the origin from the molecular centre in various ways[12,13] and combination of both effects,[12,14,15] in an attempt to obtain better agreement with experimental data.

2. At large separations of the molecules the nett force is attractive and may arise from three distinct types of interaction. Molecules which do not have permanent electric moments, are attracted because of the so called dispersion forces. The origin of these is non-classical, but they may be visualised as arising from the attraction of instantaneous dipoles and higher electric moments which occur in the in phase oscillations of the electron clouds of the molecules. The leading term of this force varies as the inverse seventh power of molecular separation,[16,17] and results from the interaction of instantaneous dipoles. Inverse higher power dependences arise from instantaneous dipole-quadrupole (R^{-9}), quadrupole-quadrupole (R^{-11}),etc.

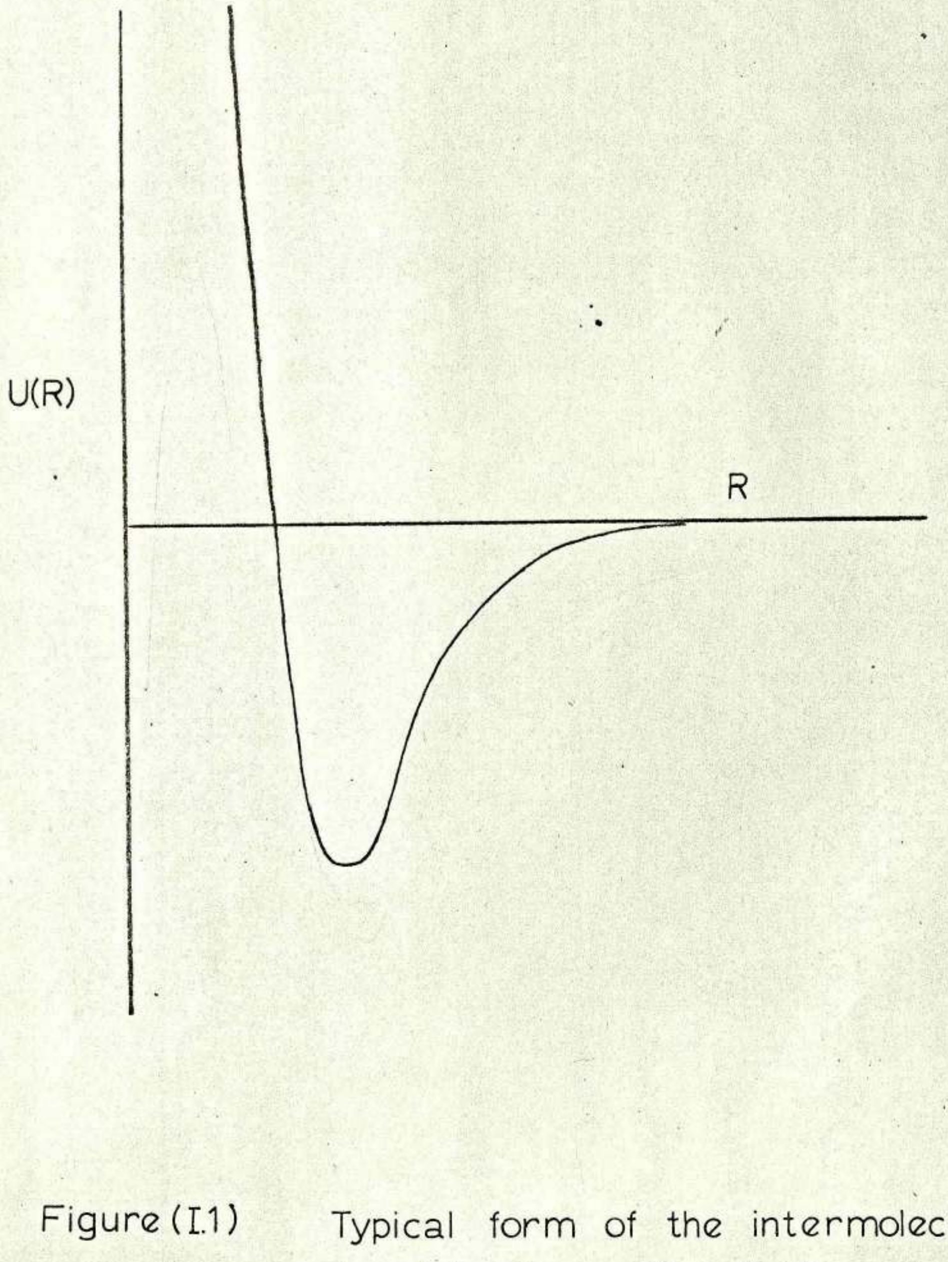


Figure (I.1) Typical form of the intermolecular potential energy function interactions. For simple molecules dispersion forces are spherically symmetrical. Improvements to the representation of these forces have included the displacement of their origin from the molecular centre[12-15] but they are usually accounted for by taking only the leading term in R^{-7}. They have also been approximated by other functional forms.[18-20]

3. Molecules with permanent electric moments have attractive forces arising directly from the interaction of these moments and also those arising from the polarisation of one molecule by the permanent moments of the other. These forces have dependences on separation of R^{-4}(dipole-dipole), R^{-5}(dipole-quadrupole), R^{-7}(dipole-induced dipole), etc They also depend on the relative orientation of the molecules. They have usually been represented by a point dipole at the centre of the dispersion forces,[21-23] but polarisation and quadrupole moments have been included[11] and the asymmetry of the charge distribution has been described more comprehensively and adequately by displacing the dipole from the centre of the molecule.[24,25]

The total effect of all these forces produces a potential energy curve of the form shown in Figure (I.1). Of the many different attempts that have been made to represent this curve analytically, none has entirely succeeded.[26] Success in this context is judged by the ability to describe or to predict quantitatively various observable quantities.

The description of the macroscopic properties of matter in terms of the forces between molecules is a problem of statistical mechanics. In the case of dilute gases, where interaction is important only for small numbers of molecules, and for crystalline solids, where the regularity of the lattice aids computation, the relationships are generally well defined.[1] For liquids and dense gases which have some degree of short range order but long range disorder, the situation is less satisfactory. It has been usual until quite recently to assume that the energy of a group of molecules was adequately described by the sum of energies of interaction of all the possible pairs (the assumption of pairwise additivity). This is now known not to be exactly true,[27,28] but all the corrections which must be made for non-additivity have not been definitely established.[29,30] Indeed, until pair interactions can be adequately described there is no satisfactory way of assessing whether many-body effects have been correctly allowed for.

Because of this problem it has seemed more appropriate to concentrate on those properties which result from interactions between pairs of molecules only, which means effectively restricting attention to certain gas phase properties.

The most widely studied of these is undoubtedly the second compressibility virial coefficient, B, defined by equation (I.1).

$$z = \frac{PV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2} + \ldots \qquad (I.1)$$

Various transport coefficients, that for viscosity in particular, the zero pressure limit of the Joule-Thomson coefficient, the second refractivity[31,32] and second dielectric virial coefficients[33-35] are amongst other properties that have been measured in order to obtain information about the intermolecular energy of pairs of molecules. In addition a number of more direct methods of study have been used, notably molecular beam investigations. Because of the difficulties associated with the extraction of useful information from the values of bulk properties, the more direct methods are likely to find increasing use in the future.

In order to obtain values of the intermolecular potential energy from bulk properties, it is necessary, with only a few exceptions, to assume a functional form for the potential energy, and to incorporate a few (usually two or three) adjustable parameters. The expression for the property is then obtained in terms of these parameters by the methods of statistical mechanics; by fitting this expression to the experimental data, values for the parameters are obtained. This indirect method is necessary because the intermolecular separation is not a single valued function of the intermolecular energy, except in the repulsive region, so that a direct inversion is mathematically impossible.[36] It is only where the macroscopic properties are largely determined by the repulsive region, that is at high temperatures, that a direct inversion is possible.[37,38] Because of the necessity of assumption of a model, the amount of information which may be obtained from measurements of one property is limited to values of the adjustable parameters. However the true potential function will be able to describe one property over its complete temperature range, and also different properties over their temperature ranges, with the same values of these parameters. For the simplest molecules, the rare gases, measurements are available over a wide temperature range for a number of different properties, and some detailed molecular beam experiments have also been made. Nevertheless, no potential has been reported which can reconcile the second virial coefficient data and the beam scattering results with the coefficient of viscosity at high temperatures. No entirely satisfactory explanation has been made for this discrepancy.[26]

For polar gases, reliable experimental information is very much more sparse, and less effort has been expended on the theory of such systems, partly as a result of not being able to explain satisfactorily the behaviour of the simpler systems. However, useful information may be gleaned from the study of these gases. This is so because there are observable effects which are obviously too large to be explained away by the known inadequacy of the representation of the spherically symmetrical, non-polar forces. This is particularly so for the second dielectric virial coefficient, $\mathcal{B}$,[24,39] which is defined by equation (I.2).

$$ {}_{T}P = \frac{\varepsilon-1}{\varepsilon+2} V_m = \mathcal{A} + \frac{\mathcal{B}}{V_m} + \frac{\mathcal{C}}{V_m^2} + \cdots \qquad (I.2) $$

This coefficient is more sensitive to both the precise charge distribution in the molecule and the overall shape of the molecule than is the second compressibility virial coefficient, but the experimental difficulties in making the measurements, and the consequent large experimental errors,[34,41] have been a major factor limiting their use. This increased sensitivity to shape and charge distribution can best be seen from the statistical mechanical expressions for the two coefficients,[1,41] equations (I.3) and (I.4).

$$ B = \frac{N}{2\Omega} \int \left\{ 1 - \exp(-U_{12}/kT) \right\} d\tau_2 \qquad (I.3) $$

where U_{12} is the potential energy of a pair of molecules and $\int d\tau_2 = \Omega V_m$, the integration being over all positions of molecule 2.

$$\mathcal{B} = \frac{2\pi N^2}{9kT\Omega} \int \left\{ \langle\mu_{12}\rangle^2 - 2\mu_0^2 \right\} \exp\left(-U_{12}/kT\right) d\tau \qquad (I.4)$$

where $\langle\mu_{12}\rangle$ is the dipole moment of the pair of molecules at the instant of collision and μ_0 is the permanent dipole moment of an isolated molecule. The expression for $\mathcal{B}$ contains the additional factor $\left\{\langle\mu_{12}\rangle^2 - 2\mu_0^2\right\}$ in the integral, and this introduces the increased dependence on molecular shape and charge distribution.

In this research group the simultaneous measurement of gas compressibility and dielectric virial coefficients at pressures up to about two atmospheres and over a fairly restricted temperature range, and interpretation of this data, has been made for some years for both pure gases and two-component mixtures.[41,43] The results have not always been self-consistent.[43] While this might be the result of inadequate models, the experimental errors in both sets of measurements have diminished the reliability of conclusions in this respect, or at least reduced the amount of information that could be obtained from the results.

Accordingly the investigation of these properties has proceeded by replacing the original dielectric virial coefficient apparatus with a more sensitive bridge method, which when used in conjunction with a

Burnett type of expansion method does not require compressibility virial coefficients for evaluation of the dielectric virial coefficient from the data.[35,44] At the same time, an investigation of possible means of improving the measurement of the compressibility virial coefficient was undertaken, so that the results of the two separately determined virial coefficients could be combined to give more definite information about the relative performance of trial potential functions.

The principal difficulty in the density determinations has been attributed to the fact that the gases being studied frequently have relatively high boiling points and so, being at a pressure nearer the saturated vapour pressure, they are much more strongly adsorbed on to the walls of any containing vessel than, for example, the permanent gases. The problems this poses arise mainly from the difficulty in assessing how many molecules are actually in the gas phase at any particular time during the measurements.[45,46] Little accurate experimental work on such gases is reported in the literature, and the methods which have been used are not without objections.

Three types of approach have been made:

1. An attempt to eliminate significant adsorption effects in the design of the apparatus; the density balance method is such an approach.

Surface moments of the two balance arms are equalised so that the moments of adsorbed gas are equal and opposite, and thus cancel. This is less easily achieved in practice because of the differing ratio of real to geometric area for different specimens of fused quartz.[47] The fact that, for various reasons which are considered in Chapter III, fused quartz is the preferred material of construction for density balances, and working quartz very frequently produces some amount of 'bloom' (quartz volatilised in the flame and then condensed onto cooler nearby parts) of a finely divided and hence highly adsorptive nature, further complicates the problem of equalising real surface moments. Density balances have further disadvantages, the main one being the difficulty of achieving a stable balance point, this probably arising from the slow ageing of quartz.[48-50]

2. If measurements are made in vessels of differing surface to volume ratios, the value of the second virial coefficient corrected for adsorption should be obtained by an extrapolation to zero surface-to-volume ratio.[51] This method is applicable to most methods for measuring virial coefficients, but the problem mentioned already of differing ratios of real to geometric surface areas for different specimens, at least for glass vessels, makes such an approach

of doubtful value. In addition, the functional form of the extrapolation required is not necessarily linear, so the procedure is further complicated.

3. Measurement of the adsorption isotherm of the gas being investigated should enable a suitable correction for adsorption to be applied.[46,52-55] The adsorption isotherm determination has not always been made in the vessels used for the virial coefficient determination, so that the problem of the determination of real surface area may again introduce uncertainties into the correction which must be applied. With metal vessels, the greater ease of obtaining reproducible metal surfaces reduces the importance of this consideration.

It must be emphasised that for many gases, where adsorption effects are relatively small, such procedures can be perfectly valid, because uncertainties in the adsorption correction will be higher order effects. Accurate results have been obtained in this way, for example, for the inert gases at low temperatures.[56,57] In addition, measurements made by methods which theoretically should show errors from adsorption may not in fact do so. Thus Lambert and co-workers[56] found no difference in values of the second virial coefficient obtained for ethanol, methanol, acetone and benzene from a Boyle's Law apparatus, whether or not it was filled with glass wool. On the other hand, Hamann and Pearse[59] observed effects, which they attributed to adsorption, during measurements on methyl bromide and methyl chloride in a compressibility apparatus.

It is clear that for gases which may be strongly adsorbed, there cannot be any certainty that any of the approaches outlined above will be satisfactory in practice. What is really required is a method where adsorption effects are measured on the same surfaces as those used during the virial coefficient determination. Furthermore, the measurements of adsorption and of the virial coefficient should be done in the absence of mercury confining surfaces because strongly adsorbed gases may adsorb on and possibly dissolve in the mercury, which will introduce errors.

A consideration of these requirements showed that they might be met by using a density balance operating on the lines of the electromagnetic balances which have been described in the literature for measurements of sorption and magnetic susceptibility. In view of the infrequent use of a density balance for virial coefficient determination, and some of the unsatisfactory results which have been obtained with density balances, such a statement requires some further justification.

Firstly, the recent extensive development of vacuum microbalances (see for example reference 60) indicated that a density balance with a more stable zero point than that of previously described balances might be constructed with a reasonable certainty of adequate performance. Secondly, such balances, because they are used in a vacuum or controlled atmosphere, usually incorporate an electromagnetic method of weight measurement. If a density balance were equipped with such a means for altering the balancing density, a much more simple procedure for obtaining readings at a variety of balancing densities would be available. Such a density balance should also be very much more reproducible than the ordinary density balance because the density measurements may be related to a <u>difference</u> in currents so that balance stability over one hour or so only is required (the period for a density measurement), and the stability required over the run period is that of the current-density relationship, which is defined by the geometry of the system alone.

However, by far the most important advantage which should accrue from the use of a suitable electromagnetically operated density balance is that the problems posed by adsorption can be minimised and residual effects can then be corrected for. The only surfaces on which adsorption matters from the point of view of the determination of virial coefficients are those of the moving parts of the balance. Thus a constant surface only is involved. This means that the results are not complicated by the effects of adsorption as they are in the conventional methods which require changes of volume. The procedures used either produce new surfaces or result in adsorbed films being covered by mercury. In addition to this the area moments of the two arms can be equalised to within 5 or 10%[48] so that adsorption effects can be considerably reduced. It is shown later (Chapter II) that the effect of non-ideality and the major effects of uncompensated adsorption in the data from a suitable density balance should be separable, so that it should then be possible to measure both the extent of gas imperfection, that is, the magnitude of the second virial coefficient, and the extent of adsorption on the balance. The adsorption is effectively measured on exactly the same material which is used for the density determinations, and at the same time, and so there is much more certainty in the correction to be applied and therefore in the value of the second virial coefficient obtained. In practice, the correction is not obtained as a directly observable experimental quantity, but is accounted for in evaluating the second virial coefficient by the normal procedure of taking the ratio of slope to intercept of a suitable plot. In view of all this, the writer feels it something of an anti-climax that for none of the gases studied was an effect actually observed which could be definitely assigned to adsorption.

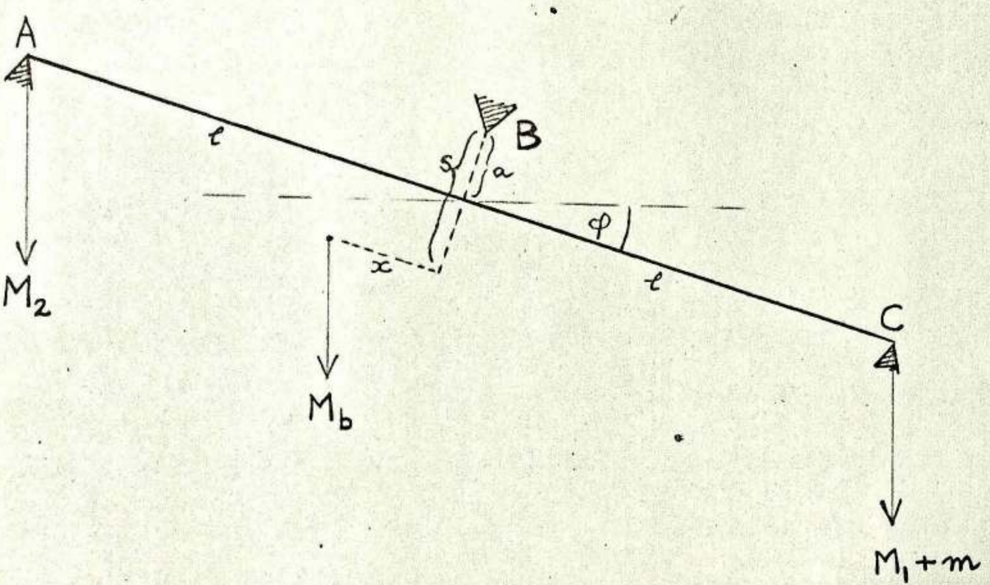


Figure (II.1) The forces on an asymmetrical balance beam

CHAPTER II

THEORY OF THE DENSITY BALANCE

In general, a density balance does not have a symmetrical beam so the simple balance theory[61,62] must be slightly modified. The forces acting on the beam are represented in Figure (II.1) B is the primary fulcrum, A and C, the secondary fulcrums, of the beam ABC. AC is 2ℓ units long, B is a units above the line passing through A and C, and the centre of gravity of the beam lies s units below B, and is displaced x units from the line drawn through B, perpendicular to AC. M_b is the mass of the beam and M_2 is the mass required acting downwards at A to counterbalance exactly the mass M_1 acting downwards at C. The addition of a small mass, m, causes the beam to turn through the small angle, φ.

Taking clockwise moments about B at equilibrium, and ignoring the small torsional moment which may arise, if the primary fulcrum is a fibre, wire or ribbon,

$$(M_1 + m)(\ell.\cos\varphi - a\sin\varphi) = M_2(\ell.\cos\varphi + a\sin\varphi) + M_b(x\cos\varphi + s.\sin\varphi) \quad (II.1)$$

From equation (II.1):

$$\tan\varphi = \frac{(M_1 - M_2)\ell - M_b x + m\ell}{(M_2 + M_1 + m)a + M_b s} \quad (II.2)$$

Clockwise moments about B at balance ($m=0$, $\varphi=0$) gives:

$$M_1\ell = M_2\ell + M_b x \tag{II.3}$$

and substituting equation (II.3) into equation (II.2) gives:

$$\tan\varphi = \frac{m\ell}{(M_2 + M_1 + m)a + M_b s} \tag{II.4}$$

m is small relative to M_1+M_2, so $M_1+M_2 \simeq M_1+M_2+m$, and equation (II.4) becomes:

$$\tan\varphi = \frac{m\ell}{(M_1 + M_2)a + M_b s} \tag{II.5}$$

and so,

$$m = \frac{(M_1 + M_2)a + M_b s}{\ell}\tan\varphi \tag{II.6}$$

Differentiation of equation (II.6) gives the <u>sensitivity</u> defined as $\frac{dm}{d\varphi}$.

$$\frac{dm}{d\varphi} = \frac{(M_1 + M_2)a + M_b s}{\ell}\sec^2\varphi \tag{II.7}$$

Since φ is small, $\sec^2\varphi \simeq 1$ and equation (II.7) becomes:

$$\frac{dm}{d\varphi} = \frac{(M_1 + M_2)a + M_b s}{\ell} \tag{II.8}$$

It is convenient also to define a <u>sensibility</u> which is the minimum mass change that can actually be observed and measured reproducibly, and so depends on the method of measuring φ.

Equation (II.8) shows that in order to obtain the ideal of a very sensitive balance with sensitivity independent of load, a should be zero, M_b and s small and ℓ large. For M_b to be small and ℓ large, the balance beam is made as thin as is consistent with a rigid structure. s is made small by various techniques described in Chapter III.

For a balance operated under constant load conditions, M_2 and M_1 are constant, and the weight changes are measured by applying an equal and opposite weight or force change on the same side of the beam. The expression for the sensitivity remains unaltered, so it can be seen that a does not require to be zero for a sensitivity independent of measured weight change. a must nevertheless be small for a very sensitive balance.

OBTAINING VIRIAL COEFFICIENTS FROM DENSITY BALANCE DATA

There are a number of different ways in which second virial coefficients may be measured with density balances, depending largely on the type of balance used. There are essentially three different forms of the density balance, of varying complexity, and these may be labelled as types A, B and C:

A. The simple balance, balancing at one predetermined density.

B. The balance which has provision for the addition of riders of some sort, to enable the balance to operate at more than one different, but still predetermined, densities.

C. The balance which can be brought to balance in gases of any density, by means of an electromagnetic control or by an adaptation of the ordinary semi-micro chemical balance.

A. For this type of balance there is only one method for obtaining second virial coefficients.[34] This is based on the fact that at equal densities of different gases the balance will be deflected by equal amounts. This is strictly true only when the moments due to adsorbed gas on the two arms of the balance are adequately equalised, if no change of zero occurs between balance in the first and in the second gas, and if the difference in volume of the flotation bulb due to the difference of pressures is insignificant. When these conditions are met:

$$d_1 = d_2 \qquad \text{(II.9)}$$

where d is gas density,
subscript 1 is for gas 1 and
subscript 2 for gas 2.

and so, from the virial expansion of density in terms of powers of the pressure:

$$\frac{M_1p_1}{RT_1 + B_1p_1} = \frac{M_2p_2}{RT_2 + B_2p_2} \text{ in the usual notation} \qquad \text{(II.10)}$$

On re-arranging, equation (II.11) is obtained.

$$B_2 = \frac{M_2}{M_1}\cdot\frac{RT_1}{p_1} + \frac{M_2B_1}{M_1} - \frac{RT_2}{p_2} \qquad (II.11)$$

Thus molecular weights, or at least ratios, must be assumed to obtain values of B_2 and, in practice, this is the major disadvantage of the method. The reason for this is more obvious if order of magnitude error calculations are made.

From equation (II.11):

$$\delta B_2 \simeq \frac{M_2}{M_1}\left[\frac{RT_1\delta p_1}{p_1^2} + \frac{R\delta T_1}{p_1} + \delta B_1\right] + \frac{RT_1}{p_1}\left[\frac{\delta M_2}{M_1} + \frac{M_2\delta M_1}{M_1^2}\right] + \frac{R\delta T_2}{p_2} + \frac{RT_2\delta p_2}{p_2^2}$$

Taking $M_1=44, M_2=60$, $p_1=50$cm Hg, $p_2=37$cm Hg, $T_1=T_2=300^\circ$K, $R=6.2\times10^3$cc.cm Hg.mole^{-1}degree^{-1}, $\delta p_1=\delta p_2=2\times10^{-3}$cm Hg, $\delta T_1=\delta T_2=0.01^\circ$C, $\delta B_1=1$cm^{3}mole^{-1}, $\delta M_1=\delta M_2=0.1$:

$$\delta B_2 = 200 \text{ cm}^3\text{mole}^{-1}$$

of which about 190 cm^{3}mole^{-1} is due to the error in M_1 and M_2.

If $\delta M_1 = \delta M_2 = 0.01$, $\delta B_2 = 30$ cm^{3}mole^{-1},

and if $\delta M_1 = \delta M_2 = 0.001$, $\delta B_2 = 10$ cm^{3}mole^{-1}.

To obtain all the gases with impurity levels sufficiently low that their molecular weights are known to ± 0.001 would not only be tedious, but probably would require facilities for bakeout between gases to avoid contamination from the more strongly adsorbed ones.

B. For a balance of this type, it is possible to circumvent the difficulty arising from uncertainties in molecular weight.[47] An arrangement which is essentially the same, and for which the data may be treated in the same way, is that of two or more similar balances pre-adjusted for different balancing densities.[41] In theory the method can also be used for a single balance with the balancing density altered, by fusion on or off of quartz, for each point. Practically, there are objections to this method (see Chapter III).

T_1 may be assumed to be equal to T_2 (small corrections may be applied if this is not strictly true), and then equation (II.11) can be rearranged to give:

$$\frac{p_1}{p_2} = \frac{p_1}{RT}\left[\frac{M_2}{M_1}\cdot B_1 - B_2\right] + \frac{M_2}{M_1} \qquad \text{(II.12)}$$

From equation (II.12) it can be seen that the slope, S, and the intercept, I, of a plot of p_1/p_2 against p_1 will be given by:

$$RT.S = \left[\frac{M_2}{M_1}\cdot B_1 - B_2\right] \qquad \text{(II.13)}$$

$$I = \frac{M_2}{M_1} \qquad \text{(II.14)}$$

and therefore, from equations (II.13) and (II.14):

$$B_2 = IB_1 - RTS \qquad \text{(II.15)}$$

Thus by actually measuring the ratio of molecular weights of the gas of unknown virial coefficient and a standard gas, the requirement of knowledge of molecular weight is reduced to a requirement that the molecular weight be constant, although the constancy necessary is still a stringent limitation. If the molecular weight errors are not to be significant, the constancy in M_2/M_1 must be less than the measurement error in p_1/p_2. If $p_1=p_2=50$ cm Hg, and $p_1=p_2=0.002$ cm Hg, $\delta(p_1/p_2)=8\times10^{-5}$. If this equals $\delta(M_2/M_1)$, and $M_1=M_2=60$, the changes in M_1 and M_2 that can be tolerated are about ± 0.002 in either. Assuming that this can be achieved, the error in B_2 is given by equation (II.16).

$$\delta B_2 = I\delta B_1 + B_1\delta I + RS\delta T + RT\delta S \qquad \text{(II.16)}$$

If pressures are measured over the range 10 to 50 cm Hg, $B_1=-100\text{cm}^3\text{mole}^{-1}$, $R=6.2\times10^3$ cc.cm Hg.mole^{-1}degree^{-1}, $T=300^\circ$K, $S=3\times10^{-4}$cm Hg^{-1}($B_2=500\text{cm}^3\text{mole}^{-1}$), $I=1$, $\delta T=0.02^\circ$C, $\delta B_1=1\text{cm}^3\text{mole}^{-1}$, $\delta S=10^{-5}$cm Hg^{-1}, $\delta I=5\times10^{-4}$, then

$$\begin{aligned}\delta B_2 &= 1 + 0.05 + 0.04 + 18\\ &\simeq 20 \text{ cm}^3\text{mole}^{-1}\end{aligned}$$

This error would be larger than that actually obtained from a plot of four or five points, which might be expected to lead to a probable error of about half this, i.e. 10 cm^{3}mole^{-1}, in the value of B_2 obtained. The improvement over the type A balance is significant, and in addition, a value of the molecular weight of the second gas which can be obtained if that of the standard gas is known, gives some guide to the worth of the results.

C. For a balance of this type a further method is available. Effectively this uses the current reading (for an electromagnetic balance) or the weight reading (for a chemical balance) in place of the standard gas used above for the calibration of the balance. If the weight added to the bulb side to bring the balance to null is m, and the effective volume of the bulb is V_e, then after Di Zio et al.[63] we can write:

$$d = \frac{m}{V_e} = \frac{M}{V_m} \quad \text{in the usual notation.} \tag{II.17}$$

Substituting this into the virial expansion in terms of inverse powers of the molar volume, and taking terms to the second:

$$\frac{p}{m} = \frac{RT}{MV_e} + \frac{RTB}{(MV_e)^2}\, m \tag{II.18}$$

Thus a plot of p/m versus m has slope, S_m, and intercept, I_m, given by equations (II.19) and (II.20).

$$S_m = \frac{RTB}{(MV_e)^2} \tag{II.19}$$

$$I_m = \frac{RT}{MV_e} \tag{II.20}$$

and so

$$B = \frac{RTS_m}{(I_m)^2} \tag{II.21}$$

Alternatively, and analogously, if the pressure virial series is used instead of the density series:

$$\frac{p}{m} = \frac{RT}{MV_e} + \frac{B}{MV_e}\cdot p \tag{II.22}$$

and $$B = \frac{RTS_p}{I_p} \qquad \text{(II.23)}$$

For a balance weighing electromagnetically, if i' is the weight proportional current, then $m = ki'$, where k is a constant, and the expressions corresponding to equations (II.18) and (II.22) are:

$$\frac{p}{i'} = \frac{RTk}{MV_e} + \frac{RTk^2B}{(MV_e)^2}\, i' \qquad \text{(II.24)}$$

$$\frac{p}{i'} = \frac{RTk}{MV_e} + \frac{kB}{MV_e}\, p \qquad \text{(II.25)}$$

and the expressions for B are:

$$B = \frac{RTS_i}{(I_i)^2} \quad \text{(II.26)} \quad \text{and} \quad B = \frac{RTS_p}{I_p} \qquad \text{(II.27)}$$

Since an electromagnetic balance has been used in this work the errors in the current form of the equation will be considered. From equation (II.27):

$$\delta B = \frac{RT}{I_p}\delta S_p + \frac{RS_p}{I_p}\delta T + \frac{RTS_p}{(I_p)^2}\delta I_p \qquad \text{(II.28)}$$

If pressures are measured in the range 10 to 50 cm Hg, with an accuracy of 0.002cm Hg, currents with an accuracy of 0.001%, I_p=60, S_p=0.003, then δI_p=0.01, δS_p=3×10^{-4} and the other values are those used above,

$$\delta B = 9 + 0.006 + 0.02$$

$$\simeq 10 \text{ cm}^3\text{mole}^{-1}$$

Once again with a series of five points, a probable error of about half this, that is, about

5 $cm^3 mole^{-1}$, would be expected. The improvement over the p_1/p_2 plot arises from the fact that the error from the δS term, the largest contributor, is about halved because the current measurements may be made significantly more accurately than the pressure measurements, and errors arise from only one set of pressure readings rather than two sets.

So far, the discussion of errors has included only those arising from pressure, temperature and molecular weight. There are, however, other sources of error for density balance measurements, so these and the methods of accounting for them will now be considered. The ensuing discussion is concerned especially with C type balances, because these are more suitable for accurate virial coefficient work, but it is also appropriate for B type balances.

Given a balance of adequate sensitivity and zero point stability, it is necessary to know also the effects of adsorption, bulb volume variation and non-linearity of the current-force relationship for the interaction of the magnet with the solenoid.

The forces which act on the balance beam at null in a gas of density, d, and pressure, p, are shown in Figure (II.2)(a) and the moments these exert about the pivot are shown in Figure (II.2)(b), where a, b, c, e, are constants. M is the total mass of

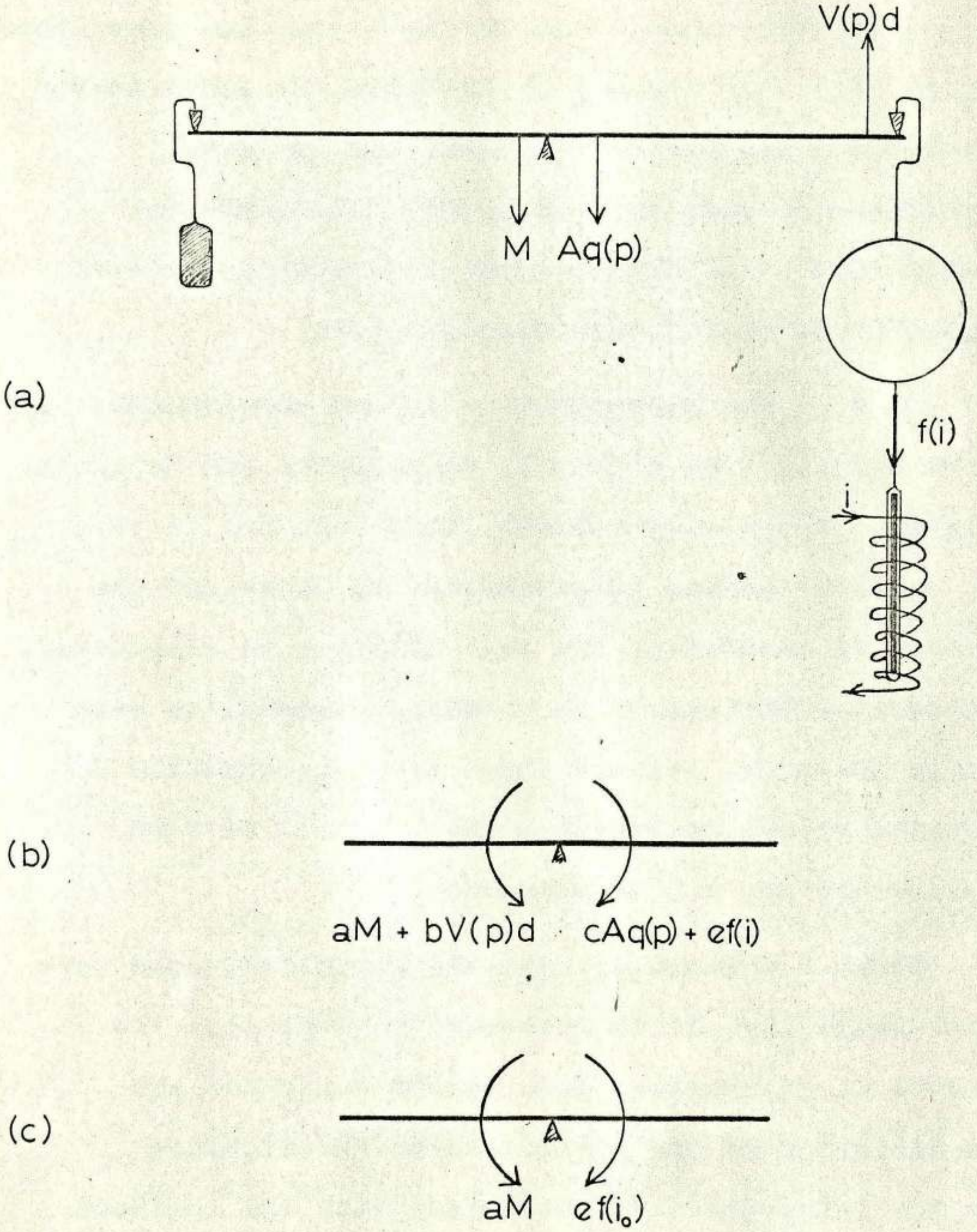


Figure (II.2) The forces on an electromagnetically compensated density balance at null the moving parts and acts through their centre of gravity. A is the total surface area of the moving parts, and q(p) is the mass of gas adsorbed per unit of area on the balance and so is a function of pressure. The force Aq(p) acts through the centre of area of the moving parts. V(p) is the total volume of the moving parts of the balance, and is a function of pressure. The upthrust V(p)d acts through the centre of volume of the balance. f(i) is the force exerted on the magnet by the field of the solenoid, and so is a function of the solenoid current, i.

At null, therefore, we can write:

$$aM + bV(p)d - cAq(p) - ef(i) = 0 \tag{II.29}$$

The moment aM will also include any constant forces acting on the magnet as a result of, for example, the earth's field, nearby magnetic material, etc.

In a vacuum, d and p are both zero and $i = i_o$, so the moments are as shown in Figure (II.2)(c), and:

$$aM - ef(i_o) = 0 \tag{II.30}$$

Combining equations (II.29) and (II.30) gives:

$$bV(p)d - cAq(p) - e\left[f(i) - f(i_o)\right] = 0 \tag{II.31}$$

Forms must now be chosen for V(p), q(p) and f(i). The theoretical expression for the dependence of the volume of a uniformly thin spherical shell on pressure is $V(p) = V_o - hp$, where V_o is the volume in a vacuum and h is a constant (see Appendix II). This expression is used for $V(p)$. The adsorption isotherm, defined above as mass adsorbed per unit area equals $q(p)$, is taken as $q(p) = lp$, where l is a constant, for convenience. In equation (II.31) c is effectively the horizontal displacement of the centre of area from the balance pivot. It is made small in the balance design, so the error introduced by this approximation should be of second or higher order only. $f(i)$ is theoretically directly proportional to current. To account for possible inaccuracies, for example, in the winding of the solenoid, polarisation by the solenoid field, the form $f(i) = m(1+ni)i$ is used. n is a constant which is expected to be very small, and since i_o is also small $f(i) - f(i_o)$ can be equated to $m(1+ni')i'$, where $i' = i - i_o$.

Inserting these expressions into equation (II.31) and rearranging gives:

$$d = \underset{\overset{\uparrow}{\text{adsorption}}}{rp} + s(1 + \underset{\overset{\uparrow}{\text{nonlinearity}}}{ni'})i' + \underset{\overset{\uparrow}{\text{bulb contraction}}}{stpi'} \qquad \text{(II.32)}$$

where r, n and t are small compound constants depending on the balance dimensions and the constants introduced in the paragraph above. s is the approximate proportionality constant between d and i'. When this expression is combined with the virial equation in the pressure form, equation (II.33) is obtained if second and higher order terms (cross products of small numbers) are ignored.

$$\frac{p}{i'} = \frac{sRT}{M-RTr} + \left[n + \frac{RTst}{M-RTr} + \frac{Bs}{M-RTr}\right] p \qquad (II.33)$$

Equation (II.33) is an expanded form of equation (II.25). For a plot of p/i' versus p,

$$B = \frac{RT}{I_p}\left[S_p - n - tI_p\right] \qquad (II.34)$$

The effect of adsorption is cancelled out as a result of taking the ratio of slope to intercept. If runs are done on two gases of different molecular weights, and hence different intercepts, for which values of the second virial coefficient are known, the constants for the nonlinearity of the current force relationship and for the contraction of the bulb can be evaluated. Further runs may be made on other gases to provide a check on this. As an additional check, these constants should have approximately the same values at different temperatures.

It is worth mentioning that although the pressure and current (density) dependent effects above have been labelled bulb contraction and nonlinearity effects, any small effect with a dependence on pressure or on current will be incorporated in the relevant constant. The significance of this will emerge later. (Chapter V)

WORKERS	YEAR	REF	MAIN PIVOT	MATERIAL OF BEAM AND BULB	BALANCE TYPE *	APPROX SENSIBILITY (gms)	BALANCE USED FOR STUDYING	ANYTHING ELSE OF INTEREST
Steele and Grant	1909	64	Knife edge	Fused quartz	-	$4x10^{-9}$ A) 10^{-7} B)	Apparatus development	Made two balances, A for light loads, B for heavier.
Whytlaw-Gray and Ramsay	1910	65	Knife edge	Fused quartz	-	$2x10^{-9}$	Radioactive disintegration of radium	
Whytlaw-Gray and Ramsay	1912	66	Knife edge	Fused quartz	-	$2x10^{-9}$	Atomic weight of radium.	
Aston	1913	67	Knife edge	Fused quartz	A	10^{-6}	Separation of neon isotopes	First density balance proper.
Taylor	1917	68	Quartz fibre	Fused quartz	A	10^{-8}	Density and atomic weight of He.	
Stock and Ritter	1926,1928	69	Pin in cup	Fused quartz	A,C	$2x10^{-6}$	Boron and silicon hydrides	A number of balances described. First electromagnetic density balance
Rodebush and Michalele	1929	70	Pin in cup	Fused quartz	A	10^{-5}	Vapour density of NH_4Cl at elevated temps (300°C)	
Whytlaw-Gray, Cawood and Patterson	1931	49	Quartz fibre	Fused quartz	B	$4x10^{-9}$	Atomic weight of Xe.	Introduction of suspension of buoyancy bulb.
Lehrer and Kuss	1933	71	Knife edge	Fused quartz	C	$7x10^{-7}$	Apparatus development	Extension of Stock's ideas.
Woodhead and Whytlaw-Gray	1933	72	Quartz fibre	Fused quartz	B	$3x10^{-8}$	Atomic weight of C from limiting density of CO.	
Cawood and Patterson	1937	47	Quartz fibre	Fused quartz	B	$4x10^{-9}$	Atomic weights of C, N, F.	
Simons	1938	73						
Roberts, Emelens and Briscoe	1939	74	Quartz fibre	Fused quartz	A	$7x10^{-8}$	Vapour density of deteramines.	
Cassado, Massie and Whytlaw-Gray	1949	54	Quartz fibre	Fused quartz	B	$2x10^{-8}$	Molecular weight and B for n-propane.	
Johnson and Nash) Lundin, Harris and Nash)	1950,1951 1952	75, 76	Pin in cup	Fused quartz	C	10^{-6}	Vapour phase association of carboxylic acids.	
Cassado, Massie and Whytlaw-Gray	1951	77	Quartz fibre	Fused quartz	B	$2x10^{-8}$	Molecular weight and B for C_6H_6 linearity of PV isotherm	Used moveable ball bearing in centre of beam to alter balancing density.
Lambert and Phillips	1951	48	Quartz fibre	Fused quartz	B	10^{-8}	Molecular weight and B for N_2 and CH_4	Introduction of sensitivity adjustment by hanging weights on additional hooked fibre.
Simons, Sheirer and Ritter	1953	78	-	Nickel,gold plated	C	10^{-7}	Apparatus development	Automatic nulling version of an earlier balance.
Reeves and Whytlaw-Gray	1955	45	Quartz fibre	Fused quartz	B	$2x10^{-8}$	Atomic weight of Xe.	
Bottomley, Remmington and Whytlaw-Gray	1958	79	Quartz fibre	Fused quartz	B	$2x10^{-8}$	B for C_6H_6.	
Dunlop, Murphy and Bedford	1958	80	-	Fused quartz	C	10^{-7}	B for n-C_6F_{14}	
Buckingham and Raab	1961	34	Pin in cup	Fused quartz	A	10^{-5}	B for some polar vapours	Used deflection of beam as measure of density.
Lawley and Sutton	1963	43	Knife edge	Fused quartz	B	$4x10^{-7}$	B for 2 component mixtures.	
DiZio, Abbott, Zibello and Van Ness	1966	63	Knife edge	Aluminium alloy	C	10^{-5}	Virial coefficient of n-C_6H_{14}; apparatus development.	Used Ainsworth semi-microbalance
Turner	1966	41	Quartz fibre	Fused quartz	A	$4x10^{-7}$	B for various gases and mixtures	Used two A type balances to obtain effect of a B type balance.
Laing	1967	81	Metal ribbon	Aluminium alloy	C	$2x10^{-7}$	Density balance used for pressure measurements.	
Tisinger	1967	82	Pin in 'V'	Stainless steel beam, aluminium and brass float and counter balance, all gold plated.	C	$5x10^{-6}$	Compressibility of oxygen - apparatus development.	Operates at pressures up to 37 atmospheres.
This work	1969		Quartz fibre	Quartz	C	$3x10^{-8}$	B for some polar gases	

* A type balance operates at one predetermined density.

B type balance operates at more than one, but still predetermined, density.

C type balance has continuous coverage of density over its measuring range.

<u>TABLE (III.1.)</u>

SUMMARY OF DENSITY BALANCES DESCRIBED IN THE LITERATURE

CHAPTER III

DENSITY BALANCE DESIGN

A density balance is essentially a micro- or an ultramicro-balance used to measure the buoyant upthrust on a 'flotation' volume immersed in a gas. The principle was first used, in reverse, by Steele and Grant[64] in 1909, who used the upthrust on a bulb to counterbalance the downward force due to the object being weighed. The pressure of the gas providing the upthrust was measured, and with knowledge of its compressibility and the volume of the bulb, this gave a value of the upward force equal to the unknown downward one. Their balance, constructed from fused silica, had a knife edge pivot and the bulb and sample pan were hung on a quartz fibre fused to the beam. It was mounted in a vacuum tight case.

Since then a number of density balances have been described in the literature, with a variety of different designs and uses. These are summarised in Table (III.1).

It is of interest to compare density balance design with that of the so called 'vacuum' micro-and ultramicro-balance - a balance designed to measure very small weight changes due to adsorption, absorption of a physical or chemical nature, chemical and thermo-chemical changes and interaction with a strong magnetic field (magnetic susceptibility measurements) at pressures in the range several cm Hg to high vacua. Such balances have sensitivities similar to that required for a density balance, and may measure weight changes of a similar order; they are therefore very relevant to a consideration of density balance design. The design of vacuum ultramicro- and micro-balances has been extensively and authoritatively reviewed by Rhodin[83] and Gulbransen[84] in 1953 and by Behrndt[85] in 1957, and subsequent developments are very adequately covered in the six volumes of Vacuum Microbalance Techniques for 1960 to 1967[60]. The theory and applications of vacuum microbalance techniques have also been reviewed in 1965.[62] Consequently, no attempt will be made here to provide a complete coverage, but any relevant parallels and contrasts with density balance design practice will be pointed out.

The design of chemical micro- and semimicro-balances is also relevant, especially since a semimicro-balance has been used, with very little modification, as a density balance.[63] A comprehensive review of the theory, design and performance of chemical balances available in America was published recently[86] and includes information about almost all balances available in this country.

MATERIAL OF CONSTRUCTION

Fused silica (quartz, fused quartz) has usually been used for the construction of density balances, and this is explained by the following desirable properties of quartz:

1. It has low density.
2. It has a high strength to weight ratio.
3. It has a low coefficient of thermal expansion.
4. It is readily available, pure and homogeneous, as rods, plates, tubes, etc.
5. It is chemically inert to almost all gases.
6. Chemical cleaning of quartz is easy.
7. Quartz does not occlude gases.
8. For many gases adsorption on quartz is not significant.[87,88]
9. Strong, thin, flexible quartz fibres can be drawn[89] and fused directly without the use of cements.
10. The elastic properties are nearly perfect; there is little flow or creep, and so torques in fibres can be small and reproducible.

Its major disadvantages seem to be that it is a poor conductor of electricity and so electrostatic charges can build up and interfere with the balance, and also that it ages slowly so that the gradual relief of strains set up during the manufacture of the balance may cause the zero point to wander erratically. The ordinary glass annealing oven has fans to ensure temperature uniformity, and the vibration from these can damage a delicate balance.

Of the four metal density balances described, Tisinger's[82] was for use up to pressures of 35 kg/sq cm (about 37 atmospheres), so that a hollow glass bulb could not be used. As will be seen later, one object in density balance design is to have equal adsorption on either arm, so that if a metal 'float' is used the rest of the balance should be made from or plated with the same metal, and so the whole balance was made from metal. Of the other three metal balances, one seems to have been a prototype only,[78] another,[63] an ordinary semimicro-balance in a special metal chamber, was said by the authors not to have given reproducible results with chemically more reactive gases, and the other[81] was used for pressure measurements using a commercially available metal vacuum micro-balance.

Vacuum micro-balances have often been made from quartz but Dural[91] and Invar[92] have also been used. The present situation is that a commercial balance made from aluminium alloy satisfies the requirements of most users of vacuum micro-balances, so these will probably be used increasingly.

There is, however, a further consideration to be taken into account in the case of balances used for sorption studies, magnetic susceptibility measurements and thermogravimetric analysis. In such investigations, the problems which arise because of temperature gradients along the beam may be minimised by having a beam with both low thermal expansion and high thermal conductivity.[93]

Taking both effects into consideration, there is little to choose between quartz and Dural. It must also be borne in mind that adsorption on the balance is likely to be of greater importance in the case of a density balance which is generally used at higher pressures. This is more readily minimised if one material only is used in the construction,[63] an aim that is more readily met with a fused silica construction than by using metals. This is even more so in the case of an electromagnetically operated balance.

TYPE OF MAIN PIVOT

The following types have been used for density balances:

1. Knife edge This was used in Steele and Grant's original instrument[64] and in some later ones.[43,65-67,71] It is difficult to grind a suitable knife edge in fused silica, and the knife edge is easily chipped subsequently if not handled with great care.[68] Sapphire or agate knife edges can be cemented to the beam to circumvent this, but there is a further more important disadvantage. In a very sensitive balance, the knife edge has a tendency to 'walk',[49] i.e. alter its position on the plate or shallow groove where it rests, and so extreme care when using the balance and good insulation from vibration and jolting is essential for good results. The long term stability will inevitably be poor because of the

susceptibility to shock. A chemical balance, which has a lower absolute sensitivity may be used with a larger bulb to give the necessary ratio of sensitivity to range,[63] but this type of instrument does not perform well in a gas line. The variety of materials used in its construction complicates the problem of adequately equalising the moments of adsorbed gas on the two arms.

2. Pin and cup Flame drawn tungsten points in quartz cups,[69,75,76] tungsten points in sapphire V's[82] and quartz points in quartz cups[34] have all been used for density balances. The last of these was shown to be less satisfactory than a knife edge pivot.[45] Sapphire (gramophone) needles in quartz cups have been used in a less sensitive adsorption balance,[94] and electropolished tungsten points in parabolic quartz cups were used to very good effect in a sorption balance[95] with ultramicrogram sensibility and very small long term zero drift. The balance was, however, susceptible to shock, though not to vibration. One of the commercially available micro-balances (Sartorius[96]) uses a pivot of this type. Thus it seems that such a pivot can be very satisfactory, but close attention to the detailed shape of the pin and cup is necessary.

3. Fibre, wire or ribbon The type of pivot used most frequently in density balances is a quartz fibre fused to the quartz beam. In other micro-balances, a ribbon clamped to a metal beam[97], a tungsten wire cemented with

fused silver chloride to a quartz beam[98] and a quartz fibre fused to a quartz beam[88,99] have all been used. Most commercially available balances use this type of pivot: Cahn (metal ribbon) [100], R.I.I.C.(wire)[101], C.I.(wire)[102], Oertling (quartz fibre)[103].

For a density balance there seems to be little to choose between the use of a well made pin in cup pivot and the use of a ribbon, fibre or wire, although the precision of control needed for the profile of the cup, and the equipment necessary for electropolishing the tungsten points, makes this type of pivot less easily fabricated. With a quartz balance beam, a quartz fibre is as easily used as a metal ribbon or wire, and has the further advantage of needing no cement. However, by using a wire cemented in a groove cut to a jig controlled depth,[98] or a pin/cup fused on in a jig,[95] it is possible to construct a balance with predetermined sensitivity. This can not be achieved using a drawn fibre with any certainty, so that where this is used, some means must be provided for subsequent adjustment of the sensitivity (see later).

ALTERATION OF BALANCING DENSITY

A density balance is of very restricted use if it can be used at only one density (see Chapter II). Many methods have been employed in order to make measurements or comparisons of density over a range of values, or in the case of vacuum micro-balances, to measure over a range of weight changes.

The simplest method is to use the deflection of the balance as a measure of the density of the gas surrounding the bulb,[34] or of the weight of the sample.[50] This is a linear relationship over a restricted range (see above), but the limits are not wide, so that the ratio of range to sensitivity is small.

An alternative method is to fuse pieces of quartz on or off the (quartz) beam or, more conveniently, to add or remove riders on the bulb or load side of the beam.[46,49] This provides a range of values but can be tedious in operation because the balance case must be opened between each set of readings. The limitations imposed by this method can be tolerated with a density balance used only for comparisons of density, but are unacceptable in the case of vacuum micro-balances, or in the case of density balances used in the direct measurement of density, where the weight change to be measured is not necessarily known prior to the experiment.

There are, moreover, objections to the addition or removal of quartz by fusing because such a process inevitably sets up strains in the balance, and the slow easing of these strains is reputedly a factor in the zero drift of the balance (see above). Furthermore, any intense heating of quartz is liable to cause 'bloom' (silica volatilised in the flame and condensed on cooler parts of the balance), the finely divided nature of which can lead to problems from non-compensated adsorption. Even opening the case to add or remove riders would be better avoided because in so doing the balance is almost inevitably subjected to some shocks. This alters the zero point, and so calibration is necessary each time this is done.

Accordingly, methods have been evolved for changing the balancing density or load from outside the case. One method used a piece of soft iron in the centre of a hollow beam, which could be moved along the beam by a magnet outside the case,[104] and another[77] has employed a ball bearing which could also be moved in this way inside the beam, which had depressions to locate the ball bearing. Neither of these could give reproducible balancing points and so calibration was necessary after each move.

A more successful approach was that of Di Zio et al.[63] who used a semimicro chemical balance enclosed in a special chamber. Leak tight glands in the casing enabled the balance and weights to be operated by the normal linkages, so that the upthrust on the bulb could be measured continuously, with the limitation being that of the normal resolution of the balance.

Electromagnetic methods have been widely used for vacuum micro-balances, with very many different designs. Magnet-magnet[69], magnet-coil[75,76,95], coil-magnet[96,97,100-102] coil-coil[94] and induced magnet-coil[99] interactions have all been used (the first word referring to the movable member attached to the beam and the latter to the member outside the case) in density or vacuum micro-balances, and most of these have been used in a variety of configurations. Those which are potentially of most use for high accuracy work are:

1. A long permanent magnet is sealed inside the beam and centred relative to it. A large electromagnet directly beneath this provides a controlled field by a measured current. The current is directly proportional to the moment exerted on the beam, and hence to balancing density.[75,76] The principal disadvantage to this method is that to exert a given moment on the beam, a much larger current is needed than with either of the next two methods.

2. A long permanent magnet is incorporated with a hangdown fibre, or hung below the load (bulb or sample pan). The magnet hangs in a solenoid of small diameter mounted on the outside of the hangdown limb. This arrangement was used in the sensitive adsorption balance of Czanderna and Honig.[95]

3. A moving coil meter type of arrangement may be used with a coil, attached to the centre of the beam,

which moves in the uniform field of a suitably shaped permanent magnet. Current is fed to the coil along the two metal pivoting wires or ribbons. This method is used in all the commercial electromagnetic micro-balances.[96,100-102]

Of these three, the last two are more promising for a balance with a large ratio of range to sensitivity, where it is necessary to have relatively very constant currents, which aim is achieved more readily with small currents. For a density balance, the magnet in solenoid arrangement has the advantage over the moving coil design that the parts in contact with the gas (the magnet) can be encased in the same material as that from which the balance is made very much more readily. The major disadvantages of the magnet in solenoid arrangement are the markedly greater sensitivity to stray magnetic fields, and, depending on design details, possibly also to level changes.

ATTACHMENT OF FLOTATION VOLUME

Density balances have usually been used with gases at pressures of only up to one atmosphere and, since the load on the pivot is to be minimised, the flotation volume in those described in the literature almost invariably is a hollow, thin-walled glass bulb. The exception is the aluminium float used by Tisinger[82] for pressures up to 37 atmospheres.

The contraction of a thin walled bulb with increasing external pressure can give rise to errors in two distinct ways[71]:

1. With a bulb fused directly on to the beam, the centre of mass of the bulb will move relative to the pivot, thus altering its weight moment and hence the balancing density.
2. The upthrust on the bulb will change because of its volume change, and again this will alter the balancing density, though in the opposite sense to 1.

Lehrer and Kuss[71] applied theoretical corrections for both errors, but as 1. is markedly larger[47] and may be circumvented by hanging the bulb on a thin fibre, as a design principle, this should be done. If, as is likely, the bulb wall is of an uneven thickness such a theoretical correction will be inadequate. The effect of 2. can be measured experimentally with an electromagnetically operated density balance, and the appropriate correction applied (see Chapter II).

COMPENSATION FOR ADSORPTION

First order correction for adsorption is achieved by equalising the apparent surface areas on the two arms of the balance beam using an area counterbalance, which may conveniently serve as a mass counterbalance also. It was found with one balance[47] that even with such compensation adsorption caused significant errors, and this was traced to the different ratio of real to apparent surface of a blown quartz bulb, and a quartz cover slip. A trial and error adjustment for this was applied by using the balance to determine the molecular weight of sulphur dioxide. Sulphur dioxide is heavier than the other gases for which the balance was to be used and is adsorbed to a larger extent than many other gases.[87] Thus, any inequalities in area would give rise to a large effect. The area counterbalance was altered in size until a good result was obtained, when it was found that the ratio of apparent areas (bulb to plate) was 4:3.

An alternative technique which has been employed is to flame the bulb and area counterpoise and so approximately equalise the ratio of real to apparent areas.[48]

With an all metal balance, the equalising of real to apparent surface ratios should be more easily achieved, by plating with a suitable metal; gold has been used by Tisinger[82] and is used in the models of the Cahn[100] balances designed for work in high vacua.

METHODS USED FOR OBTAINING REQUIRED SENSITIVITY

The problem has been approached in two ways:

1. A balance of largely unknown sensitivity is made and is then adjusted by one of several techniques.
2. By the use of an appropriate design, jigs can be

used to construct a balance of predetermined sensitivity. This method has been used with some adsorption balances.[95,98]

The adjustment of the sensitivity of a quartz balance was originally accomplished by removing or adding small pieces of quartz to a peg on top of the beam and so lowering or raising the centre of gravity of the beam. The operation is tedious, and because of the slow ageing of quart, a few weeks may be required after each adjustment before the balance attains a stable zero and the effect of the adjustment can be measured exactly.[105] Furthermore, such operations are liable to produce 'bloom', the objections to which are outlined above.

Lambert and Phillips[48] have introduced a much more satisfactory method. The beam is provided with an additional, hooked fibre, drawn from a point appreciably above (or below) the axis of the beam. A preliminary sensitisation is carried out as above, the balance is aged by baking at 200°C for several hours and then left for some weeks before use. Final adjustments to the sensitivity are then made by adding quartz weights to the hooked fibre.

DIFFICULTIES MET WITH IN USE OF A DENSITY BALANCE

The main problem is that of zero point instability. This can arise for a balance with a knife edge or a pin in cup pivot from jarring or level changes which alter the relative positions of the balance beam and frame. In the case of a quartz fibre pivot, mechanical shock and vibration can apparently cause zero changes also, and this has been attributed to the setting up or easing of strains in the balance.[48] It is therefore important to minimise any vibration by suitable mounting of the balance, and to use the balance with the utmost care to avoid jarring of any kind. In this connection the electromagnetically compensated balance has the advantage that the beam can be very gently moved by fine adjustment of the control current. Furthermore, since a vacuum reading can be taken before and after each density measurement, the number of readings at risk if the balance should be accidentally jarred is one at most.

Apart from sudden changes, the zero may drift for a variety of reasons. The slow easing of strains set up during the manufacture of the balance is one such cause. This can be largely eliminated by the ageing treatment which was introduced by Whytlaw-Gray[49] and which has been outlined above. The slow condensation of mercury vapour on the balance beam has been reported to occur even when gold mercury traps are used,[106] and this also can give rise to zero drift. The author has experienced no such effect when tin foil mercury traps were used. Condensation of vacuum grease on the balance has also been suggested as a possible source of zero drift.[105] This seems unlikely to occur with modern, low vapour pressure greases, but in any case it can be eliminated by the use of 'O' ring sealed joints and greaseless vacuum stopcocks. In all these cases the electromagnetically operated balance has the advantage that the zero point is required to be stable over much shorter periods, viz. the time required for one density reading (about one hour) rather than the time required for four or five readings.

The other important possible source of trouble is from the inadequacy of simple corrective procedures for adsorption of the gas on to the balance beam and bulb. Alteration of balance zero was observed by Stock[69] who, using a balance with no area counterpoise, noted that weight was gained on the bulb side, and lost slowly by prolonged evacuation. When the apparent area moments were equalised no such effect was observed, within the limitations imposed by the relatively low sensitivity of his balance. Cawood and Patterson[47] equalised real surface moments by the trial and error method described above. This procedure was necessary because of the unlikely and inconsistent values of the molecular weights they obtained for ethylene, carbon dioxide and nitrous oxide, gases which would not normally be expected to be adsorbed to a significant extent. More recently, in this research group, density balance measurements have given a second virial coefficient for fluoroform[34] subsequently shown to be in error by 100 cm^{3}mole^{-1} in

200 $cm^3 mole^{-1}$,[25] and have implied a positive second virial coefficient for bromomethane.[41] Other measurements for bromomethane, chloroethane and trimethylamine have given virial coefficients considerably more negative than those reported by other workers and also those reported here.[41] These observations have all been attributed to errors arising from adsorption on the balance.

The author has, however, observed no errors which indicated that significant adsorption was occurring during the course of the work described in the later chapters. Furthermore, measurements of adsorption on a quartz micro-balance of similar design to that of balances used for density determination showed that for a gas as readily liquefied as propane, even if no area counterpoise were used, the error introduced into the determined second virial coefficient would be of the order of 5 to 10 $cm^3 mole^{-1}$ at 25°C.[54] Polar vapours would be expected to be adsorbed to a somewhat greater extent and so the errors in the virial coefficient would also be larger but probably by no more than an order of magnitude.

It seems likely that the error in the second virial coefficient for fluoroform and the implication of a positive virial coefficient for bromomethane quoted above might be accounted for, in part at least, by errors in the molecular weights which had to be assumed because a simple single-density balance was used (see Chapter II). The other measurements for bromomethane, chloroethane and trimethylamine were made using two balances operating at different densities. Both balances had the flotation bulb fused directly to the beam and it seems probable that the errors were introduced by contraction of the bulb, as outlined above.

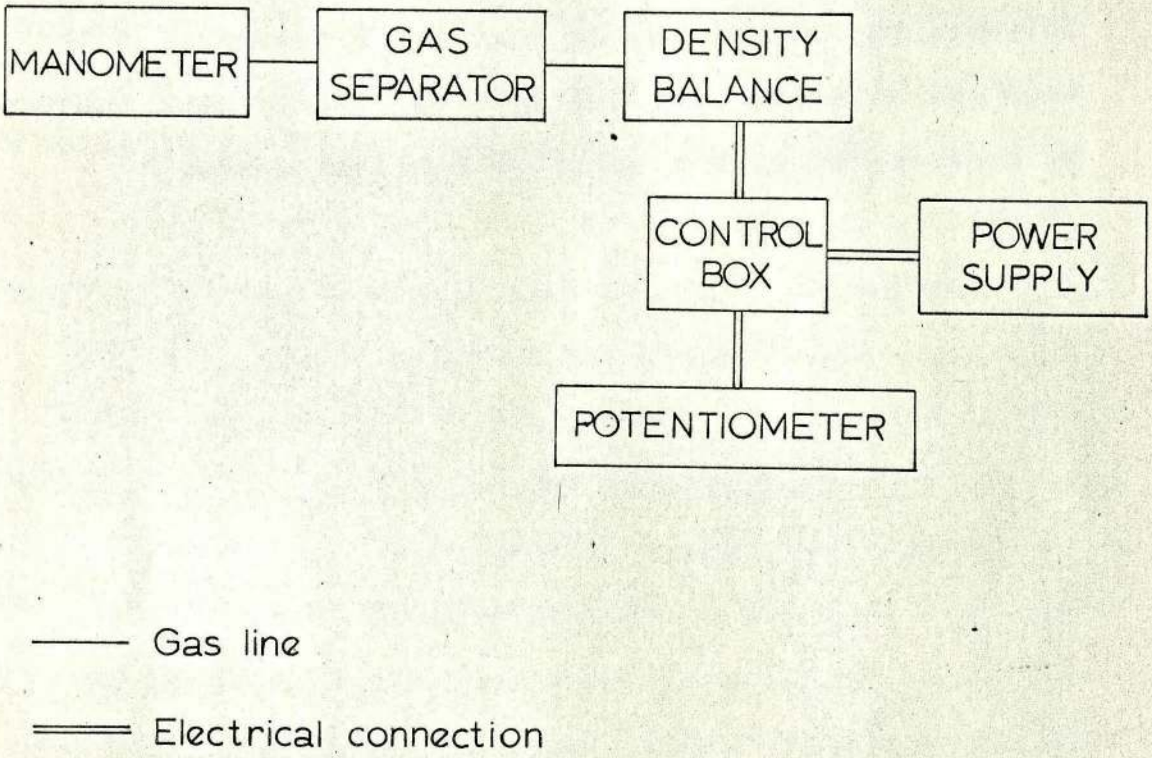


Figure (IV.1) Block diagram of the apparatus

CHAPTER IV

DESCRIPTION OF APPARATUS USED

The apparatus has been built to measure virial coefficients by the method outlined in Chapter II. The requirements may be summarised:

1. A manometer capable of measuring pressures up to 50cm Hg with an accuracy of about ±0.001cm Hg.
2. A density balance able to compare densities up to 4×10^{-3} gm.cm^{-3} to within one part in 5×10^{5} of the higher densities with a limiting accuracy of $\pm4\times10^{-9}$ gm.cm^{-3} at the lower end of the range.
3. Control of the temperature of the gas in the balance case to about ±0.01°C.

In addition to these conditions, in order to extend the range of gases which can be studied to include those which interfere with the surface properties of mercury or actually react with mercury, a separator with a sensitivity of 0.0005cm Hg is required.

The apparatus is shown schematically in the block diagram, Figure (IV.1).

THE MANOMETER ASSEMBLY

The manometer assembly is similar to that of Lambert and Phillips[48] and is described in detail elsewhere.[107] It consists basically of a thin-walled, glass U-tube and calibrated glass scale enclosed in a casing with glass front and back through which thermostatted water is passed. A microscope with an eyepiece graticule on which one division equals 0.001cm Hg is mounted on the case, and provision is made for it to be moved in three mutually perpendicular directions, for focussing on the menisci and scale graduations. The scale and menisci are illuminated by a normal, diffuse light from behind. Moveable shrouds are used to improve the clarity of meniscus images. The level of mercury in the manometer can be altered without allowing oxygen to come into contact with the mercury.

After the manometer had been set up vertically, using a plumb line and sensitive spirit level, the tubes were washed by drawing up into them warm chromic acid, distilled water, and 50% nitric acid, in succession, and then thoroughly rinsed several times with distilled water. The tubes were then evacuated to dry them, and triple-distilled mercury admitted via the mercury handling system.

The performance of the manometer has been marred by the occurrence of a zero error, arising from a slight lean of the assembly from the vertical, three different values of which have applied at different times during the experiments, viz. zero, -0.007 cm Hg, -0.010 cm Hg. The change in tilt is probably due to the lack of rigidity of the bench and bolted-up stand on which the manometer rests. This bolted-up stand has now been replaced by a welded one. The correction is fairly readily verified by checking with a spirit level the inclination of one of the microscope carriage surfaces to the horizontal.

Pressures can be measured with a resolution of ±0.0002 cm Hg by estimation of each meniscus position to 0.1 eyepiece graticule division. The measured pressure is then corrected for glass scale imperfections,[107] capillary depression,[108] the temperature of the glass scale and mercury, and for any zero error to give a value of pressure in cm Hg at 0°C and under local gravity. If the nonlinearity is defined as irregular deviations from a strictly linear relationship between observed and true pressures, the combined linearity and reproducibility of the pressure reading with these corrections as a function of true pressure is about ±0.002 cm Hg, provided that the meniscus heights differ by less than about 30%, which means in practice that the mercury must be run up the tubes prior to making a reading. The most likely limiting factor in the linearity is the calibration of the glass scale, and in the reproducibility it is errors due to refraction and the relatively large corrections for capillary depression arising from the use of 11.5 mm diameter tubes. These were used because of their ready availability. The nonlinearity errors are probably

Length of beam	15cm
Diameter of beam	0.1cm
Diameter of framework rod	0.2cm
Weight of bulb in air	0.68gm
Diameter of bulb	3cm
Volume of bulb	14cm^3
Weight of magnet in sheath	1.2gm
Length of magnet	5cm
Diameter of magnet	0.2cm
Period of swing of balance	17sec

Table (IV.1)

the larger by a considerable margin. (See Chapter VII for detailed account of error assessment.)

THE DENSITY BALANCE ASSEMBLY

The balance follows the design of Lambert and Phillips,[48] with the essential modification of the provision of an electromagnetic method for bringing the beam to null in gases of differing densities. The magnet in solenoid arrangement was the method adopted. (See Chapter III) At the time the decision was taken, no commercial balances using the moving coil principle were on the British market. The technical problems of the latter arrangement made it unacceptable.

The many alterations to the original balance and case which have been found necessary or desirable during the course of setting up the apparatus are described in detail in this section, together with the reasons for their incorporation.

The balance proper is shown in Figure (IV.2) and in its case in Figure (IV.3), and Table (IV.1) gives the principal dimensions. The magnet and bulb are hung on the same arm of the balance and the other hangdown fibre now holds only a counterbalance weight, instead of the original arrangement of magnet on one arm and bulb on the opposite arm. This means that the balance is

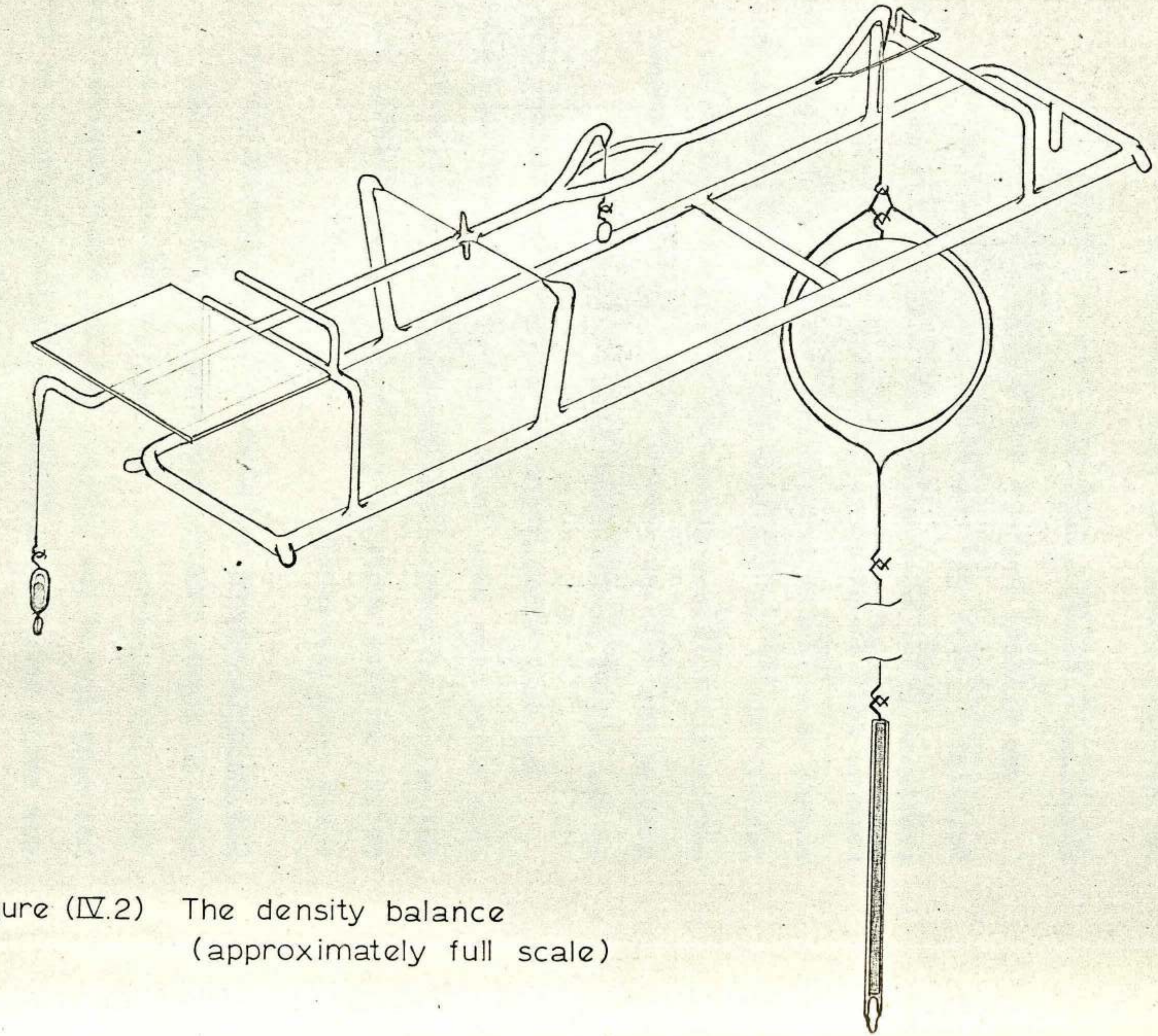


Figure (IV.2) The density balance
(approximately full scale)

operated under a constant, although increased, load and eliminates the troublesome alteration in sensitivity arising from the fact that the hangdown and main (pivoting) fibres could not easily be made colinear within the required limits (the main fibres to be no more than ±0.003 cm from the line joining the points from which the hangdown fibres are drawn). The magnet is actually hung about 6 cm below the bulb, for reasons mentioned later. A special stirrup was used to prevent any change in the relative position of the magnet and solenoid which would occur with bulb contraction were the magnet hung directly on the bulb. All the hooks on the stirrup, extension fibre and magnet sheath are V-shaped to prevent rotation of the magnet which was suspected of causing zero point changes in the balance during some of the early measurements.

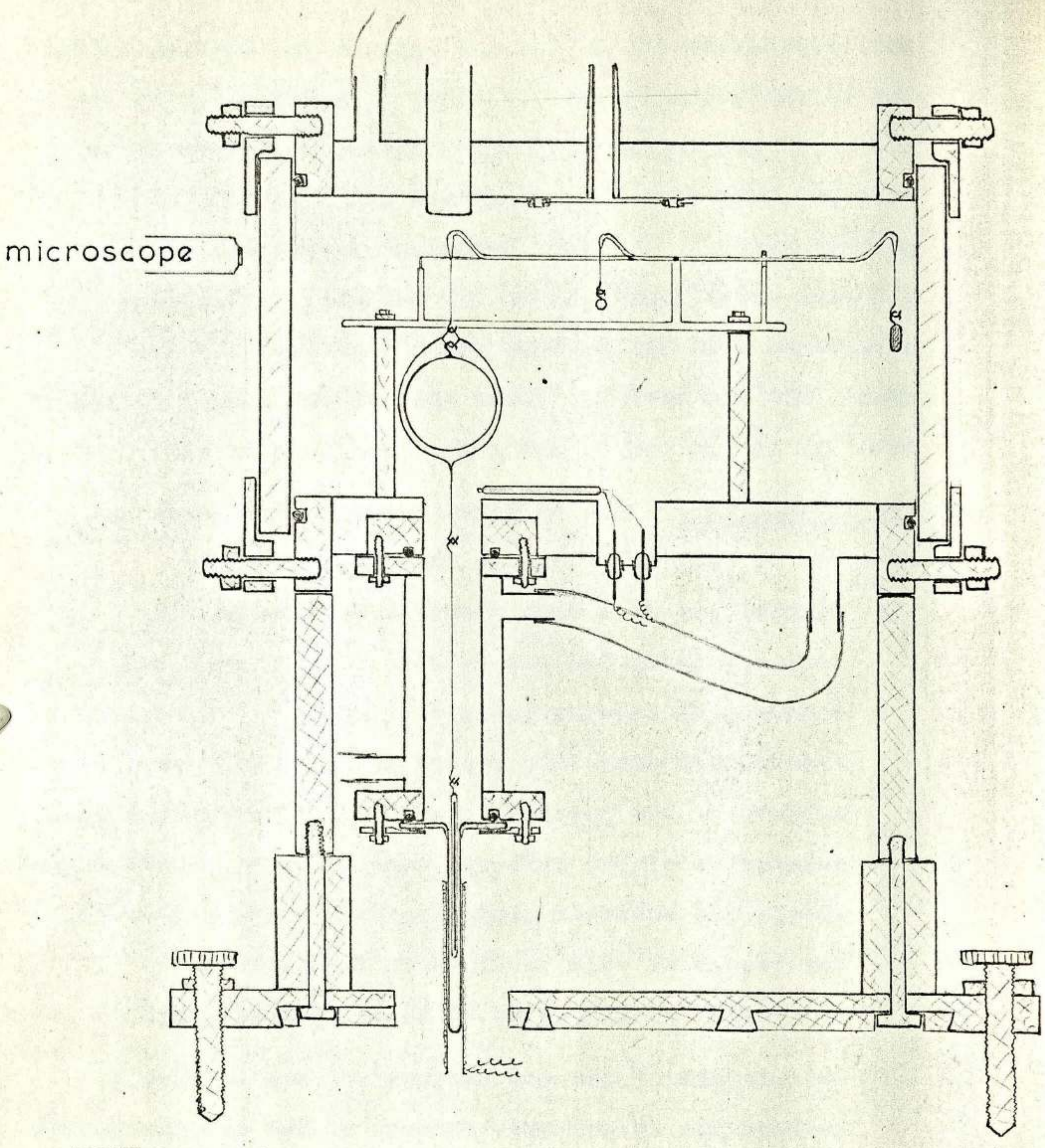
The counterweight is a mercury filled quartz bulb rather than a solid quartz weight, in order to reduce its volume and thus reduce changes due to buoyancy in the total load on the beam, which might cause second order effects on the constancy of sensitivity.

The period of swing of the balance as it was used was about 17 seconds, and the resolution was 3×10^{-8} gm, which with a bulb of volume 14 cm^3 is equivalent to a resolution of density of 2×10^{-9} $gm.cm^{-3}$. The repeatability of the balance, and hence its precision, when used as a null instrument can depend not only on the balance itself but on the stability of the resistance across which the potential drop associated with the solenoid current is measured, and on the accuracy and stability of the potentiometer. The most important factor has probably been the zero point stability of the balance. Under the conditions used the balance has a repeatability of about 3×10^{-7}gm over the lower half of the range, rising to 6×10^{-7}gm at the top of the range (see Chapter VII).

<u>The balance case</u> The original glass balance case was found to be unsuitable in two important respects:

(a) Despite the fact that previous workers in this research group had had no difficulties with the build-up of electrostatic charge,[34,41,43] trouble was experienced from this source during early tests on the balance. One possible reason for this was the small separation of the bulb and case and also of the magnet sheath and solenoid limb which was finally adopted. The result of this would be to make even a relatively small amount of charge significant.

(b) Measurement of the gas temperature was difficult, because the temperature control of the air thermostat was not as good as anticipated, largely because of inadequate mixing arising from our inability to obtain a sufficiently vibrationless fan. This meant that the temperature in the balance case had to be measured with a resolution of 0.01°C and an



▨ Glass in cross section

▨ Metal in cross section

● Viton A 'O' ring

Figure (IV.3) Cross section of the balance in its case (approximately half scale) accuracy of 0.1°C, by a short time response method. Most such methods have temperature sensing elements which also have a significant pressure dependent response; although a thermistor was used it had a marked dependence on the pressure of gas in the balance case up to about 10cm Hg and a significant one over the whole range of pressures used (10 to 50 cm Hg). This is a thermal conductivity effect, and so, as expected, there was also a difference from gas to gas.

To circumvent both these difficulties, it was decided to use a metal balance case with a jacket through which thermostatted water could be pumped, Figure (IV.3). Non-magnetic stainless steel was selected as the material for construction of the case, so that measurements could be made on most gases and so there would be no interference with the magnetic compensation. About 1 cm thick, 12.6 cm diameter plate glass discs were readily available so these were used for the end windows. They were sealed with Viton A 'O' rings and retained by a clamping ring bolted by six studs to the end flange. To facilitate the construction, the end windows were not water-jacketted. Since the air thermostat is retained, this does not affect temperature control of the balance which is normally better than ±0.005°C short term, and ±0.02°C long term, at 25°C and about two or three times these values at 40° and 50°C.

A thermometer well is provided to enable the temperature of the case to be measured with a Beckman thermometer, and a thermistor was also used inside the case in the earlier experiments, to measure changes in gas temperature and so ensure that the gas had come to thermal equilibrium. This was to enable measurements to be made as soon as possible after introduction of the gas, a point which might have been of importance if the zero of the balance had been markedly subject to drift with time.

The thermistor resistance was measured using a Pye Wheatstone bridge, connection through the case being via two of four ceramic lead-throughs provided (the other two are spare). The thermistor has a resistance of 2,000 ohms and a temperature coefficient of $-3.1\%/^{\circ}$C at 20°C. An external Pye Scalamp galvanometer was used. The resistance could be measured with four figure resolution, so that temperature changes of about 0.002°C were observable at 25°C.

The balance is mounted inside the case on two stainless steel supports, to which the frame of the balance is clamped by a crossbar which is screwed down.

The microscope which is used for viewing the balance is mounted on one of the end plate clamps on ½" diameter brass rods. The microscope has an eyepiece scale and variable magnification. The almost normal angle that the microscope makes with the end plate has a fine adjustment over a small range. This enables a fiduciary pointer on the balance frame to be set on a suitable graduation of the eyepiece scale by tilting the microscope. The position of the beam pointer when the beam is at the top stop is used to check that no change occurs in the magnification of the microscope. The beam is brought to balance by nulling on a suitable graduation between the frame pointer and balance pointer at top stop. The microscope is normally used with a magnification of about X100, so that nulling of the balance can be achieved to ±0.001 cm.

The water jacket of the balance case is supplied by a centrifugal pump with thermostatted water from a 25 litre tank lagged with expanded polystyrene. A 500 watt blade heater is supplied from a Variac transformer, the output of which is switched by a Gallenkamp electronic relay. A 0° to 50°C Electro-methods mercury contact thermometer is the sensing element and temperatures in the range of 25° to 55°C can be used with the present arrangement.

The balance case is connected to the gas and vacuum lines by a standard B14 taper joint sealed with black wax. A baffle plate is fitted inside the case over this opening to prevent jets of gas striking the balance, and so to minimise the risk of accidental damage.

Before setting up the balance and casing, they were thoroughly washed using a warm solution of Quadrilene detergent in 50% aqueous methanol, and then rinsed repeatedly with distilled water and dried by evacuating the case in which the balance was placed temporarily. After this, care was taken to handle the balance and case as little as possible, and in any case this was usually done with thoroughly degreased tools.

The balance case is mounted on a stand made from a ½" Dural plate base, with lead weighting and four levelling screws. Two uprights, slotted and screwed to the base, hold the balance case by the end flanges with four screws. The stand rests on a ¾" thick marble slab which is screwed to the Handy Angle frame of the air thermostat. The marble originally rested on a ⅛" thick sheet of polyether foam which was intended to damp out vibration. However, it gave rise to non-reproducible changes of vacuum null current, presumably because of changes of level of the balance, and so it was removed. This greatly reduced the zero point changes and actually seemed to improve the insulation from vibration, perhaps by increasing the mass being vibrated. The air thermostat is an expanded polystyrene box built on a Handy Angle frame, mounted on a ½" thick Dural base 32" x 24", which is fitted with three levelling screws. An Electro-methods regulator is mounted next to the balance case. Air is blown across a heating element by a fan blade powered by a motor outside the thermostat; the motor is mounted on the wall of the room to minimise transmission of vibration to the balance. The heating element has two separate manganin windings on a Pyrex rod frame, one of resistance 50 ohms, one of reistance 30 ohms. The former is supplied with 12 volt a.c. when the thermostat is operating at 40° and 55°C and switched off for operation at 25°C; the latter is supplied by a Variac transformer, with a relay operated by the regulator switching the transformer secondary. The Variac is adjusted at each temperature to give equal on and off times. It was found essential to remove the regulator adjusting magnet when using the balance because of interference with the balance magnet. For the same reason, the relay was mounted a long way from the balance. The air thermostat is operated at approximately the same temperature as the balance case water jacket (±0.05°C). There was no significant change in balancing density with a temperature difference one hundred times larger (5°C). The air thermostat is clamped with four G clamps, which allow for level adjustment while maintaining a rigid fixing, to a table loaded with three sandbags to improve its stability and insensitivity to vibration. The table is separate from the bench and framework used for mounting the rest of the apparatus.

<u>The solenoid</u> has 300 turns of 28 SWG enamelled copper wire wound on a 0.01 cm thick aluminium former of diameter 0.08 cms. The aluminium stock from which the former was made was selected for its low ferro-magnetism.[*] It has a resistance of 1.6 ohms. The windings are encased in polystyrene to minimise movement. The solenoid is an interference fit on the glass limb in which the magnet hangs and is further fixed in position with black wax.

The diameter of the solenoid was reduced from the original 1.2 cm to minimise the change in sensitivity with deflection experienced with the original solenoid. The field at a point on the axis of a circular solenoid is $2\pi ni(\cos\phi_2-\cos\phi_1)$,[109] where i is the current, n the number of turns per unit length and $2\phi_1$ and $2\phi_2$ the angles subtended at the point by the two ends of the solenoid. $(\cos\phi_2-\cos\phi_1)$ will change with displacement along the axis but, over any particular range, this change will be reduced by making the ratio of length to radius of the solenoid larger. The location of the magnet relative to the solenoid also affects the constancy of force on the magnet at a given current with displacement.

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[*] The selection process used was waving the metal near a N.M.R. magnet and the piece which had least effect was that used.

The range over which the force changes least is approximately symmetrical about the position of maximum force, a relationship which is very conveniently used when setting the solenoid position. This position occurs with the magnet roughly halfway into the solenoid. (See Appendix I).

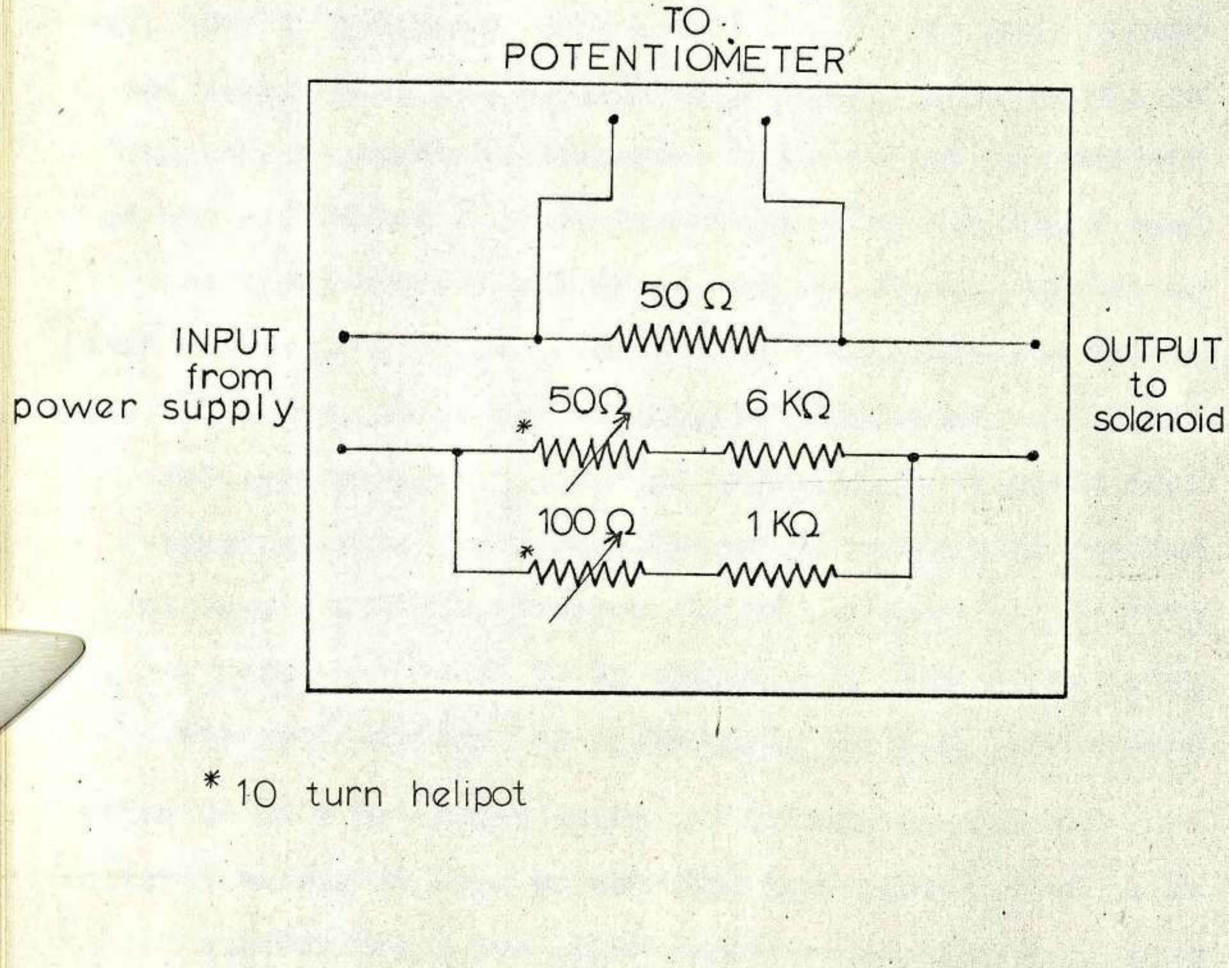
It was originally intended to mount the solenoid directly on the main case with a Viton A 'O' ring seal, but because parts of the case were not entirely non-magnetic this arrangement gave rise to a sensitivity markedly dependent on the deflection of the balance, with the balance actually top heavy at one end of the swing. The balance was also very sensitive to the movement of magnetic or magnetisable material some distance from the balance: in particular the null current (or alternatively and equivalently the balance position) depended on whether a lift 30 feet away was up or down. This effect probably arose because of a larger absolute change in the strength of the earth's field in the vicinity of magnetisable material, but could also have been an effect in change of level of the balance. A temporary arrangement with magnet and solenoid moved about 6 cm lower showed that in this position the effect due to the lift was not observable. Accordingly, a 6 cm long water-jacketted brass extension tube was made which sealed with Viton A 'O' rings between the case and the solenoid. The brass stock was selected in the same way as the aluminium used for the solenoid former. This extension could be gold plated inside if the balance were to be used for gases which react with brass.

With the extension fitted, however, the magnet was then situated some 12 cm below its point of suspension with the result that small changes in level of the balance case caused relatively large displacements of the magnet relative to the solenoid and balance case. This caused changes in the balance null current at constant density, due to the non-constant magnetic environment. Aligning the magnet as centrally as possible by eye in the solenoid made the level sensitivity insignificant.

For the range of densities to be covered (0 to 4×10^{-3}gm.cm^{-3}) with the magnet and solenoid used, the range of current required is 0 to 40 milliamp. The current was originally supplied by three 75 amp-hour lead-acid accumulators connected in parallel. When thermostatted, these provided an adequately stable current over periods of up to half an hour, but showed drifting over longer periods. Moreover, they required up to six or seven hours to settle down at the higher currents to a sufficiently stable value for measurements to be made.

It was decided to eliminate the settling down period and for greater convenience during measurements to replace the accumulators with a Solartron model AS1413 stabilised d.c. power supply. Because the current supplied by this unit can readily be adjusted very finely, and there is a negligible settling down time after adjustment, this also offered the very considerable advantage of using the balance as a null instrument. Whereas, with the original arrangement for which the current could not be easily altered, it would have been necessary to make five or six separate readings of current and pressure in the vicinity of the required balancing pressure, in order to make a plot of pressure versus balance deflection and so to obtain a value equivalent to the null current, one or two measurements now suffice. Apart from saving time, this also means that the period over which zero drift can take place is drastically reduced. Furthermore, the balance itself can be operated at intrinsically lower sensitivity because, in the author's experience, it is possible to null by a factor of at least ten more sensitively than it is possible to read displacement.

The d.c. output of the power supply is 0 to 40 volts at up to 0.5 amps, the unit can be used in either constant current or constant voltage mode, and a preliminary investigation showed that the latter gave less noise and a more stable output. The voltage output can be adjusted in steps of 0.1 volts with an additional continuous setting over any 10 volt interval of the range. In fact, the resolution of this continuous control was not



* 10 turn helipot

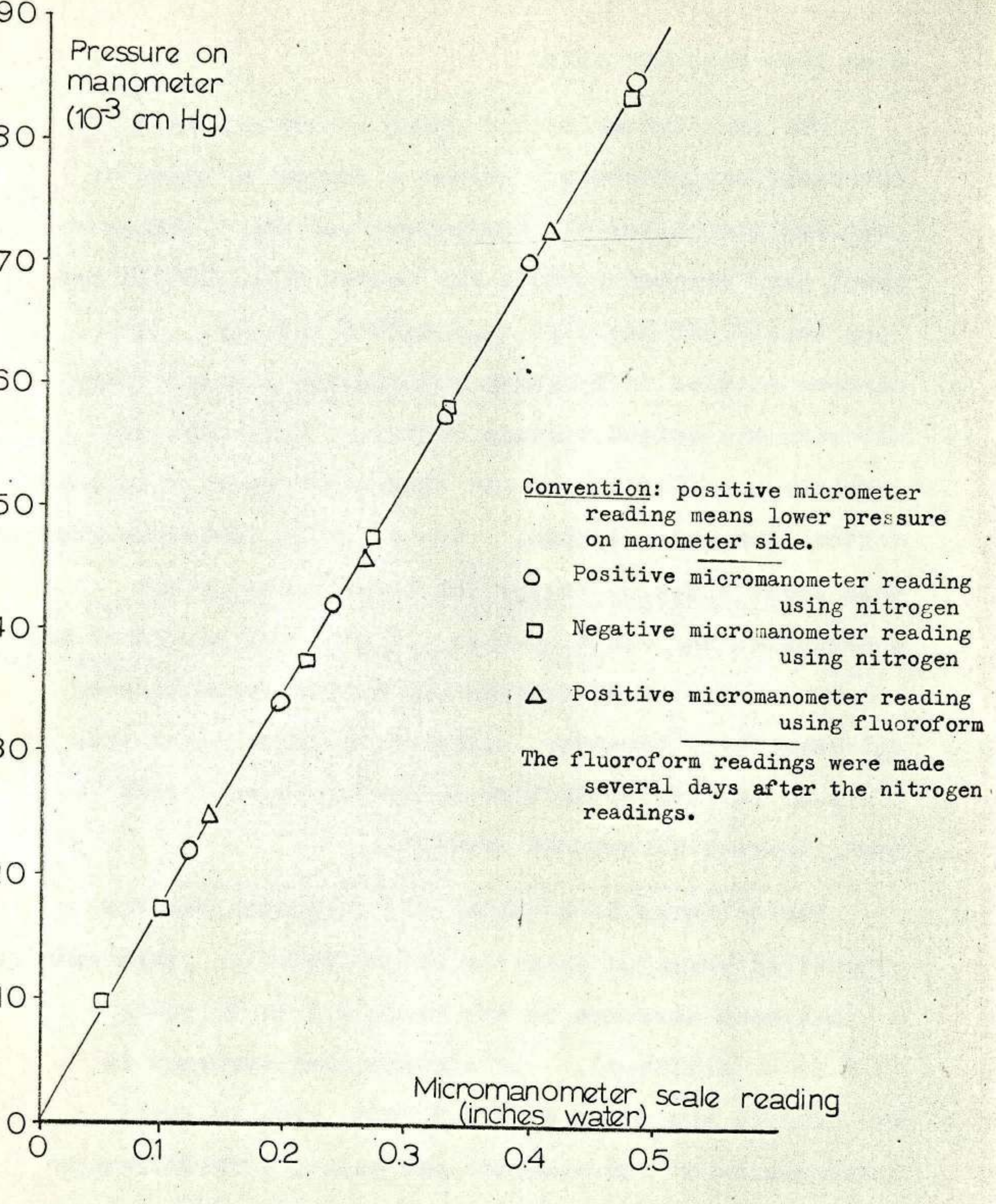
Figure (IV.4) Control box circuit

much less than 0.1 volt.

The performance of the power supply has been extremely satisfactory. After a couple of weeks of settling down after the instrument was first connected up, short term current control was better than 0.0001% and long term drift was less than 0.001% per day. The current settled to a steady value a few minutes after altering the output voltage setting; this time was probably a reflection of the external circuit - i.e. the control box and solenoid. Any noise at frequency greater than about 1 c.p.s. in the output voltage was not observable, nor did it matter, because the period of the balance was about 17 seconds and of the potentiometer galvanometer 2 seconds; noise of frequency less than 1 c.p.s. was evidently less than 1 micro volt peak to peak, because it was not detected.

The solenoid is supplied via a control box the circuit of which is shown in Figure (IV.4). This enables a continuous coverage in the range 0.5 to 40 volts (0.5 to 40 milliamp). If a continuous coverage is required in the range 0 to 0.5 volt, e.g. in early measurements of the balance zero point, a three decade resistance box (0 to 1,110 ohm) and a 10 Kohm resistance may be plugged in in series with the solenoid.

Currents are measured as the potential drop across the 50 ohm resistance in series with the solenoid. This



Figure(IV.5) Calibration of micromanometer is a 0.1% Rivlin wire wound resistor. A Pye (catalogue number 7568) vernier potentiometer is used and measures 0 to 1.8 volts in steps of 10 micro-volt. A Tinsley type 4500A mirror galvanometer is used with a Tinsley type 4309A series resistance and the path length of the light adjusted so that 10 micro-volt is equivalent to a deflection of 5 mm on the scale. Thus readings are readily made to ±1 micro-volt (which is equivalent to 2×10^{-9}gm.cm^{-3}, or 0.00013cm Hg of nitrogen, or 3×10^{-8}gm).

THE SEPARATOR

That used was a differential micromanometer made by Hilger-Watt, with a beryllium copper diaphragm and a capacitative sensor on either side to measure deflection. It has a range of about +0.1cm Hg to -0.1cm Hg and a meter scale with about 0.004cm Hg per division. Readings were interpolated to 0.1 of a division (0.0004cm Hg) with a probable accuracy of better than ±0.001cm Hg. The separator was calibrated against the manometer, readings being taken for pressure differences in both senses and for these applied to the manometer in both senses. The relationship between meter deflection and pressure was found to be linear within better than ±0.0005cm Hg over the whole range of the separator, Figure (IV.5).

The makers recommend a maximum overload of about 1cm Hg but accidental overloads of up to 10cm Hg have occurred without change in the calibration and with a zero shift of less than 0.002cm Hg.

The instrument has the disadvantage that it is made from a number of materials which might be attacked by gases, but it was used simply to prevent the 'stickier' gases getting into the manometer and so to avoid the possibility of contamination of the mercury and/or the manometer tube walls.

Oxygen free nitrogen was supplied from a 2 litre globe to the manometer side of the separator which is also connected to a further 2 litre globe insulated with expanded polystyrene. This has two purposes:

(a) It minimises the effects of temperature changes of unlagged parts of the connecting line on the pressure of nitrogen in the separator and the manometer.

(b) It allows small changes in the pressure of nitrogen to be made more readily.

A Budenberg stainless steel, differential Bourdon tube pressure gauge was used to equalise the pressures of nitrogen and of the gas in the balance case roughly, before the gases were admitted by needle valves to the micromanometer. The Budenberg gauge has a range of about 50cm Hg and divisions at 5cm Hg intervals. It was possible to equalise the pressures on either side to about ±0.5cm Hg.

Provision was made for equalising pressure on the

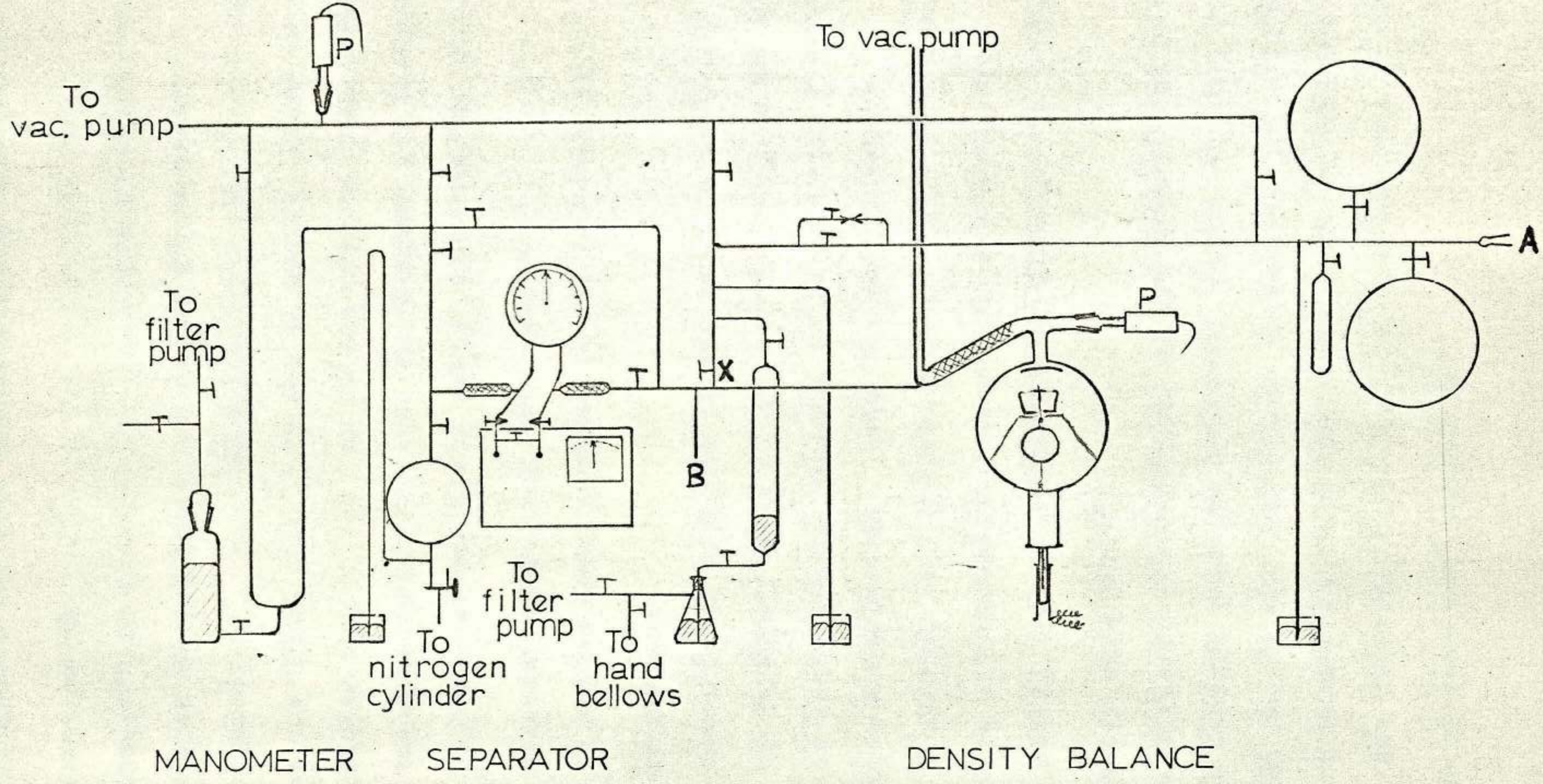
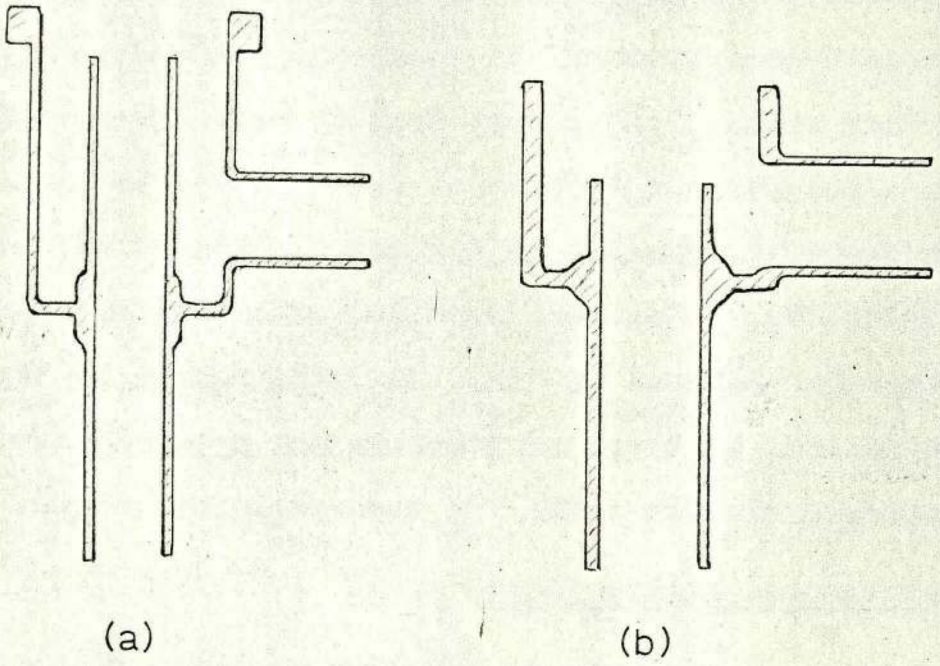


Figure (IV.6) Line drawing of gas line

two sides of the micromanometer with a ¼" Edwards-Saunders Speedivalve. This was done after each point, and the zero of the separator noted. It was necessary to do this because the separator has a significant temperature coefficient and also because when there is a difference in dielectric constant between the gas in the balance case and nitrogen, this introduces a zero shift. This results from the fact that the meter deflection depends on the relative capacitances between the diaphragm and a fixed plate on either side. An attempt to calibrate the zero shift as a function of dielectric constant difference was unsuccesful, because it was not a constant effect from day to day. However, provided that the zero was noted for each pressure reading, the calibration of meter deflection in terms of pressure was constant during the entire period in which the separator was in use.

THE GAS AND VACUUM LINES

These are shown in the line drawing, Figure (IV.6) Pyrex tubing is used except for connections between the micromanometer and Budenberg gauge where ¼" copper tubing is used for convenience. 4mm Springham greaseless stopcocks are used throughout with a few exceptions: greased taps are used on some of the gas storage flasks; needle valves (Edwards model OS1D) are used for admission of gas to the micromanometer, and a ¼" Edwards-Saunders Speedivalve is used to short across the micro-


(a) (b)

Cross section, approximately full scale

Figure (IV.7) (a) Unmodified and (b) modified glass body for 10mm Springham greaseless stopcock manometer; a 10mm Springham greaseless stopcock with a modified glass body, Figure (IV.7) is used on the balance case vacuum line.

Tin foil traps are used to prevent mercury vapour entering the balance case, condensing on the balance, and so causing zero point changes,[106] and also to prevent it reaching the separator and amalgamating with the beryllium copper diaphragm.

Rough manometers indicate the pressure in the nitrogen reservoir and the gas line and Pirani gauge heads in the vacuum line and over the balance case are used for measuring the vacuum.

Pumping is by mercury diffusion pump backed by a rotary oil pump. Two 18mm diameter vacuum lines are used, one for the gas line, and a direct one for evacuating the balance case, so avoiding the necessity of pumping through a number of 4mm greaseless stopcocks. To improve the speed of evacuation of the balance case a 10mm Springhams greaseless stopcock was used but with the glass part modified as shown in Figure (IV.7) to enable larger diameter tubes to be used and give a more straight-through path.

The gas line also includes a volume adjuster, originally intended for use in obtaining the equivalent of a null current when accumulators were to be used for the solenoid power supply. It is not now needed for this purpose but is conveniently used to compensate for the pressure drop caused by adsorption of the 'stickier' gases and to bring the separator back on scale. It is essentially a mercury piston operating in a tube of 2cm diameter. The pressure over the mercury in the flask at the bottom of the tube is increased or decreased as necessary using a hand bellows or filter pump respectively, so that on opening the tap at the base of the tube mercury flows in or out.

CHAPTER V

EXPERIMENTAL METHOD

This chapter describes the method in which the required readings were made, and their interpretation to obtain virial coefficients.

It was found during early tests on the balance, that magnetic or magnetisable materials moved near the balance case frequently interfered with the balance magnet. It was therefore of some importance to ensure that this did not occur during a run; the precautions taken included removal of the balance operator's watch, pen and key ring, and care to avoid any such materials in clothing.

In doing a run on a gas, the aim is to obtain a series of values of pressure, null current and temperature for the gas under equilibrium conditions, for a series of different pressures, and so to make a plot of p/i' against p (Chapter II). For the 'sticky' gases an equilibrium pressure was not obtained after several hours because the pressure fell continuously. However, it was found that if the average of the values of the null current measured before and after the pressure readings were used, the ratio p/i' was sensibly independent of time. This procedure was used satisfactorily with a difference of null current as large as a few hundred micro-volts in one volt, between the two values of null current. All measurements were made in this way.

When a run was to be made, the gas sample was connected on the previous evening, usually at A, Figure (IV.6), by flexible stainless steel tubing with standard B10 taper ends, sealed with Apiezon L vacuum grease. For bromomethane, chloroethane and trimethylamine, the sample was kept in a glass trap with a Springham greaseless stopcock, as a liquid under its own vapour pressure at room temperature, and was sealed on at B, Figure (IV.6). The mercury was run out of the manometer and volume adjuster, and the whole apparatus evacuated overnight, with the balance at null.

The run was commenced by making readings of i_o (the vacuum null, or zero, current), usually three times at ten minute intervals, or until it had settled to a stable value (±5 micro-volt) for two successive readings. The mercury was run slowly into the manometer until it half-filled both limbs. The balance was then carefully swung to the top stop with the least possible jarring, by using the control box fine current control, and the power supply output was then set to zero.

When the separator was in use, the needle valves and Speedivalve were closed, and gas was slowly introduced to the balance case to a suitable pressure by closing and opening the appropriate taps. Only for the 'sticky' gases was the volume adjuster used, so for other gases, this was shut off at the start of the run. The tap between the balance case and the gas line was closed, and then gas in the gas line was frozen back into the sample container, using liquid nitrogen, and the gas line was evacuated. This was done to minimise contamination of greased taps on any other gas reservoirs connected to the gas line. When the separator was in use, nitrogen was next admitted to the manometer and the Budenberg gauge to an approximate null. Both needle valves were then simultaneously slowly opened so as to admit gas and nitrogen to the separator, while keeping the meter on scale. When these were fully opened, any necessary corrections to the nitrogen pressure were made by slightly opening the tap to the nitrogen reservoir, or to the vacuum line, as appropriate. In this way, the pressures were balanced to within about 0.01 cm Hg.

The balance was now carefully brought from the top stop by increasing the power supply setting to about 1 volt less than the expected value and then slowly increasing by 0.1 volt steps, while the balance was being watched all the time. When the pointer started to swing, the control box coarse and fine controls were used to obtain a null. It was found to be important not to allow the balance to swing much below the null position used (about 14 eyepiece division, which equals 0.075cm, below the top stop) or otherwise some time would be required for the null current to settle to a stable value. This was interpreted as arising from the magnetisation, followed by slow demagnetisation, of material near the magnet in its lower positions. The potentiometer was then roughly balanced, so as to be ready to read the current in the solenoid, and the manometer mercury next run up about 0.5cm, in order to equalise the meniscus heights. The glass scale graduations nearest to and above each meniscus were identified and noted. If it was now necessary to adjust the pressures to bring the separator back on scale, and it usually was for the 'sticky' gases, this was done using the volume adjuster, and the balance case and separator then closed off from the volume adjuster with tap X, Figure (IV.6). This minimises the non-thermostatted volume. When the pressure of the gas was adjusted, this was done in such a way as to take account of the pressure drop likely to occur before a measurement was actually made, so that the separator would be used near its zero. The current would then require altering to bring the balance back to null, and the potentiometer was reset correspondingly. This whole procedure took about 10 or 15 minutes, and the gas was then left for a further 15 to 20 minutes. This allowed the gas to reach thermal equilibrium, and the rate of pressure drop to decrease sufficiently for the averaging procedure described above to be valid.

About half an hour after the last vacuum null reading before the gas was admitted, a set of readings were made in the order:

null current
temperature of the balance case
separator pressure reading
temperature of the manometer
position of the upper meniscus
height of the upper meniscus
position of the lower meniscus
height of the lower meniscus
separator pressure reading
null current
temperature of the balance case
time

Before the separator was incorporated, the pressure reading of this instrument was, of course, not made. It took about 5 minutes to read and record these values.

From time to time various other readings were included, for example, the resistance of the thermistor was measured in the early runs to ensure that the gas had come to thermal equilibrium, the temperature of the 50ohm resistance across which the potential drop was measured to give the solenoid current, was measured to assess whether a correction arising from its temperature coefficient was necessary.

These readings were repeated after 5 or 10 minutes had elapsed, to obtain three sets of values, originally, and two sets later. Repetition of the readings was originally intended to improve the precision of the readings, but it became apparent that the reproducibility of observation was better than the accuracy. This was, for example, because of the different shapes of the mercury meniscus on different occasions and errors in the calibration of the glass scale (see Chapter VII for a further discussion). Two sets of readings were then usually made as a guard against observational and recording errors. They also served to show how well the averaging procedure was working, when the null current and pressure were changing.

After the final repetition the balance was gently moved to its top stop, using the control box fine control, the tap to the separator was shut, and after opening and closing appropriate taps, the gas was frozen back into the reservoir using liquid nitrogen. The separator was then short circuited and the zero point noted. After this the balance case, separator, manometer and gas line were evacuated.

As soon as the Pirani gauge came on scale, the current was set to the expected vacuum null value and the apparatus was left for about 25 or 30 minutes. The vacuum null current was then measured as before, until two values at ten minute intervals agreed. These were usually the first two values although for the 'stickier' gases it took longer for adequate evacuation. In the majority of cases they were sensibly the same as the original vacuum readings. In the few cases where this was not so, whichever value gave a better fit for the point on the p/i' versus p plot was chosen for the subsequent calculation. This was done rather than taking the average of vacuum readings, because the observed zero drift of the balance over periods of weeks implied a trivial change in one hour, and so a more likely explanation for a more than trivial change was a less gentle than usual movement of the balance against its stops. Such an effect was occasionally observed when the author had been aware of having jarred the beam slightly, although it did not occur on every such occasion.

The procedure of filling the balance case was then repeated at other pressures until readings had been obtained at five, or occasionally six, different pressures. The five pressures were approximately 10, 20, 30, 40 and 50cm Hg; the order in which the points were obtained was deliberately varied from gas to gas and was usually one of 30,50,20,40,10, 10,40,20,50,30, 20,40,50,10,30, 40,20,10,50,30, or similar orders selected so that any systematic change in molecular weight of the gas would be obvious.

At the end of a run, after the last vacuum null current reading, the mercury was run out of the manometer and volume adjuster, and the whole apparatus was evacuated overnight. Typically it took about 7 or 8 hours to do one run.

Runs were made at temperatures of 25°, 40° and 55°C, on a variety of different gases. When it was desired to change the temperature at which the balance case was thermostatted, it was considered advisable to slacken one of the clamps holding the balance frame on to the uprights inside the casing to prevent it breaking as a result of some slight expansion of the latter. This was always done and the clamps were retightened after the thermostats had been altered and the balance case left for a few hours to reach equilibrium. The case was evacuated for several days before starting runs at a different temperature.

EXTRACTION OF VIRIAL COEFFICIENT FROM RAW DATA

The values of p/i' and p had first to be obtained. Corrections were applied to the measured distance between the meniscus levels because of the glass scale imperfections and because there are not exactly 100 eyepiece divisions to 0.1cm.[107] The capillary depressions were then obtained from Cawood and Patterson's data,[108] and the appropriate difference added to the pressure. The average separator meter scale reading was converted to cm Hg from the calibration graph, Figure (IV.5) and this was added, together with the manometer zero point error, in the appropriate sense. The final step was to correct for the temperature of the manometer, converting the readings to values for mercury at 0°C and for the glass scale at 20°C, the temperature at which it was calibrated.

This conversion is given by:

$$p_o = p\left[0.999934 - 1.785\times10^{-4}t_{man}(^{o}C)\right]$$

The vacuum null current was then subtracted from the null current in the gas and the corrected pressure divided by this value. Finally the ratio p/i' was corrected for small differences of the balance case temperature at each point from the essayed control temperature using:

$$\Delta(p/i') = (p/i').\Delta T/T$$

The best straight line fit to the experimental values was obtained using a weighted least squares programme on the laboratory computer (Elliot 903). The weighting used was 1,2,3,4,5 for the 10,20,30,40,50cmHg points respectively. This is strictly justifiable only if the corrected glass scale linearity is much better than the reproducibility of meniscus setting and observation. Since the same optical system that is used for observing the meniscus was also used for calibrating the glass scale, this is unlikely to be so. If the nonlinearity of the corrected glass scale readings is the major effect, and arises from random errors in calibration, the weighting should be $\sqrt{1}, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}$. However, a trial fit with the two different weightings showed insignificant differences in the value and standard deviation of both the slope and intercept, and the former was used because it is more readily handled with the available programme.

A trial was also made of the relative merits of the p/i' versus p and p/i' versus i' plots, and the differences found in the values of RTS_p/I_p and RTS_i/I_i^2 (see Chapter II) were always less than the standard deviation in the virial coefficient calculated from the standard deviation of the slopes. It was concluded that one was as good as the other and the p plot was used in the calculations.

The molecular weight of the gas was obtained from the intercept so obtained and the intercept for the same plot for a gas of known molecular weight as M_1I_1/I_2, and the value of RTS/I was computed, using the temperature to which all the balance readings were corrected.

From equation (II.34) it is seen that RTS/I will be equal to the second virial coefficient if the bulb contraction is negligible, and the current is directly proportional to the force acting on the magnet. In fact, preliminary measurements with carbon dioxide, carbon tetrafluoride, sulphur hexafluoride and sulphur dioxide showed that there was a correction of about $25 cm^3 mole^{-1}$, independent of the gas being studied, which had to be subtracted from RTS/I in order to obtain second virial coefficients which agreed with literature values.

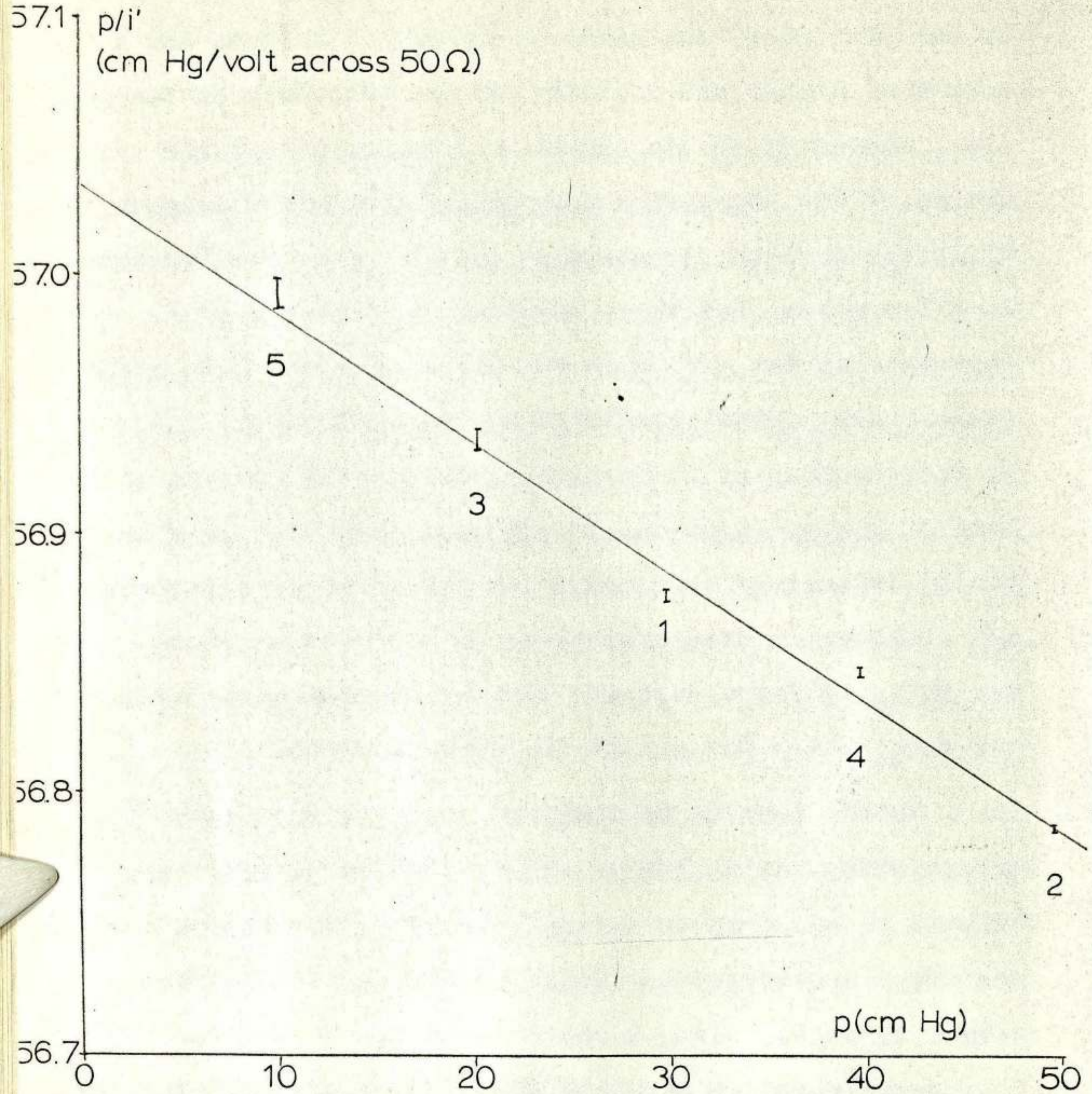
It was this observation that demonstrated the necessity of allowing for the bulb contraction. A theoretical calculation of the value to be expected for this correction gave a value of about $7cm^3mole^{-1}$ (see Appendix II). Agreement to within an order of magnitude was considered a reasonable indication that the factor responsible for the correction had been correctly identified. Furthermore, the experimental value obtained would be expected to be numerically larger than the theoretical value for a uniformly thin spherical shell as was indeed found. A blown bulb might very well have a non-uniform thickness, and the additional contraction of thin parts would be more than the smaller contraction of the thicker parts relative to a uniform shell.

During the first series of measurements at 25°C, however, the value of the correction factor had clearly changed from about $25cm^3mole^{-1}$ to about $48cm^3mole^{-1}$, as shown by runs on standard gases at the beginning and end of the series. A close examination of the plots showed where this had probably occurred, so that there was no difficulty in assigning the most probable value of the correction for each run. Subsequent runs at 40° and 55°C gave values for the virial coefficients which have confirmed the values obtained at 25°C. Faith in the reliability of this correction factor was nevertheless shaken. It is not impossible that the contraction of a thin bulb with pressure could have more than one value if, for example, a thin part had behaved rather like a click gauge. However it seemed rather a remote possibility, so other possible sources of such an effect were considered.

In the derivation of equation (II.34), although the contraction of the bulb was considered, the mathematics would hold for any effect with such a pressure dependence. The only one of the many considered which seemed at all likely was that the position of the solenoid relative to the magnet might change slightly with pressure changes in the balance case; the solenoid is mounted directly on the balance case. This effect would be in addition to the bulb contraction. There are a number of ways in which such a pressure dependence could change. In an attempt to prevent any further changes, before commencing the series at 40°C all the joints between the glass solenoid limb and the main part of the balance case were tightened and have not been moved since. The correction factor has not changed during a series of measurements since then, although it does of course vary slightly from temperature to temperature.

The other possibilities of error considered in equation (II.34) are non-linearities in the relationship between the solenoid current and the force on the magnet, and unbalanced adsorption. There has been no indication of a significant effect from the former, and it is considered that deviations from linearity of the current/force relationship are less than 0.001%. The latter would give rise to a first order effect on the intercept of the p/i' plot, and hence on molecular weight, and a second or higher order effect on the linearity of the plot, depending on the extent of adsorption and the nature of the adsorption isotherm. Molecular weights differing from the theoretical values have been obtained in a few cases, but there has been no indication of curvature of the p/i' plot in excess of that which might occasionally arise coincidentally and within the limits of the accuracy of the pressure and current measurements. Some of the cases of non-theoretical molecular weights can be definitely ascribed to the presence of impurities, and although in others there is no definite evidence for this, it seems unlikely that unbalanced adsorption was significant for any of the gases studied.

It has been shown (Chapter II) that for the full potential of the manometer and balance to be realised, it must be possible to obtain successive samples of the gas under investigation with a constancy of molecular weight of better than ±0.004 from sample to sample. This requirement is a fairly stringent one. 0.003mole% of an impurity of molecular weight 30 units less (or more) than that of the gas being studied, causes a molecular weight 0.001 different from the theoretical value. To ensure that any systematic change in molecular weight due to handling the gas is detected, the readings at different pressures must not be made in ascending or descending order. Such a change will then be observable, as can be seen from



The numbers immediately under the experimental points show the order in which readings were made.

Figure (V.1) The p/i' versus p plot for fluoroform at 25°C (Run B7), showing the effect of a gradual change of the molecular weight.

the p/i' plot for fluoroform at 25°C, Figure (V .1). This shows one of the most pronounced effects encountered. The order in which the readings were made is shown, and the effect of a slight decrease in molecular weight is obvious from the graph. For comparison, the vertical lines indicate the errors which would be associated with the values of p/i' for errors in p of ±0.001cm Hg.

There was a further effect, arising from molecular weight changes, observed in the case of bromomethane at 40°C. In this case the balance case was filled from a trap containing liquid bromomethane by allowing the trap to warm up to the temperature at which the vapour pressure was the desired filling pressure. The procedure was used for experimental convenience. The second virial coefficient obtained in this way was approximately the same as that obtained at 25°C, where the trap was also used, but was kept at room temperature, and the amount of gas which was admitted to the balance case was controlled by the tap on the trap. However, the molecular weight obtained at 25°C was 94.52, whereas the theoretical weight is 94.95, so a lower molecular weight impurity was present. The molecular weight obtained at 40°C with the different technique was 93.86, implying that the impurity concentration had been increased.

A mass spectographic investigation of the sample indicated that chloromethane was the impurity and so a further sample of bromomethane was prepared. Only by rejecting a large initial fraction of the sample was it possible to reduce the chloromethane concentration to a satisfactorily low level. Bulb to bulb distillation was used and this may have accounted for the difficulty in separating the chloromethane. It would clearly have been useful to have fractionally distilled the bromomethane but a suitable low temperature column was not available and an attempt with a column cooled by circulating methanol at -5°C (bromomethane boils at 3.5°C) was unsuccessful. It was concluded that the derivation of a lower molecular weight and a more negative second virial coefficient than that expected were due to proportionally increased concentrations of chloromethane in the lower pressure points.

To eliminate the possibility of this recurring, the sample eventually prepared was admitted from a 5 litre flask in which it was all kept in the gas phase. The virial coefficient obtained in this way was in much better agreement with that expected from literature values and the result at 25°C, and the molecular weight was 94.93, only 0.02 less than the theoretical value.

CHAPTER VI

DETAILED EXPERIMENTAL RESULTS

This chapter includes details of preparation of the samples, the experimental results and the values of the second compressibility virial coefficient and molecular weight obtained. The results are set out gas by gas. The data recorded are the pressure, p, corrected to cm Hg at 0^oC and under local gravity, the difference between the null current in the gas and the vacuum null current, i', the ratio (p/i') which includes corrections for small temperature variations of the balance case, and the averages of these values for measurements made at approximately the same pressure, p_{av}, i'_{av}, and $(p/i')_{av}$ respectively. The run number and temperature, t, the slope, S, and intercept, I, of the weighted least squares plot of $(p/i')_{av}$ against p, and their standard deviations, D_s and D_i respectively are also included. Runs with prefix A were preliminary measurements with fewer points, and are not included. Runs with prefix B were the first series for the gases fluoroform, chlorodifluoromethane, chlorotrifluoromethane, dichlorodifluoromethane, 1,1-difluoroethylene and dimethyl ether at 25^o, 40^o and 55^oC. These runs were done before the separator was incorporated. Runs C were those for bromomethane, chloroethane and trimethylamine, together with one or two duplicate runs for the other gases. These were done at temperatures of 25° and 40°C after the separator was added.

Calibration of the pressure dependent correction was made for each series of runs at a particular temperature using as standards carbon dioxide, carbon tetrafluoride and sulphur hexafluoride. These gases are all readily obtainable in a fairly pure state and have virial coefficients known to within 1 or 2cm^{3}mole^{-1} in the temperature range over which measurements were made. The values used and the references are shown in Table (VI.1). The results for the calibration runs are collected at the end of the chapter.

Gas	$-B$(cm^{3}mole^{-1}) 25°C	 40°C	 55°C	refs
CO_2	122	108	97	110,111
CF_4	88	77	67	112-114
SF_6	278	250	225	113-115

Table (VI.1)

INDEX TO EXPERIMENTAL RESULTS

Calibration runs

FLUOROFORM (M = 70.02)

Matheson (98% pure) fluoroform was collected in a cold trap and a cycle of liquefying, pumping on the liquid, and freezing down was carried out until the pressure vapour at liquid nitrogen temperature, as recorded on a Pirani gauge, was less than 4microns. It was distilled once rejecting small initial and large final fractions. The sample was collected in and stored in a 5 litre glass flask closed with a greased tap and provided with a side limb for freezing down the gas in the flask.

Run B7, $t = 25^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
29.8216		0.524363		56.8721	
29.8225	29.8225	0.524374	0.524371	56.8726	56.8730
29.8235		0.524377		56.8742	
49.7337		0.875829		56.7847	
49.7327	49.7333	0.875815	0.875817	56.7845	56.7842
49.7313		0.875807		56.7834	
20.1642		0.354167		56.9342	
20.1657	20.1655	0.354187	0.354183	56.9352	56.9352
20.1665		0.354194		56.9363	
39.8617		0.701220		56.8462	
39.8606	39.8610	0.701199	0.701205	56.8463	56.8463
39.8606		0.701197		56.8465	
10.0553		0.176435		56.9915	
10.0556	10.0554	0.176434	0.176435	56.9935	56.9920
10.0552		0.176435		59.9910	

$S = -0.00499$, $D_s = 0.00019$, $I = 57.035$, $D_i = 0.007$

$RTS/I = -163 cm^3 mole^{-1}$. From B1,B2,B5, $\Delta B = 27 cm^3 mole^{-1}$

$B = -190 cm^3 mole^{-1}$ From B2, $M = 70.00$

(Fluoroform)

Run B25, $t = 40^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
29.3830 29.3827	29.3829	0.492091 0.492080	0.492086	59.7121 59.7138	59.7129
49.5848 49.5829	49.5839	0.831493 0.83486	0.831490	59.6353 59.6359	59.6356
20.2945 20.2942	20.2944	0.339695 0.339682	0.339689	59.7499 59.7511	59.7505
39.8559 39.8551	39.8555	0.667831 0.667825	0.667828	59.6846 59.6828	59.6837
10.2107 10.2101	10.2104	0.170708 0.170701	0.170705	59.8164 59.8172	59.8168

$S = -0.00415$, $D_s = 0.00016$, $I = 59.843$, $D_i = 0.006$

$RTS/I = -136 cm^3 mole^{-1}$. From B18, B19, B23, B24, B29, $\Delta B = 43 cm^3 mole^{-1}$

$B = -179 cm^3 mole^{-1}$ From B29, $M = 70.01$

Run B33, $t = 55^\circ C$

30.2102 30.2137	30.2120	0.483260 0.483259	0.483260	62.5097 62.5176	62.5137
49.9102 49.9115	49.9109	0.799248 0.799244	0.799246	62.4447 62.4456	62.4452
20.0871 20.0891	20.0881	0.321172 0.321164	0.321168	62.5467 62.5496	62.5482
40.1225 40.1176	40.1201	0.641934 0.641942	0.641938	62.5008 62.4996	62.5002
10.1569 10.1587	10.1578	0.162257 0.162259	0.162258	62.5984 62.6067	62.6026

$S = -0.00357$, $D_s = 0.00022$, $I = 62.629$, $D_i = 0.008$

$RTS/I = -117 cm^3 mole^{-1}$. From B31, B32, B39, $\Delta B = 40 cm^3 mole^{-1}$

$B = -157 cm^3 mole^{-1}$ From B39, $M = 70.00$

(Fluoroform)

<u>Run C7, t = 25°C</u>

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
39.8579 39.8588	39.8584	0.700996 0.700997	0.700997	56.8590 56.8602	56.8596
20.3845 20.3831	20.3838	0.357988 0.35800	0.357994	56.9419 56.9360	56.9390
49.9605 49.9609	49.9607	0.879477 0.879496	0.879487	56.8070 56.8063	56.8067
10.4665 10.4668	10.4667	0.183690 0.183704	0.183697	56.9791 56.9764	56.9778
29.9062 29.9081	29.9072	0.525606 0.525622	0.525614	56.8984 56.9004	56.8994

$S = -0.00439$, $D_s = 0.00008$, $I = 57.030$, $D_i = 0.003$

$RTS/I = -143 \text{cm}^3 \text{mole}^{-1}$. From C1, C2, C8, $\Delta B = 51 \text{cm}^3 \text{mole}^{-1}$

<u>$B = -194 \text{cm}^3 \text{mole}^{-1}$</u>   From C1, <u>$M = 70.03$</u>

CHLORODIFLUOROMETHANE (M = 86.48)

Matheson (99.9% pure) chlorodifluoromethane was collected in a cold trap and the solid was pumped at liquid nitrogen temperature for ½ hour. It was distilled once, rejecting a small final fraction, into a 3 litre flask.

Run B3, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.2108		0.221493		46.0999	
10.2107	10.2105	0.221485	0.221482	46.1011	46.1009
10.2100		0.221467		46.1017	
39.6793		0.865246		45.8590	
39.6775	39.6778	0.865185	0.865177	45.8601	45.8597
39.6759		0.865159		45.8597	
19.7706		0.429689		46.0114	
19.7697	19.7701	0.429670	0.429677	46.0114	46.0116
19.7701		0.429672		46.0121	
30.1373		0.656140		45.9312	
30.1366	30.1360	0.656099	0.656110	45.9330	45.9312
30.1340		0.656092		45.9295	
49.8463		1.089019		45.7717	
49.8444	49.8437	1.088930	1.088937	45.7737	45.7727
49.8403		1.088863		45.7728	

$S = -0.00808$, $D_s = 0.00008$, $I = 46.177$, $D_i = 0.003$

$RST/I = -325 cm^3 mole^{-1}$. From B1, B2, B5, $\Delta B = 27 cm^3 mole^{-1}$

$B = -352 cm^3 mole^{-1}$ From B2, M = 86.46

(Chlorodifluoromethane)

Run B20, t = 40°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
20.2272		0.418678		48.3131	
20.2271	20.2270	0.418651	0.418655	48.3160	48.3154
20.2268		0.418636		48.3170	
50.5166		1.050195		48.1022	
50.5178	50.5175	1.050193	1.050181	48.1035	48.1027
50.5182		1.050159		48.1025	
10.0738		0.208182		48.3893	
10.0727	10.0729	0.208183	0.208182	48.3838	48.3851
10.0723		0.208182		48.3821	
39.6200		0.822112		48.1850	
39.6133	39.6154	0.822083	0.822092	48.1862	48.1856
39.6129		0.822082		48.1857	
29.8012		0.617543		48.2531	
29.7991	29.8001	0.617524	0.617526	48.2551	48.2551
29.8001		0.617510		48.2570	

$S = -0.00703$, $D_s = 0.00008$, $I = 48.461$, $D_i = 0.003$

$RTS/I = -283 cm^3 mole^{-1}$. From B18, B19, $\Delta B = 40 cm^3 mole^{-1}$

$B = -323 cm^3 mole^{-1}$ From B29, $M = 86.45$

Run B21, t = 40°C

15.1333		0.313075		48.3370	
15.1341	15.1336	0.313067	0.313068	48.3422	48.3404
15.1334		0.313063		48.3414	
34.9760		0.725289		48.2168	
34.9767	34.9763	0.725284	0.725284	48.2187	48,2179
34.9763		0.725280		48.2184	
25.2395		0.522652		48,2830	
25.2396	25.2389	0.522637	0.522641	48.2883	48.2863
25.2395		0.522636		48.2875	
44.8963		0.932309		48.1506	
44.8941	44.8947	0.932271	0.932277	48.1502	48.1504
44.8938		0.932250		48.1503	

$S = -0.00656$, $D_s = 0.00008$, $I = 48.446$, $D_i = 0.003$

$RTS/I = -264 cm^3 mole^{-1}$. From B23, B24, $\Delta B = 49 cm^3 mole^{-1}$

$B = -313 cm^3 mole^{-1}$ From B29, $M = 86.47$

(Chlorodifluoromethane)

Run B38, $t = 55^{o}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
9.7498 9.7498	9.7498	0.192506 0.192501	0.192504	50.6457 50.6444	50.6450
40.0413 40.0393	40.0403	0.793508 0.793482	0.793495	50.4593 50.4588	50.4591
20.0608 20.0589	20.0599	0.396602 0.396602	0.396602	50.5791 50.5747	50.5769
50.4509 50.4472	50.4491	1.001201 1.001162	1.001182	50.3890 50.3888	50.3889
30.0025 30.0029	30.0027	0.593882 0.593873	0.593878	50.5189 50.5203	50.5196

$S = -0.00624$, $D_s = 0.00005$, $I = 50.706$, $D_1 = 0.002$

$RTS/I = -252 cm^3 mole^{-1}$. From B31, B32, B39, $\Delta B = 40 cm^3 mole^{-1}$

$B = -292 cm^3 mole^{-1}$ From B39, $M = 86.46$

Run C3, $t = 25^{o}C$

29.8999 29.8990	29,8995	0.650629 0.650614	0.650622	45.9554 45.9551	45.9553
48.5056 48.5031	48.5044	1.058806 1.058772	1.058789	45.8116 45.8108	45.8112
19.8645 19.8649	19.8647	0.431488 0.431500	0.431494	46.0371 46.0368	46.0370
39.8303 39.8298	39.8301	0.868073 0.868059	0.868066	45.8836 45.8837	45.8837
10.2420 10.2430	10.2425	0.222171 0.222186	0.222179	46.0994 46.1008	46.1001

$S = -0.00768$, $D_s = 0.00008$, $I = 46.186$, $D_1 = 0.003$

$RTS/I = -309 cm^3 mole^{-1}$. From C1, C2, C8, $\Delta B = 51 cm^3 mole^{-1}$

$B = -360 cm^3 mole^{-1}$ From C1, $M = 86.47$

CHLOROTRIFLUOROMETHANE ($M = 104.47$)

Mathèson (99% pure) chlorotrifluoromethane was purified and collected in the same way as fluoroform.

Run B8, $t = 25^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
22.0101		0.577146		38.1361	
22.0091	22.0090	0.577118	0.577122	38.1362	38.1357
22.0077		0.577101		38.1349	
50.1167		1.317764		38.0316	
50.1161	50.1161	1.317738	1.317743	38.0319	38.0317
50.1154		1.317728		38.0317	
30.7387		0.806629		38.1071	
30.7383	30.7387	0.506629	0.506630	38.1071	38.1076
30.7395		0.806632		38.1085	
10.1222	10.1225	0.265185	0.265185	38.1703	38.1713
10.1227		0.265185		38.1722	
40.3550		1.059820		38.0772	
40.3549	40.3549	1.059815	1.059815	38.0774	38.0773
40.3548		1.059813		38.0773	

$S = -0.00358$, $D_s = 0.00011$, $I = 38.215$, $D_i = 0.004$

$RTS/I = -174\,cm^3 mole^{-1}$. From B11, $\Delta B = 48\,cm^3 mole^{-1}$

$\underline{B = -222\,cm^3 mole^{-1}}$ From B2, $\underline{M = 104.47}$

(Chlorotrifluoromethane)

Run B27, $t = 40^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
9.9961 9.9963	9.9962	0.249479 0.249477	0.249478	40.0731 40.0736	40.0734
40.0497 40.0489	40.0493	1.001612 1.001618	1.001615	39.9898 39.9888	39.9893
20.0532 20.0531	20.0532	0.500835 0.500833	0.500834	40.0441 40.0441	40.0441
50.2577 50.2598	50.2588	1.258107 1.258121	1.258114	39.9522 39.9534	39.9528
30.0982 30.0980	30.0981	0.752271 0.752268	0.752270	40.0147 40.0143	40.0145

$S = -0.00299$, $D_s = 0.00005$, $I = 40.105$, $D_1 = 0.002$

$RTS/I = -145 cm^3 mole^{-1}$. From B18, B19, B23, B24, B29, $\Delta B = 43 cm^3 mole^{-1}$

$\underline{B = -188 cm^3 mole^{-1}}$ From B29, $\underline{M = 104.46}$

Run B34, $t = 55^\circ C$

20.4182 20.4183	20.4183	0.487082 0.487089	0.487086	41.9160 41.9159	41.9160
49.9290 49.9301	49.9296	1.193628 1.193627	1.193628	41.8302 41.8302	41.8302
29.9785 29.9805	29.9795	0.715732 0.715718	0.715725	41.8855 41.8879	41.8867
40.0080 40.0076	40.0078	0.955664 0.955667	0.955666	41.8654 41.8646	
10.2185 10.2185	10.2185	0.243637 0.243637	0.243637	41.9420 41.9426	41.9423

$S = -0.00282$, $D_s = 0.00007$, $I = 41.973$, $D_1 = 0.003$

$RTS/I = -138 cm^3 mole^{-1}$. From B31, B32, B39, $\Delta B = 40 cm^3 mole^{-1}$

$\underline{B = -178 cm^3 mole^{-1}}$ From B39, $\underline{M = 104.45}$

DICHLORODIFLUOROMETHANE ($M = 120.93$)

Matheson (99% pure) dichlorodifluoromethane was purified and stored in the same way as fluoroform.

Run B9, $t = 25^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
39.5613		1.210227		32.6891	
39.5613	39.5612	1.210213	1.210215	32.6895	32.6893
39.5609		1.210205		32.6894	
10.5492		0.320816		32.8824	
10.5496	10.5493	0.320821	0.320846	32.8831	32.8820
10.5490		0.320826		32.8809	
50.2460		1.541032		32.6054	
50.2477	50.2474	1.541036	1.541034	32.6064	32.6063
50.2486		1.541034		32.6071	
20.0182		0.609765		32.8294	
20.0187	20.0186	0.609763	0.609764	32.8203	32.8301
20.0189		0.609763		32.8306	
30.0483	30.0484	0.917205	0.917205	32.7607	32.7608
30.0484		0.917205		32.7608	
12.4805	12.4804	0.379506	0.379506	32.8862	32.8858
12.4802		0.379506		32.8654	

$S = -0.00725$, $D_s = 0.00010$, $I = 32.974$, $D_i = 0.004$

$RTS/I = -409 cm^3 mole^{-1}$. From B11, $\Delta B = 48 cm^3 mole^{-1}$

$B = -457 cm^3 mole^{-1}$ From B11, $M = 121.05$

(Dichlorodifluoromethane)

Run B26, t = 40°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
30.0220 30.0225	30.0223	0.872507 0.872505	0.872506	34.4027 34.4033	34.4030
48.8225 48.8232	48.8229	1.424065 1.424054	1.424060	34.2823 34.2830	34.2827
19.5918 19.5919	19.5919	0.568211 0.568207	0.568209	34.4729 34.4733	34.4731
39.9922 39.9914	39.9918	1.164465 1.164472	1.164469	34.3404 34.3408	34.3406
9.9090 9.9092	9.9091	0.286760 0.286763	0.286762	34.5414 34.5422	34.5418

$S = -0.00656$, $D_s = 0.00004$, $I = 34.602$, $D_i = 0.001$

$RTS/I = -370 cm^3 mole^{-1}$. From B18, B19, B23, B24, B29, $\Delta B = 43 cm^3 mole^{-1}$

$B = -413 cm^3 mole^{-1}$ From B29, $M = 121.07$

Run B36, t = 55°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.1013 10.1015	10.1014	0.279385 0.279839	0.279537	36.1572 36.1571	36.1572
39.9617 39.9619	39.9618	1.110675 1.110663	1.110669	35.9819 35.9824	35.9822
20.0379 20.0386	20.0383	0.555119 0.555115	0.555117	36.0982 36.0994	36.0988
49.8402 49.8379	49.8391	1.387633 1.387615	1.387624	35.9192 35.9185	35.9189
29.9511 29.9507	29.9509	0.831014 0.831012	0.831013	36.0439 36.0436	36.0438

$S = -0.00604$, $D_s = 0.00005$, $I = 36.222$, $D_i = 0.002$

$RTS/I = -341 cm^3 mole^{-1}$. From B31, B32, B39, $\Delta B = 40 cm^3 mole^{-1}$

$B = -381 cm^3 mole^{-1}$ From B39, $M = 121.03$

1,1-DIFLUOROETHYLENE (M = 64.04)

Matheson (99% pure) 1,1-difluoroethylene was purified and stored in the same way as fluoroform.

Run B6, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.1708		0.163349		62.2642	
10.1707	10.1707	0.163342	0.163344	62.2663	62.2657
10.1707		0.163341		62.2667	
49.9646		0.805049		62.0640	
49.9641	49.9643	0.805027	0.805035	62.0651	62.0647
49.9643		0.805030		62.0651	
29.3780		0.472350		62.1954	
29.3782	29.3781	0.472354	0.472351	62.1953	62.1955
29.3781		0.472349		62.1957	
40.2697		0.648208		62.1247	
40.2686	40.2691	0.648201	0.648201	62.1236	62.1245
40.2691		0.648194		62.1251	
20.1342		0.323550		62.2290	
20.1327	20.1332	0.323538	0.323544	62.2267	62.2271
20.1327		0.323543		62.2257	
11.8938		0.190951		62.2866	
11.8923	11.8928	0.190948	0.190948	62.2803	62.2818
11.8918		0.190946		62.2783	

$S = -0.00545$, $D_s = 0.00017$, $I = 62.342$, $D_i = 0.006$

$RTS/I = -163\,\mathrm{cm^3\,mole^{-1}}$. From B1, B2, B5, $\Delta B = 27\,\mathrm{cm^3\,mole^{-1}}$

$\underline{B = -190\,\mathrm{cm^3\,mole^{-1}}}$ From B2, $\underline{M = 64.04}$

(1,1-Difluoroethylene)

Run B28, $t = 40^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.3409 10.3410	10.3410	0.158178 0.158176	0.158177	65.3801 65.3832	65.3817
39.9228 39.9223	39.9226	0.611796 0.611789	0.611793	65.2597 65.2597	65.2597
20.6921 20.6911	20.6916	0.316700 0.316698	0.316699	65.3415 65.3393	65.3404
50.1581 50.1576	50.1579	0.769313 0.769311	0.769312	65.2038 65.2038	65.2038
30.0590 30.0593	30.0592	0.460380 0.460376	0.460378	65.2991 65.2998	65.2995

$S = -0.00454$, $D_s = 0.00009$, $I = 65.435$, $D_i = 0.004$

$RTS/I = -135 cm^3 mole^{-1}$. From B29, $\Delta B = 39 cm^3 mole^{-1}$

$B = -174 cm^3 mole^{-1}$ From B29, $M = 64.02$

Run B35, $t = 55^{\circ}C$

10.0673 10.0675	10.0674	0.147111 0.147108	0.147110	68.4370 68.4414	68.4392
40.1092 40.1061	40.1077	0.587071 0.587065	0.587068	68.3194 68.3184	68.3189
20.3434 20.3440	20.3437	0.297511 0.297507	0.297509	68.3833 68.3841	68.3837
50.0639 50.0615	50.0627	0.733201 0.733200	0.733201	68.2844 68.2792	68.2818
30.0989 30.0981	30.0985	0.440268 0.440263	0.440266	68.3672 68.3688	68.3680

$S = -0.00380$, $D_s = 0.00014$, $I = 68.473$, $D_i = 0.005$

$RTS/I = 114 cm^3 mole^{-1}$. From B31, B32, B39, $\Delta B = 40 cm^3 mole^{-1}$

$B = -154 cm^3 mole^{-1}$ From B39, $M = 64.02$

DIMETHYL ETHER (M = 46.07)

Matheson (99% pure) dimethyl ether was purified and stored in the same way as fluoroform.

Run B10, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.1277	10.1266	0.117141	0.117129	86.4571	86.4567
10.1267		0.177128		86.4584	
10.1253		0.117117		86.4546	
39.6588	39.6563	0.461635	0.461606	85.9095	85.9094
39.6537		0.461577		85.9093	
19.8162	19.8168	0.229687	0.229687	86.2748	86.2777
19.8173		0.229686		86.2799	
19.8170		0.229687		86.2783	
30.3591	30.3570	0.352706	0.352676	86.0748	86.0762
30.3572		0.352676		86.0766	
30.3548		0.352646		86.0772	
49.9550	49.9467	0.582908	0.582801	85.6995	85.7011
49.9458		0.582792		85.7010	
49.9393		0.582704		85.7027	

$S = -0.01900$, $D_s = 0.00012$, $I = 86.655$, $D_1 = 0.005$

$RTS/I = -408 \text{cm}^3 \text{mole}^{-1}$. From B11, $\Delta B = 48 \text{cm}^3 \text{mole}^{-1}$

$B = -456 \text{ cm}^3 \text{mole}^{-1}$ From B11, $M = 46.06$

(Dimethyl ether)

Run B30, $t = 40^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.2654 10.2649	10.2652	0.113122 0.113111	0.113117	90.7534 90.7584	90.7559
40.0082 40.0052	40.0067	0.443229 0.443181	0.443205	90.2632 90.2628	90.2630
19.9965 19.9936	19.9951	0.220692 0.220679	0.220686	90.6116 90.6064	90.6090
50.0500 50.0439	50.0470	0.555575 0.555512	0.555544	90.0927 90.0942	90.0935
30.1555 30.1526	30.1541	0.333454 0.333433	0.333444	90.4457 90.4427	90.4442

$S = -0.01702$, $D_s = 0.00015$, $I = 90.947$, $D_i = 0.0006$

$RTS/I = -366 cm^3 mole^{-1}$. From B29, $\Delta B = 39 cm^3 mole^{-1}$

$B = -405 cm^3 mole^{-1}$ From B29, $M = 46.06$

Run B40, $t = 55^\circ C$

10.1632 10.1620	10.626	0.106937 0.106926	0.106932	95.0346 95.0332	95.0339
39.8753 39.8696	39.8725	0.421614 0.421571	0.421593	94.5962 94.5924	94.5743
20.4032 20.4015	20.4024	0.215092 0.215080	0.215086	94.8576 94.8551	94.8564
49.8811 49.8744	49.8778	0.528289 0.528232	0.528261	94.4173 94.4176	94.4175
29.9894 29.9885	29.9890	0.316609 0.316587	0.316598	94.7237 94.7275	94.7256

$S = -0.01524$, $D_s = 0.00012$, $I = 95.179$, $D_i = 0.005$

$RTS/I = -328 cm^3 mole^{-1}$. From B31,B32,B39, $\Delta B = 40 cm^3 mole^{-1}$

$B = -368 cm^3 mole^{-1}$ From B39, $M = 46.06$

BROMOMETHANE (M = 94.95)

Two samples were used. The one used for the measurements at 25°C was prepared from technical grade bromomethane supplied by Merck, by shaking the liquid over mercury to remove elemental bromine. The solid was then pumped at liquid nitrogen temperature, passed over phosphorous pentoxide to remove water, and finally distilled into a glass trap closed with a greaseless stopcock. The sample eventually used at 40°C was obtained from B.D.H. laboratory grade reagent by repeated distillation and collecting the sample shown mass spectrometrically to contain the least methyl chloride (less than ½%).

Run C4, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
29.9727 29.9648	29.9688	0.714786 0.714596	0.714691	41.9324 41.9326	41.9325
50.0043 49.9817	49.9930	1.198269 1.197759	1.198014	41.7305 41.7294	41.7299
10.4264 10.4285	10.4275	0.247289 0.247338	0.247314	42.1530 42.1531	42.1531
20.4202 20.4193	20.4198	0.485782 0.485749	0.485766	42.0358 42.0368	42.0363
39.6796 39.6656	39.6726	0.948394 0.948087	0.948241	41.8387 41.8375	41.8381

$S = -0.01046$, $D_s = 0.0009$, $I = 42.252$, $D_i = 0.003$

$RTS/I = -461 \text{cm}^3\text{mole}^{-1}$. From C1, C2, C8, $\Delta B = 51 \text{cm}^3\text{mole}^{-1}$

$B = -512 \text{cm}^3\text{mole}^{-1}$ From C1, $M = 94.52$

(Bromomethane)

<u>Run C18, $t = 40^{\circ}C$</u>

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
20.0377 20.0217	20.0292	0.455959 0.455654	0.455807	43.9568 43.9489	43.9529
37.7992 37.7894	37.7943	0.863411 0.863301	0.863356	43.7898 43.7842	43.7870
49.8942 49.8849	49.8896	1.143036 1.142835	1.142936	43.6611 43.6606	43.6609
10.2279 10.2281	10.2280	0.232211 0.232216	0.232214	44.0553 44.0560	44.0557
28.7465 28.7427	28.7446	0.655385 0.655303	0.655344	43.8726 43.8724	43.8725

$S = -0.00988$, $D_s = 0.00006$, $I = 44.156$, $D_i = 0.002$

$RTS/I = -437 cm^3 mole^{-1}$. From C17, $\Delta B = 45 cm^3 mole^{-1}$

$\underline{B = -482 cm^3 mole^{-1}}$. From C14, $\underline{M = 94.93}$

<u>CHLOROETHANE</u> ($M = 64.52$)

B.D.H. laboratory grade reagent was distilled through a phosphorus pentoxide tube into a cold trap. The liquid was then pumped until the vapour pressure at liquid nitrogen temperature was less than 1 μ on a Pirani gauge. It was then distilled into a glass trap closed with a greaseless stopcock.

(Chloroethane)

Run C5, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$)p/i')_{av}$
30.4258 30.4180	30.4219	0.496776 0.496640	0.496708	61.2404 61.2476	61.2470
50.0016 49.9754	49.9885	0.822466 0.822017	0.822242	60.7947 60.7961	60.7954
10.3684 10.3710	10.3697	0.168068 0.168108	0.168088	61.6917 61.6925	61.6921
20.4114 20.4082	20.4098	0.332014 0.331980	0.331997	61.4774 61.4741	61.4758
39.9711 39.9623	39.9670	0.655204 0.654795	0.654900	61.0251 61.0302	61.0277

$S = -0.02284$, $D_s = 0.00008$, $I = 61.939$, $D_i = 0.003$

$RTS/I = -686\text{cm}^3\text{mole}^{-1}$. From C1,C2,C8, $\Delta B = 51\text{cm}^3\text{mole}^{-1}$

$B = -737\text{cm}^3\text{mole}^{-1}$ From C1, $M = 64.48$

Run C11, t = 40°C

p	p_{av}	i'	i'_{av}	(p/i')	$)p/i')_{av}$
29.7150 29.7035	29.7093	0.461398 0.461265	0.461332	64.4081 64.4018	64.4050
10.3644 10.3646	10.3645	0.159963 0.159960	0.159962	64.8003 64.8018	64.8011
49.8439 49.8171	49.8305	0.778851 0.778462	0.778657	64.0024 63.9999	64.0012
39.0888 39.0790	39.0839	0.608664 0.608494	0.608579	64.2257 64.2274	64.2266
20.5519 20.5505	20.5512	0.318237 0.318218	0.318227	64.5877 64.5867	64.5872

$S = -0.02009$, $D_s = 0.00010$, $I = 65.005$, $D_i = 0.004$

$RTS/I = -604\text{cm}^3\text{mole}^{-1}$. From C9,C14, $\Delta B = 38\text{cm}^3\text{mole}^{-1}$

$B = -642\text{cm}^3\text{mole}^{-1}$ From C14, $M = 64.48$

TRIMETHYLAMINE (M = 59.11)

Harrington laboratory grade reagent was distilled into a trap containing potassium hydroxide which had been dehydrated previously by heating in vacuuo. A purification procedure similar to that used for fluoroform was then used, followed by two distillations. The sample was collected in a glass trap closed with a greaseless stopcock. Measurements were made at 25°C, but before the 40°C were made, it was noticed that the Viton A diaphragm of the tap on the trap had become considerably swollen (its volume had increased about threefold). The value of the second compressibility virial coefficient obtained at 25°C agreed well with the measurements of Lambert and Strong, so it was decided to attempt no further runs on trimethylamine and so to avoid the possibility of contaminating the tap diaphragms and 'O' rings in the apparatus. As a further precaution, although there was no evidence of any contamination, those diaphragms which had been exposed to trimethylamine were replaced with new ones.

(Trimethylamine)

Run C6, $t = 25^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
30.1073 20.1023	30.1048	0.449600 0.449518	0.449559	66.9648 66.9656	66.9652
49.7550 49.7415	49.7483	0.748991 0.748795	0.748893	66.4293 66.4288	66.4291
10.3591 10.3600	10.3596	0.153594 0.153604	0.153599	66.4450 66.4465	66.4458
19.5620 19.5586	19.5603	0.291042 0.291029	0.291036	67.2137 67.2051	67.2094
40.3388 40.3328	40.3358	0.604865 0.604777	0.604821	66.6907 66.6903	66.6905

$S = -0.02596$, $D_s = 0.00026$, $I = 67.729$, $D_i = 0.010$

$RTS/I = -713 cm^3 mole^{-1}$. From C1,C2,C8, $\Delta B = 51 cm^3 mole^{-1}$

$B = -764 cm^3 mole^{-1}$ From C1, $M = 58.97$

CARBON DIOXIDE ($M = 44.01$)

B.O.C. cylinder carbon dioxide was passed slowly through a phosphorus pentoxide tube and collected in a cold trap. It was bulb to bulb distilled four times rejecting large initial and final fractions, with repeated freezing and pumping in between. A 5 litre sample was collected and stored in a glass flask closed with a greased tap.

(Carbon dioxide)

Run B1, $t = 25^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
11.7011		0.129122		90.6205	
11.7010	11.7009	0.129096	0.129105	90.6380	90.6311
11.7007		0.129097		90.6349	
50.1034		0.553776		90.4759	
50.0994	50.1006	0.553785	0.553742	90.4754	90.4765
50.0991		0.553714		90.4783	
29.5154		0.325883		90.5705	
29.5141	29.5150	0.325869	0.325874	90.5704	90.5719
29.5156		0.325870		90.5748	
40.6130		0.448657		90.5213	
40.6105	40.6109	0.448625	0.448629	90.5222	90.5222
40.6092		0.448606		90.5231	
20.1154		0.221964		90.6246	
20.1173	20.1185	0.221990	0.221984	90.6226	90.6304
20.1228		0.221998		90.6441	

$S = -0.00459 \quad D_s = 0.00018, \quad I = 90.708, \quad D_i = 0.007$

$RTS/I = -94 cm^3 mole^{-1}. \qquad \Delta B = B_{obs} - B_{lit} = +28 cm^3 mole^{-1}$

From B2, M = 44.01

Run B5, $t = 25^{\circ}C$

10.6581		0.117575		90.6494	
10.6577	10.6586	0.117560	0.117565	90.6575	90.6611
10.6600		0.117561		90.6763	
50.0609		0.553281		90.4801	
50.0596	50.0599	0.553258	0.553250	90.4815	90.4818
50.0592		0.553240		90.4837	
30.3481		0.335068		90.5730	
30.3457	30.3472	0.335051	0.335060	90.5704	90.5724
30.3477		0.335060		90.5739	

$S = -0.00457, \quad D_s = 0.00001, \quad I = 90.710, \quad D_i = 0.0005$

$RTS/I = -94 cm^3 mole^{-1}. \qquad \Delta B = B_{obs} - B_{lit} = +28 cm^3 mole^{-1}$

From B2, M = 44.01

(Carbon dioxide)

<u>Run B18, t = 40°C</u>

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
20.0105		0.210434		95.0945	
20.0099	20.0100	0.210409	0.210414	95.1028	95.1002
20.0097		0.210399		95.1033	
39.0891		0.411274		95.0465	
39.0884	39.0881	0.411255	0.411257	95.0507	95.0496
39.0869		0.411242		95.0517	
10.3678		0.108975		95.1440	
10.3687	10.3687	0.108980	0.108978	95.1495	95.1507
10.3695		0.108979		95.1577	
49.8039		0.524266		94.9988	
49.8037	49.8035	0.524244	0.524246	95.0023	95.0011
49.8029		0.524229		95.0022	
14.4611	14.4612	0.152042	0.152039	95.1104	95.1131
14.4613		0.152036		95.1158	

$S = -0.00340$, $D_s = 0.00016$, $I = 95.175$, $D_i = 0.006$

$RTS/I = -70 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 38 cm^3 mole^{-1}$

From B29, <u>M = 44.02</u>

<u>Run B23, t = 40°C</u>

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
19.8798	19.8799	0.209063	0.209057	95.0927	95.0942
19.8799		0.209051		95.0956	
39.6887	39.6901	0.417608	0.417604	95.0410	95.0378
39.6915		0.417599		95.0346	
29.7849	29.7845	0.313340	0.313335	95.0650	95.0654
29.7841		0.313329		95.0657	
49.9839	49.9833	0.526136	0.526126	95.0062	95.0070
49.9827		0.526115		95.0078	

$S = -0.00289$, $D_s = 0.00001$, $I = 95.152$, $D_i = .0005$

$RTS/I = -59 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 49 cm^3 mole^{-1}$

From B 29, <u>M = 44.03</u>

(Carbon dioxide)

Run B31, $t = 55^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
49.8452 49.8410	49.8431	0.501139 0.501124	0.501132	99.4623 99.4577	99.4600
30.1896 30.1881	30.1889	0.303379 0.303369	0.303374	99.5189 99.5148	99.5174
10.4757 10.4760	10.4759	0.105196 0.105191	0.105194	99.5933 99.5008	99.5971
39.7759 39.7737	39.7748	0.399757 0.399728	0.399743	99.5048 99.5066	99.5057
20.0802 20.0800	20.0801	0.201752 0.201745	0.201749	99.5353 99.5378	99.5366

$S = -0.00294$, $D_s = 0.00015$, $I = 99.611$, $D_i = 0.009$

$RTS/I = -60 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 37 cm^3 mole^{-1}$

From B39, M = 44.01

Run C8, $t = 25^{\circ}C$

20.0797 20.0805	20.0801	0.221510 0.221509	0.221510	90.6490 90.6530	90.6510
40.3530 40.3494	40.3512	0.445433 0.445450	0.445452	90.5887 90.5812	90.5850
49.1027 49.1021	49.1024	0.542330 0.542317	0.542324	90.5402 90.5413	90.5408
10.3023 10.3022	10.3023	0.113635 0.113635	0.113635	90.6616 90.6607	90.6612
29.9675 29.9647	29.9661	0.330653 0.330647	0.330650	90.6313 90.6245	90.6279

$S = -0.00353$, $D_s = 0.00022$, $I = 90.721$, $D_i = 0.009$

$RTS/I = -72 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 50 cm^3 mole^{-1}$

From C1, M = 44.02

(Carbon dioxide)

<u>Run C9, t = 40°C</u>

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
39.2058 39.2050	39.2054	0.412490 0.412493	0.412492	95.0496 95.0485	95.0491
10.0137 10.0144	10.0141	0.105271 0.105273	0.105272	95.1317 95.1381	95.1349
49.4745 49.4740	49.4743	0.520770 0.520759	0.520765	95.0102 95.0111	95.0107
19.8228 19.8236	19.8232	0.208418 0.208419	0.208419	95.1177 95.1196	95.1187
29.9320 29.9287	29.9304	0.314858 0.314849	0.314854	95.0728 95.0638	95.0683

$S = -0.00330$, $D_s = 0.00013$, $I = 95.175$, $D_i = 0.005$

$RTS/I = -68 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 40 cm^3 mole^{-1}$

From C14, <u>M = 44.04</u>

<u>Run C17, t = 40°C</u>

19.0481 19.0440	19.0461	0.200329 0.200296	0.200313	95.1043 95.0980	95.1012
39.8173 39.8213	39.8193	0.419064 0.419062	0.419063	95.0360 95.0462	95.0411
47.9489 47.9462	47.9476	0.504701 0.504690	0.504696	95.0258 95.0226	95.0242
10.0327		0.105461		95.1531	
30.4181 30.4162	30.4172	0.319996 0.319985	0.319991	95.0789 95.0765	95.0777

$S = -0.00309$, $D_s = 0.00014$, $I = 95.169$, $D_i = 0.005$

$RTS/I = -63 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 45 cm^3 mole^{-1}$

From C14, <u>M = 44.04</u>

CARBON TETRAFLUORIDE (M = 88.01)

Imperial Smelting Co. Isceon 14 which had been shown mass spectometrically to be more than 98% pure was collected in a cold trap and the cold liquid pumped repeatedly until the vapour pressure remained constant (at liquid nitrogen temperature it was an indicated 30microns on a Pirani gauge). It was then simple distilled once rejecting large initial and final fractions, and a 5 litre sample collected in a glass flask closed with a greased tap.

Run B2, $t = 25^{o}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
19.5130		0.430568		45.3192	
19.5427	19.5411	0.431075	0.431046	45.3348	45.3351
19.5688		0.431495		45.3512	
49.5823		1.094908		45.2844	
49.5854	49.5849	1.094966	1.094951	45.2849	45.2848
49.5879		1.094997		45.2851	
30.3240		0.669105		45.3202	
30.3208	30.3220	0.669100	0.669099	45.3158	45.3177
30.3213		0.669092		45.3171	
39.8032		0.878549		45.3056	
39.8043	39.8039	0.878541	0.878543	45.3073	45.3068
39.8043		0.878539		45.3074	
10.1116		0.223018		45.3398	
10.1108	10.1112	0.223011	0.223009	45.3377	45.3398
10.1112		0.222999		45.3419	

$S = -0.00152$, $D_s = 0.00008$, $I = 45.363$, $D_i = 0.003$

$RTS/I = -62cm^3mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 26cm^3mole^{-1}$

(Carbon tetrafluoride)

Run B11, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
30.2875 30.2877	30.2876	0.668270 0.668269	0.668270	45.3223 45.3226	45.3225
50.4654 50.4672	50.4663	1.113971 1.113981	1.113976	45.3022 45.3034	45.3028
12.6406 12.6410	12.6408	0.278801 0.278801	0.278801	45.3392 45.3406	45.3399

$S = -0.009779$, $D_s = 0.000002$, $I = 45.352$, $D_i = 0.00007$

$RTS/I = -40 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 48 cm^3 mole^{-1}$

Run B19, t = 40°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
19.6418 19.6415 19.6415	19.6416	0.412930 0.412926 0.412925	0.412927	47.5612 47.5617 47.5626	47.5618
49.7460 49.7454 49.7463	49.7459	1.046070 1.046071 1.046084	1.046075	47.5490 47.5484 47.5487	47.5487
10.2552 10.2660 10.2655	10.2656	0.215646 0.215646 0.215642	0.215645	47.5970 47.6006 47.5991	47.5989
39.4718 39.4725 39.4716	39.4720	0.829768 0.829768 0.829759	0.829765	47.5650 47.5651 47.5635	47.5646
14.4122 14.4127	14.4125	0.302847 0.302846	0.302847	47.5827 47.5846	47.5837

$S = -0.00086$, $D_s = 0.00016$, $I = 47.593$, $D_i = 0.006$

$RTS/I = -35 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 42 cm^3 mole^{-1}$

From B29, M = 88.02

(Carbon tetrafluoride)

Run B29, $t = 40^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.0593 10.0590	10.0592	0.21415 0.211416	0.211416	47.5846 47.5826	47.5836
40.0414 40.0395	40.0405	0.841786 0.841797	0.841792	47.5691 47.5670	47.5681
20.1444 20.1437	20.1440	1.046274 1.046268	0.423283	47.5513 47.5520	47.5876
49.7540 49.7525	49.7533	1.046274 1.046268	1.046271	47.5513 47.5520	47.5517
29.9979 29.9972	29.9976	0.630601 0.630598	0.630600	47.5688 47.5680	47.5684

$S = -0.00093$, $D_s = 0.0001$, $I = 47,601$, $D_i = 0.004$

$RTS/I = -38 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 39 cm^3 mole^{-1}$

Run B39, $t = 55^{\circ}C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.1797 10.1797	10.1797	0.204387 0.204384	0.204386	49.8022 49.8032	49.8027
39.9655 39.9685	39.9670	0.802743 0.802758	0.802751	49.7858 49.7856	49.7847
20.0411 20.0412	20.0412	0.402442 0.402448	0.402445	49.7960 49.7952	49.7956
49.8889 49.8886	49.8889	1.002396 1.002392	1.002394	49.7734 49.7742	49.7738
30.0923 30.0948	30.0936	0.604442 0.604444	0.604443	49.7906 49.7927	49.7917

$S = -0.00074$, $D_s = 0.00004$, $I = 49.812$, $D_i = 0.002$

$RTS/I = -30 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 36 cm^3 mole^{-1}$

(Carbon Tetrafluoride)

Run C1, $t = 25^\circ C$

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
21.2335	21.2341	0.468084	0.468103	45.3626	45.3621
21.2347		0.468122		45.3615	
50.9747	50.9758	1.124707	1.124732	45.3227	45.3227
50.9768		1.124756		45.3226	
10.1199	10.1206	0.223109	0.223126	45.3586	45.3583
10.1213		0.223143		45.3579	
39.7832	39.7842	0.877405	0.877421	45.3419	45.3422
39.7851		0.877436		45.3425	
30.1239	30.1247	0.664360	0.664374	45.3427	45.3430
30.1255		0.664388		45.3432	

$S = -0.00103$, $D_s = 0.00011$, $I = 45.378$, $D_i = 0.004$

$RTS/I = -42 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 45 cm^3 mole^{-1}$

Run C14, $t = 40^\circ C$

29.9042	29.9038	0.628295	0.628308	47.5993	47.5987
29.9033		0.628320		47.5980	
10.4842	10.4847	0.220240	0.220244	47.6113	47.6125
10.4851		0.220248		47.6137	
49.8850		1.048731		47.5727	
39.9459	39.9457	0.839393	0.839414	47.9590	47.5935
39.9455		0.839435		47.5919	
20.3459	20.3461	0.427458	0.427463	47.6029	47.6031
20.3463		0.427468		47.6032	

$RST/I = -0.00101$, $D_s = 0.00010$, $I = 47.627$, $D_i = 0.004$

$RTS/I = -41 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 36 cm^3 mole^{-1}$.

SULPHUR HEXAFLUORIDE (M = 146.07)

Sulphur hexafluoride supplied by I.C.I.Ltd. was passed slowly over phosphorus pentoxide and collected in a cold trap. It was simple distilled three times retaining only a small middle fraction each time, and a 5 litre sample collected and stored in a glass flask with a greased tap.

Run B24, t = 40°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
27.8122 27.8122	27.8122	0.972363 0.972351	0.972357	28.6040 28.6038	28.6039
46.7979 46.7990	46.7985	1.639108 1.639111	1.639110	28.5520 28.5527	28.5524
19.8221 19.8221	19.8221	0.692457 0.692466	0.692462	28.6261 28.6262	28.6262
37.6396 37.6391	37.6394	1.317069 1.317054	1.317062	28.5744 28.5717	28.5731
9.8038 9.8033	9.8036	0.341902 0.341903	0.341903	28.6743 28.6733	28.6738

$S = -0.00301$, $D_s = 0.00011$, $I = 28.690$, $D_i = 0.004$

$RTS/I = -205 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 46 cm^3 mole^{-1}$.

From B29, M = 146.02

(Sulphur hexafluoride)

Run B32, t = 55°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
10.1157 10.1153	10.1155	0.337244 0.337238	0.337241	30.0000 29.9972	29.9986
38.1871 38.1863	38.1867	1.276275 1.276302	1.276289	29.9258 29.9264	29.9261
19.9494 19.9494	19.9494	0.665586 0.665587	0.665587	29.9740 29.9744	29.9742
45.9409 45.9396	45.9403	1.536300 1.536306	1.536303	29.9054 29.9045	29.9050
29.9376 29.9384	29.9380	0.999841 0.999842	0.999842	29.9443 29.9446	29.9445

$S = -0.00261$, $D_s = 0.00003$, $I = 30.025$, $D_i = 0.001$

$RTS/I = -173 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 47 cm^3 mole^{-1}$.

From B39, M = 146.01

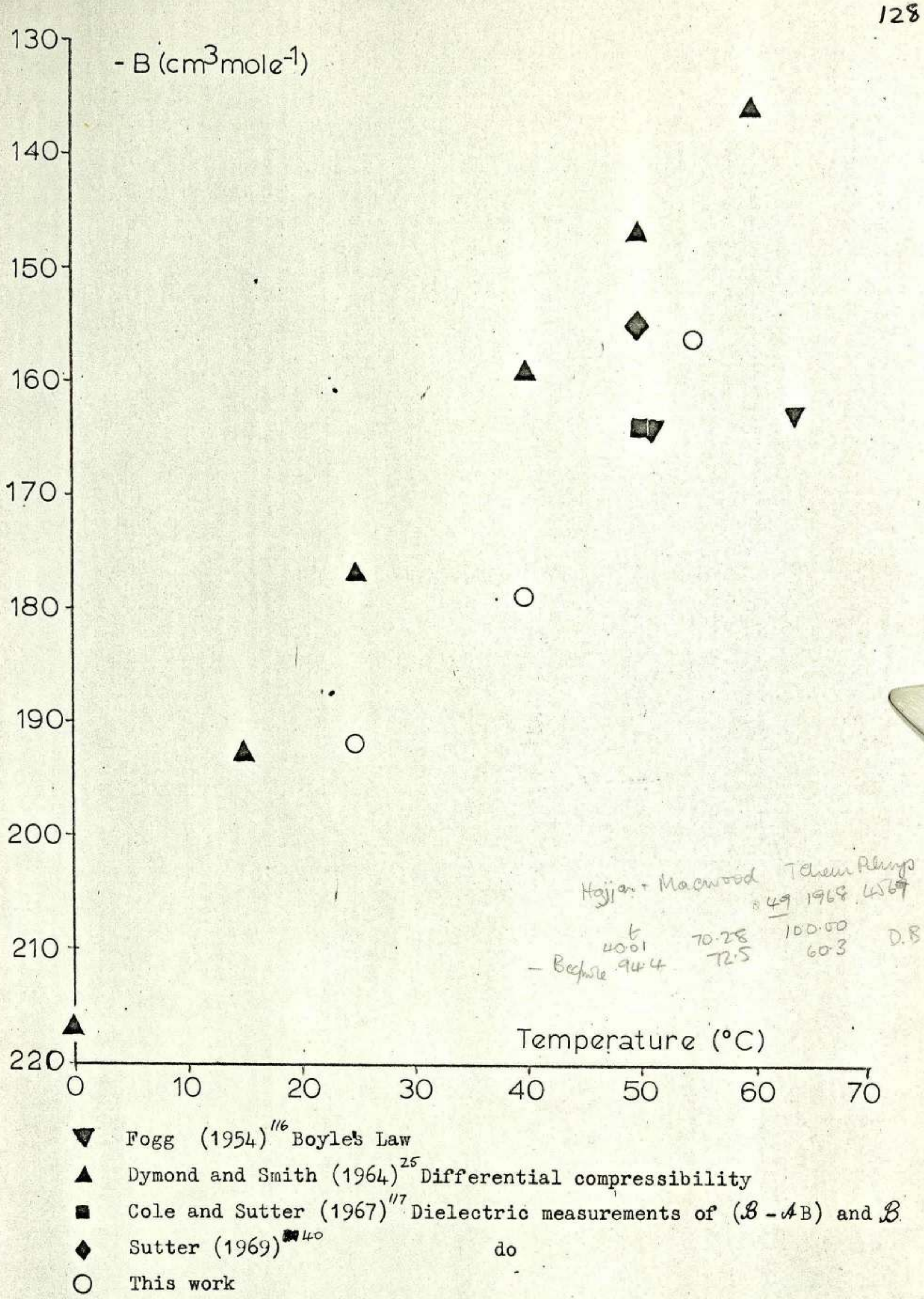
Run C2, t = 25°C

p	p_{av}	i'	i'_{av}	(p/i')	$(p/i')_{av}$
18.8660 18.8691	18.8676	0.691531 0.691603	0.691567	27.2815 27.2831	27.2823
45.1385 45.1396	45.1391	1.659643 1.659673	1.659658	27.1978 27.1979	27.1979
9.7388 9.7396	9.7392	0.356562 0.356607	0.356585	27.3127 27.3118	27.3123
36.1512 36.1536	36.1524	1.327441 1.327527	1.327484	27.2338 27.2337	27.2338
27.6400 27.6395	27.6398	1.013882 1.013937	1.013910	27.2616 27.2596	27.2606

$S = -0.00324$, $D_s = 0.00009$, $I = 27.347$, $D_i = 0.003$

$RTS/I = -120 cm^3 mole^{-1}$. $\Delta B = B_{obs} - B_{lit} = 58 cm^3 mole^{-1}$.

From C1, M = 146.04



Hajjar + Macwood J Chem Phys 49 1968 4567

t 40.01 70.28 100.00 D.B

– Before 94.4 72.5 60.3

Figure (VII.1) The second compressibility virial coeffi^ci^ent for fluoroform

Haj

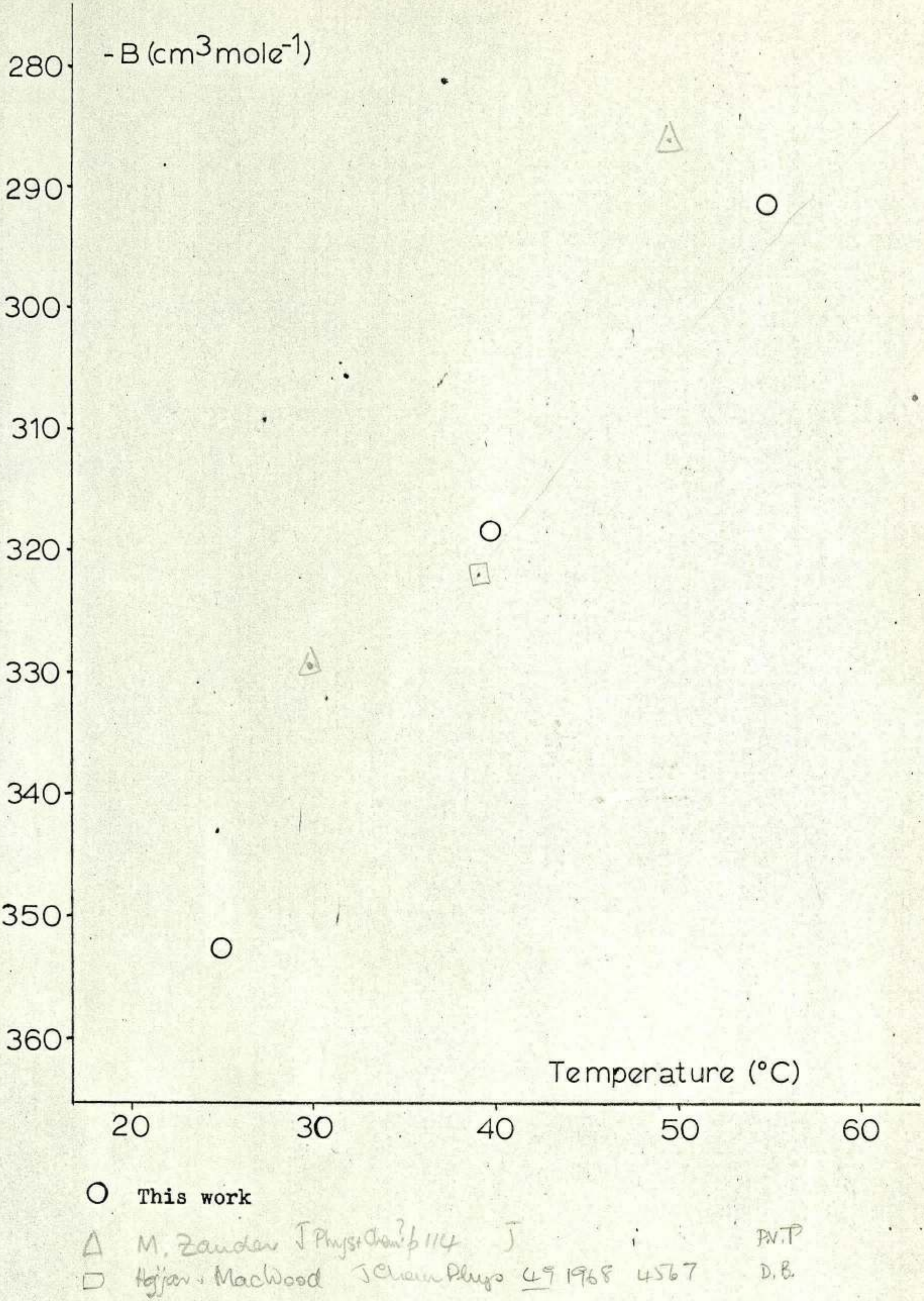


Figure (VII.2) The second compressibility virial coefficient for chlorodifluoromethane

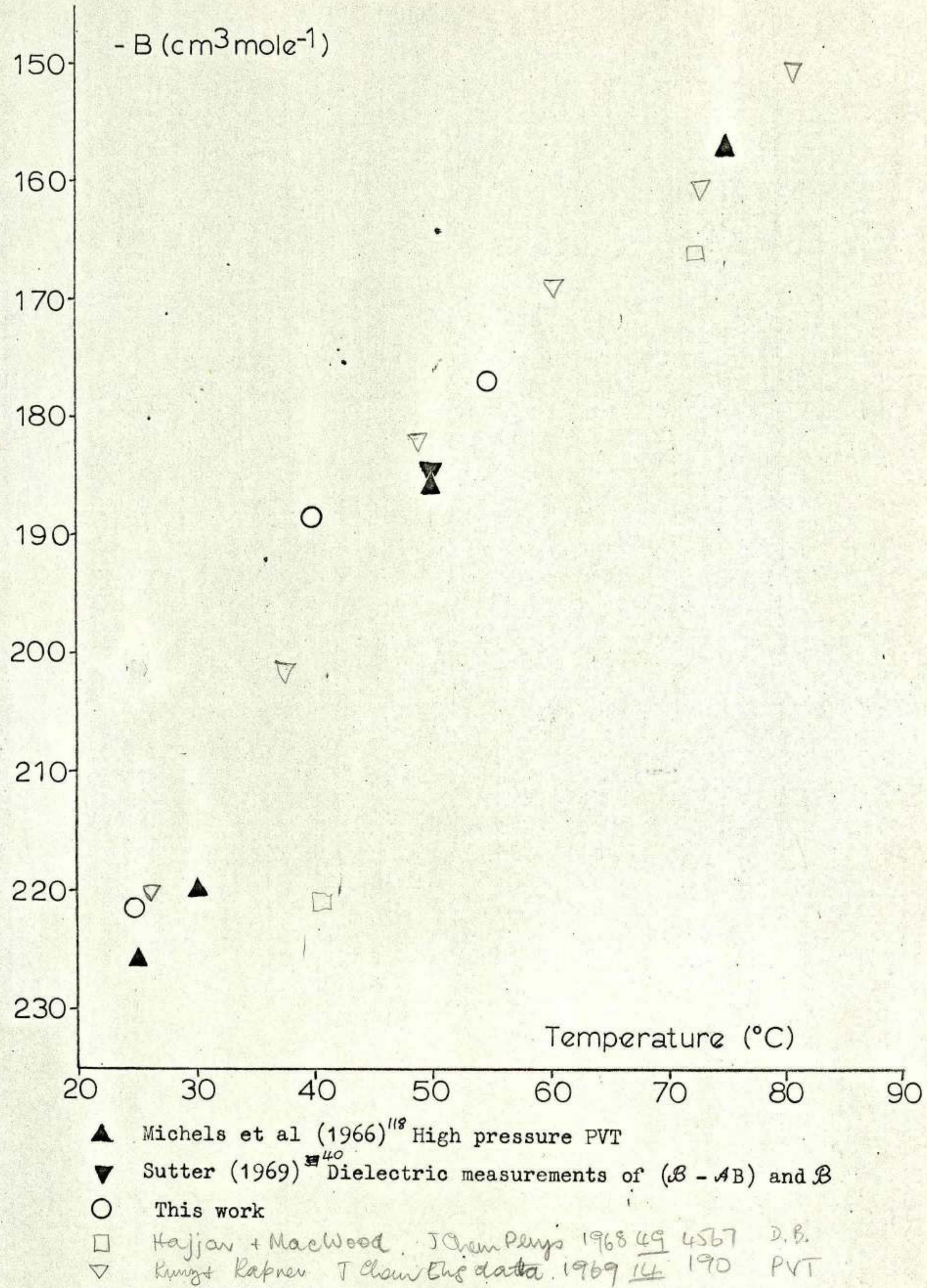
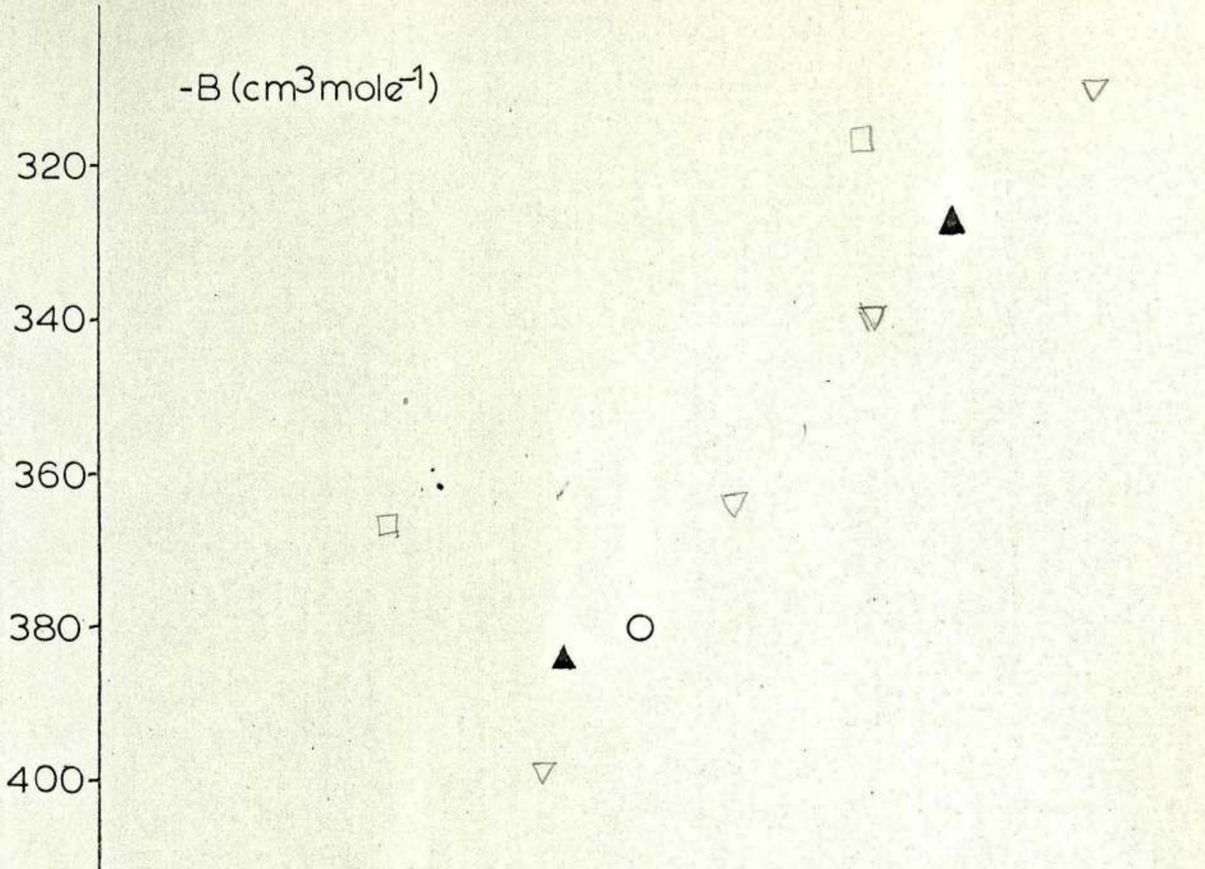


Figure (VII.3) The second compressibility virial coefficient for chlorotrifluoromethane



▲ Michels et al (1966)[118] High pressure PVT

○ This work

□ Hajjar + MacWood J Chem Phys 1968 <u>49</u> 4567 D.B.

▽ Kuby + Kapner J Chem Eng Data 1969 <u>14</u> 190

Figure (VII.4) The second compressibility virial coefficient for dichlorodifluoromethane

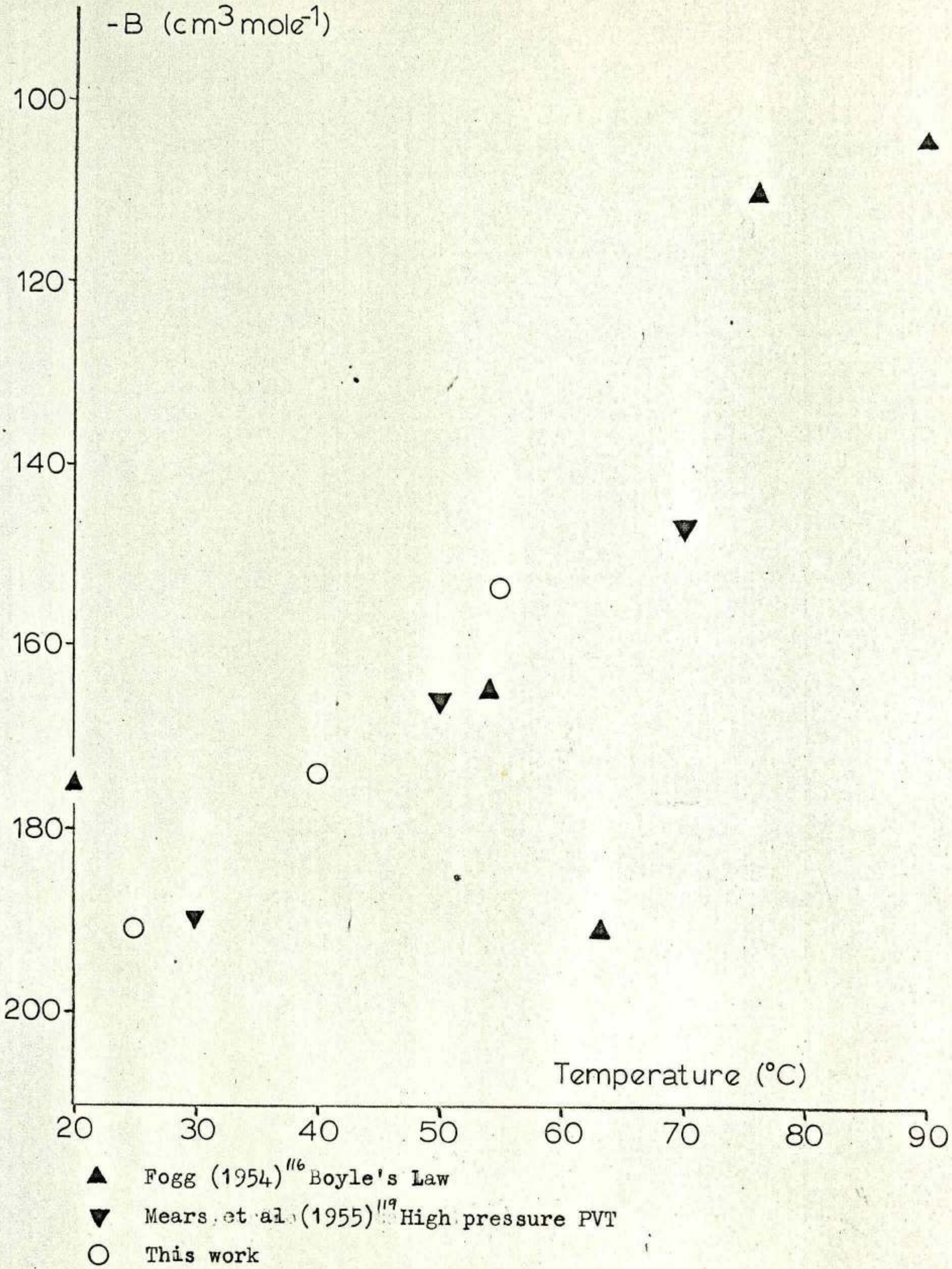


Figure (VII.5) The second compressibility virial coefficient for 1,1,difluoroethylene

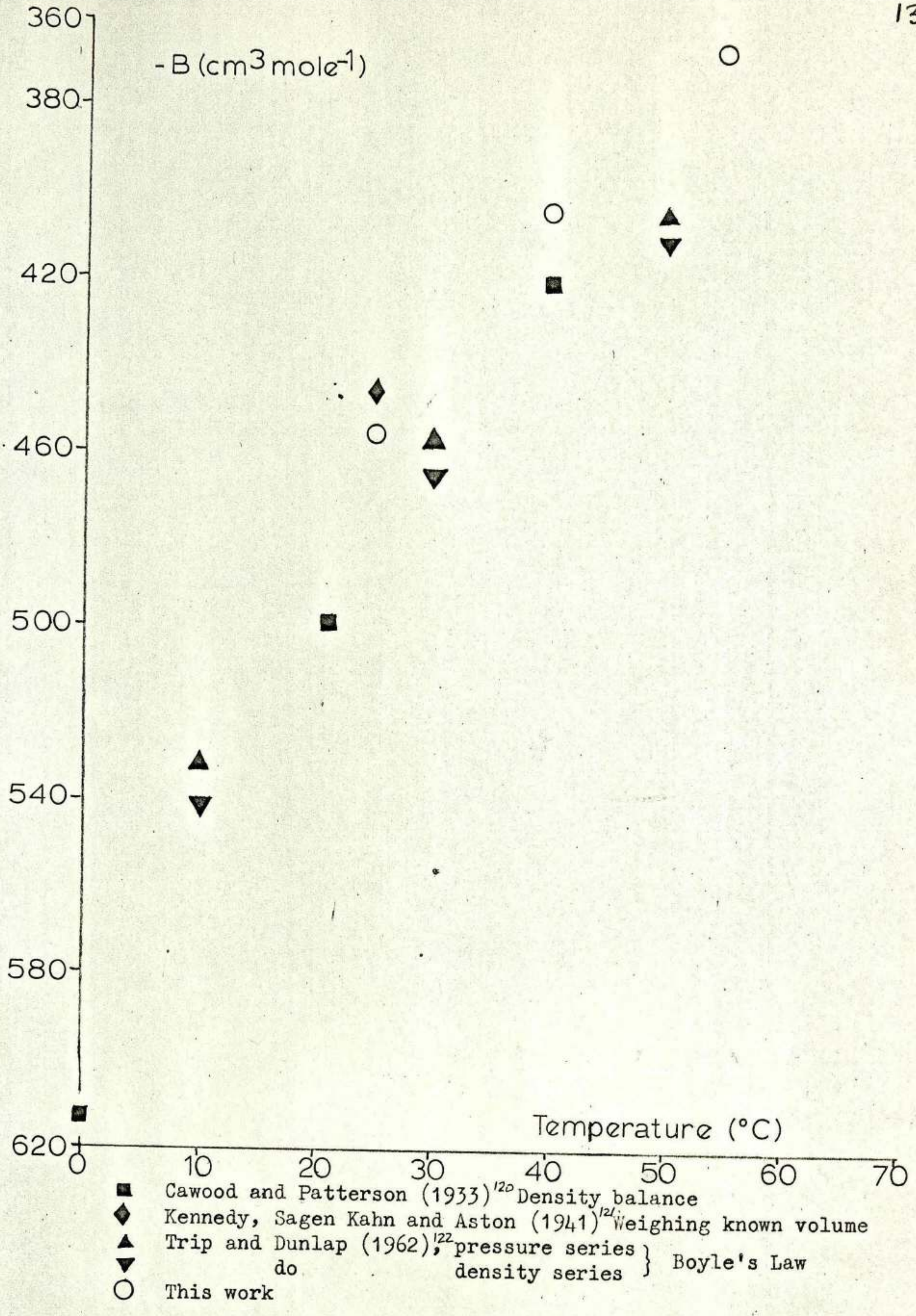


Figure (VII.6) The second compressibility virial coefficient for dimethyl ether

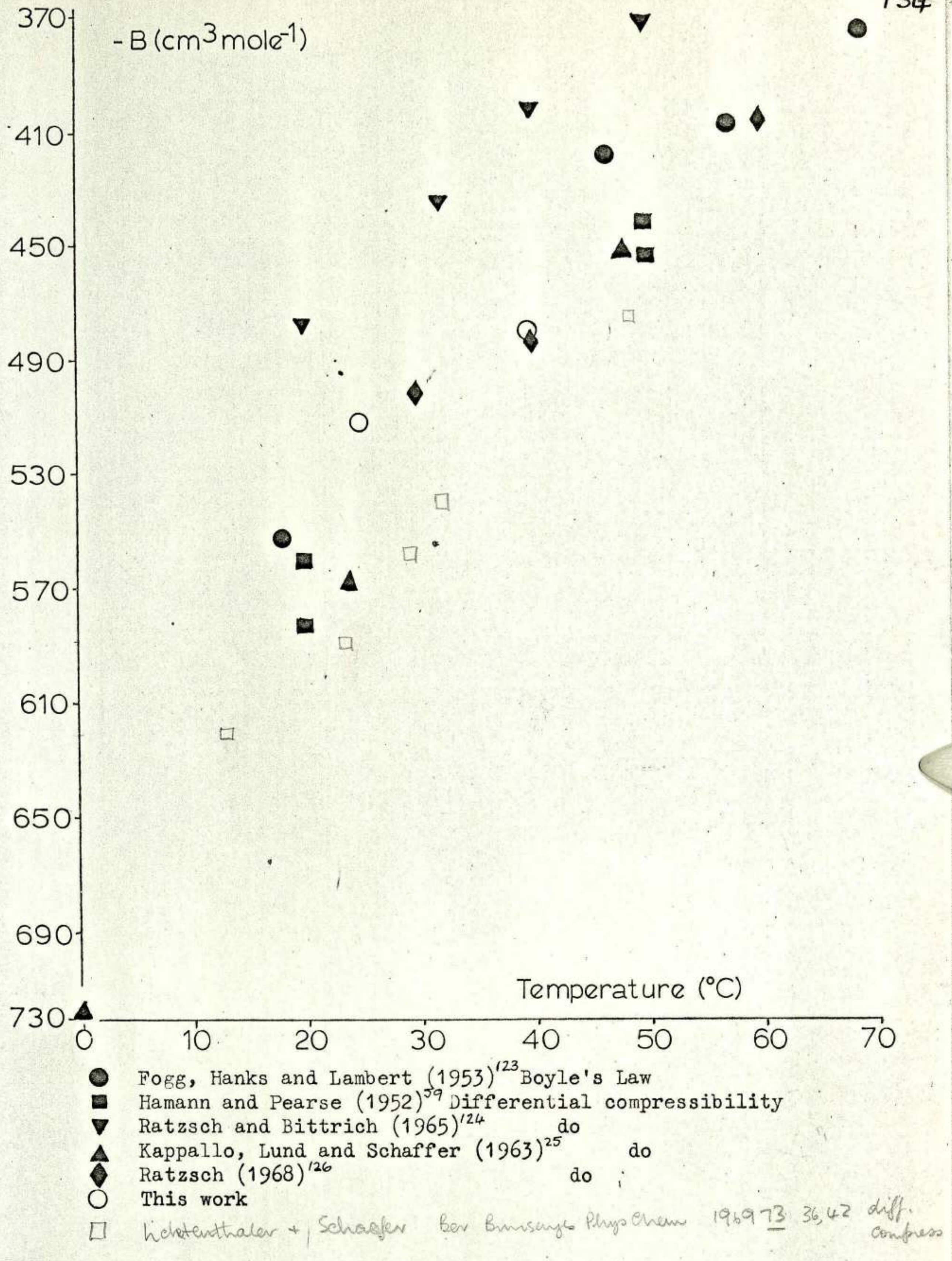


Figure (VII.7) The second compressibility virial coefficient for bromomethane

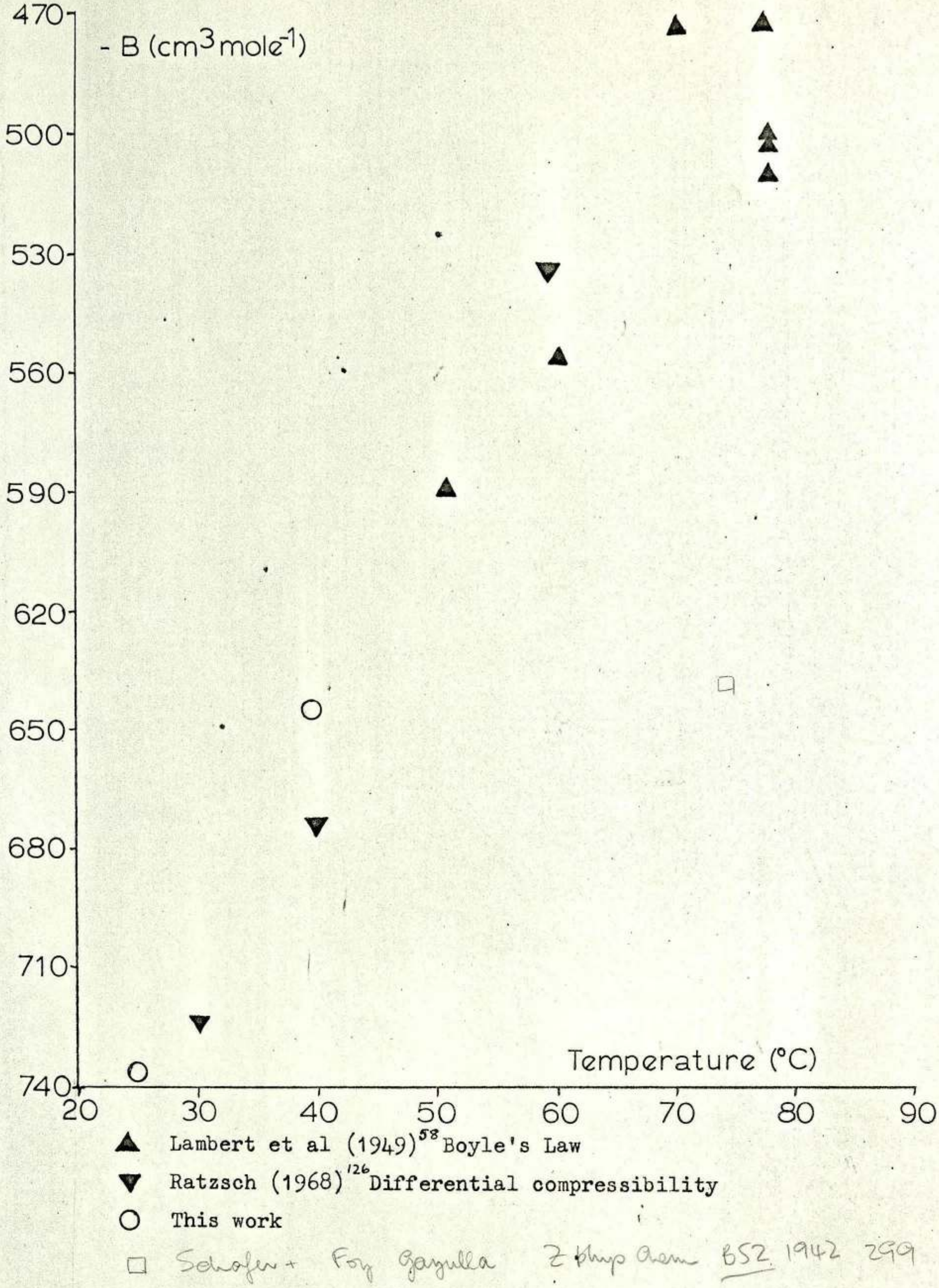
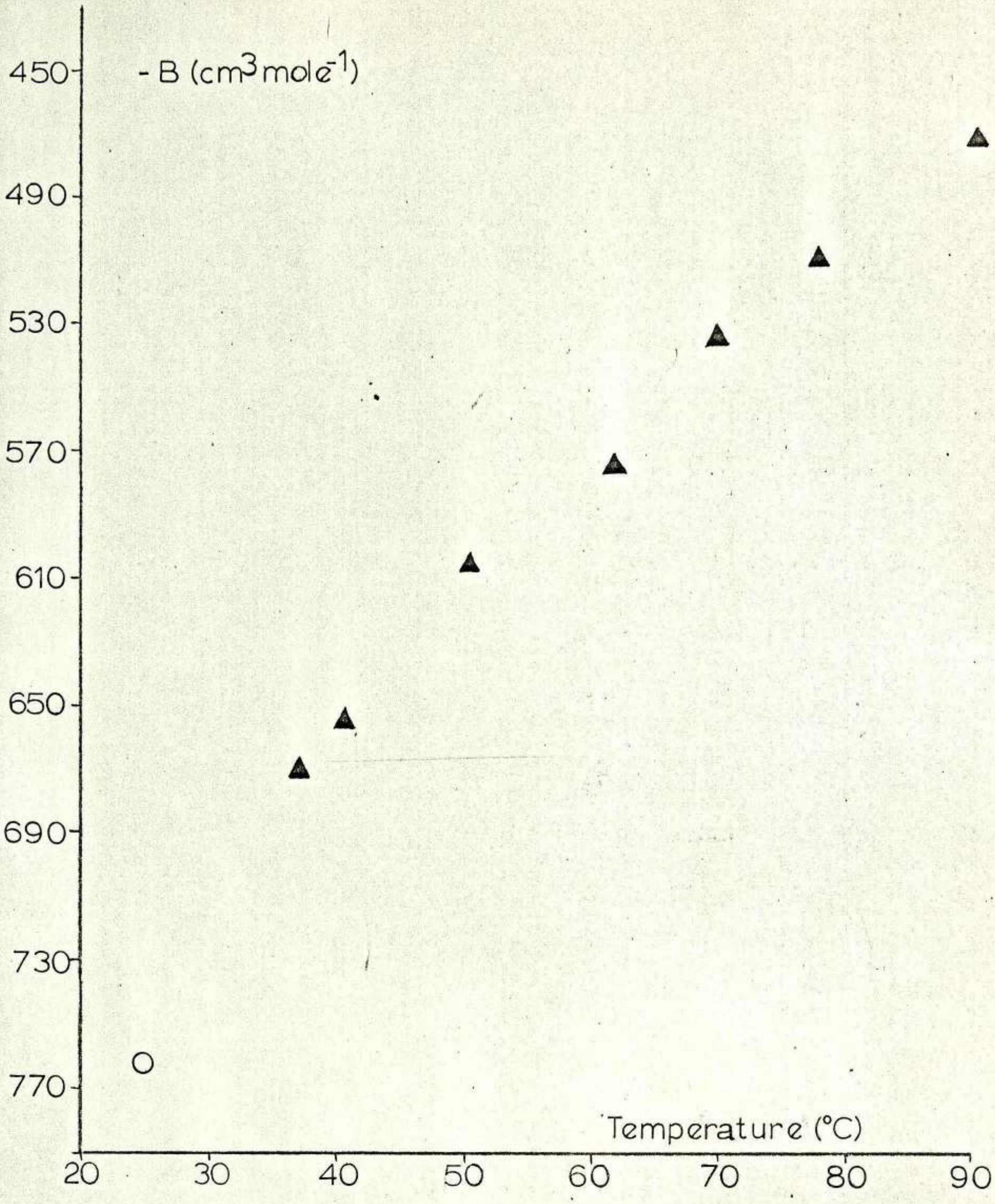


Figure (VII.8) The second compressibility virial coefficient for chloroethane



▲ Lambert and Strong (1950)[127] Boyle's Law

○ This work

Figure (VII.9) The second compressibility virial coefficient for trimethylamine

CHAPTER VII

DISCUSSION

COMPARISON WITH PUBLISHED VALUES

The plots in Figures (VII.1) to (VII.9) show the values of the second virial coefficient in the temperature range covered in this work for all the literature values traced and for those obtained herein. No attempt has been made to assess the errors in the previously reported values, but a brief description of the method used is included, together with the date of publication. The internal consistency of the values obtained in the present work is about $\pm 5\text{cm}^3\text{mole}^{-1}$ and the comparisons made show that in most cases the largest total scatter of the values reported by different workers is less than $\pm 15\text{cm}^3\text{mole}^{-1}$ so that in the worst cases the virial coefficients may be regarded as being established absolutely to about $\pm 15\text{cm}^3\text{mole}^{-1}$.

INTERPRETATION OF THE RESULTS

The results reported here have been interpreted in conjunction with his results for dielectric virial coefficients, by Barnes.[44] The following section summarises his conclusions.

Because of the restricted temperature range over which measurements were made, the only information

		Stockmayer parameters			Off centre dipole parameters		
	μ(D)	σ(Å)	$\frac{\varepsilon}{k}$(°K)	σ_{est}(Å)	σ'(Å)	$\frac{\varepsilon'}{k}$(°K)	a(Å)
CHF_3	1.65	3.68	255	5.24	3.85	215	1.07
CH_3Cl	1.86	3.74	373	5.22	4.17	280	1.16
$CH_2{:}CF_2$	1.37	2.78	343	4.50	4.70	200	0.94
CHF_2Cl	1.47	3.08	489	5.66	4.35	323	0.99
CF_3Cl	0.55	4.92	222	5.88			
CF_2Cl_2	0.50	5.16	286	6.30			
$(CH_3)_2O$	1.28	2.81	680	4.90	4.90	320	1.53
CH_4		3.62	204	4.58			
CF_4		4.05	313	5.46			
$CH_2{:}CH_2$		4.47	200	4.20			

Table (VII.1) Values of molecular parameters from Barnes.[44]

concerning the nature of the intermolecular potential that can be obtained from the compressibility virial coefficients taken by themselves is the value of the various adjustable parameters in various model functions. Table (VII.1) shows the values of the dipole moment, μ, used with the data to obtain the values of σ and ε/k for a fit to the Stockmayer potential (polar forces represented by a central point dipole) as found by Barnes from the data reported here. Also included for comparison are values of σ and ε/k for methane, carbon tetrafluoride and ethylene and values of molecular diameters estimated by Barnes from Van der Waals radii[128] and bond lengths.[129] As has been pointed out previously, the values of σ for the polar gases is considerably less than might be expected from the estimated values or from the values for the non-polar gases,[25] but the Stockmayer potential can nevertheless give a reasonable fit to experimental values of the second compressibility virial coefficient.[130] For single gases it cannot explain the observed values of the second dielectric virial coefficient quantitatively, even with the addition of polarisability, shape and quadrupole moment terms to the basic expression,[40,44] and it fails even more markedly for two component mixtures.[24] It was this sort of observation that led to the formulation of the displaced dipole model.[24,25,39] The incorporation of an additional parameter complicates the fitting of the data, and extensive trial and error calculation would be required to obtain the best values of all the parameters. However the values which were effectively selected on the basis of an expected value for σ' give a reasonable agreement with both the experimental compressibility virial coefficient and the dielectric virial coefficient over a restricted temperature range for single gases. The values of σ', ε'/k and a, the dipole displacement, are given in Table (VII.1).

In summary, the present situation is that for gases with almost spherical molecules and small dipoles (chlorotrifluoromethane and dichlorodifluoromethane) the Stockmayer model with polarisability terms is an adequate representation. For other gases, with more polar or less symmetrical molecules the introduction of a shape dependence factor for the repulsive forces and of a displacement of the point dipole from the centre of the dispersion forces enables reasonable, but not good, agreement with calculated values to be obtained for the two virial coefficients. These conclusions have been reached from investigation over a restricted temperature range, so that they should really be examined again after a more extended investigation. Measurements over a wider temperature range would also allow a more rigorous fitting of theory to the experimental data. Sutter[40] has measured second compressibility and dielectric virial coefficients for fluoroform, fluoromethane, chlorotrifluoromethane, trichlorofluoromethane and chloromethane. For fluoroform, chlorotrifluoromethane and chloromethane, agreement with the results reported here and by Barnes is generally within the combined experimental errors. His conclusions are essentially equivalent to those summarised here.

For two component mixtures the position is less convincing, and none of the available potential models can provide even an approximate description of the dielectric virial coefficients for certain mixtures, in terms of the parameters found from the single gases.

RECALCULATION OF TURNER'S DIELECTRIC DATA

Values of compressibility virial coefficients were measured for bromomethane, chloroethane and trimethylamine because Turner[41] found values differing considerably from those previously reported. It may be seen from Figures (VII.7) to (VII.9) that the results reported here, and other more recent results confirm the earlier measurements of Lambert and co-workers.[123,127] Accordingly, values of $\mathcal{B}$ have been recalculated from Turner's values of $(\mathcal{B} - \mathcal{A}B)$, using the values of the second compressibility virial coefficient, B, obtained from this work and from Lambert's work taken together. Since the dielectric measurements were essentially independent of the density measurements, the occurrence of errors in the latter does not necessarily imply errors

	Turner's Values						Corrected Values	
	t°C	$\mathcal{A}$ (a)	$(\mathcal{B} - \mathcal{A}B)$ (b)	s (c)	$-B$ (a)	$\mathcal{B}$ (b)	$-B'$ (a)	$\mathcal{B}'$ (b)
MeBr	5	85.99	110,200	4,700	1,050	+19,900	606	+58,000
	25	81.71	32,100	1,500	1,005	−50,000	521	−10,500
	40	77.29	28,300	1,000	849	−37,300	469	− 7,900
EtCl	15	107.04	76,400	1,700	977	−28,200	778	− 6,900
	25	103.91	82,300	4,600	910	−12,300	723	+ 7,200
	40	98.23	57,500	2,000	794	−20,500	649	− 6,300
NMe_3	25	29,14	17,200	900	930	− 9,900	755	− 4,800

	t°C	$\mathcal{B}$ (b)	y	ref.
MeCl	30	−6,600	600	44
	50	−3,650	300	44
	50	−4,470	200	40
MeF	50	−1,307	37	40

NOTES:

(a) Units are $cm^3 mole^{-1}$

(b) Units are $cm^6 mole^{-2}$

(c) s is the standard deviation in $(\mathcal{B} - \mathcal{A}B)$

(d) The estimated error in $\mathcal{B}'$ is about $+3,000 cm^6 mole^{-2}$

(e) y is the estimated error in $\mathcal{B}$

Table (VII.2)

in the former. Table (VII.2) shows the values of $(\mathcal{B} - \mathcal{A}B)$, $\mathcal{A}$, B and $\mathcal{B}$ found by Turner, and the values of B' used to obtain the corrected values $\mathcal{B}'$. Also included, for comparison, are values of $\mathcal{B}$ for chloromethane and fluoromethane from the results of other workers.

The erratic temperature dependence of the values of the dielectric virial coefficients obtained, means that there is little point in making a detailed assessment of the contribution from the various interaction forces such as polarisability, shape, displaced dipole etc. However, with the exception of the values for bromomethane at 5°C and chloroethane at 25°C, both of which are obtained from plots of abnormally large scatter, the results now lie in a much more reasonable range, as can be seen from comparison with the values for chloromethane[40,44] and fluoromethane.[40] It therefore seems very likely that the conclusions Barnes[44] drew from his studies which are briefly summarised above may be extended to cover these other systems.

It is worth noting that if Turner's[41] results for the compressibility virial coefficient were too large for single components, then it is probable that this is also true for his results for mixtures of these gases. In all the systems he studied such a change would increase the values of the dielectric virial coefficients obtained, making them much smaller negative numbers, and closer to values to be expected from theory and Barnes' results for mixtures. A more detailed examination of the experimental results shows that there was also some considerable change in composition for some of the mixtures, and as has been shown in Chapter II molecular weight changes are very significant in density balance studies. Turner's conclusions about the non-applicability of the displaced dipole model to mixtures should therefore be regarded with caution. Nevertheless, Barnes[44] found that when there is a possibility of hydrogen bonding between the components, the results cannot be accounted for in terms of the displaced dipole parameters found appropriate for the single components.

It seems desirable to have some more accurate values for both compressibility and dielectric interaction virial coefficients for a series of mixtures, including those where specific chemical types of interaction are expected, so that the question of the range of applicability of the displaced dipole model to such systems could be answered convincingly. Some suggestions as to how these values might be obtained are made later.

DISCUSSION OF THE APPARATUS AND METHOD

The extent to which the detailed design features of the apparatus have fulfilled their intended aim is discussed in this section, so that possible improvements may be considered and the direction in which the apparatus might be most usefully developed can be outlined. The approach to the measurement of virial coefficients described in this thesis will also be critically examined, particularly in respect of the scope of application and the limitations and disadvantages of the method in comparison with other methods. (See also reference 77.)

Performance of the apparatus

In attempting to assess the contributions to error and to scatter in the p/i' plot against p or i', there is the difficulty of separating contributions from p and from i', and this is further complicated by the possibility of errors in i' arising either from the balance itself or from the current measuring part of the apparatus. However it is possible to draw some conclusions.

1. The accuracy of the potentiometer, given by the maker, for the range used (x1) is ±0.002% or 10 micro-volt, whichever is the greater. The relative accuracy of two readings on the x1 range is ±0.001% or 10 micro-volt whichever is the greater.

2. A plot of the standard deviation of the slope of the p/i' plot divided by the intercept versus the molecular weight of the gas is shown in Figure (VII.10). The error in a single value of p/i' may be expressed:

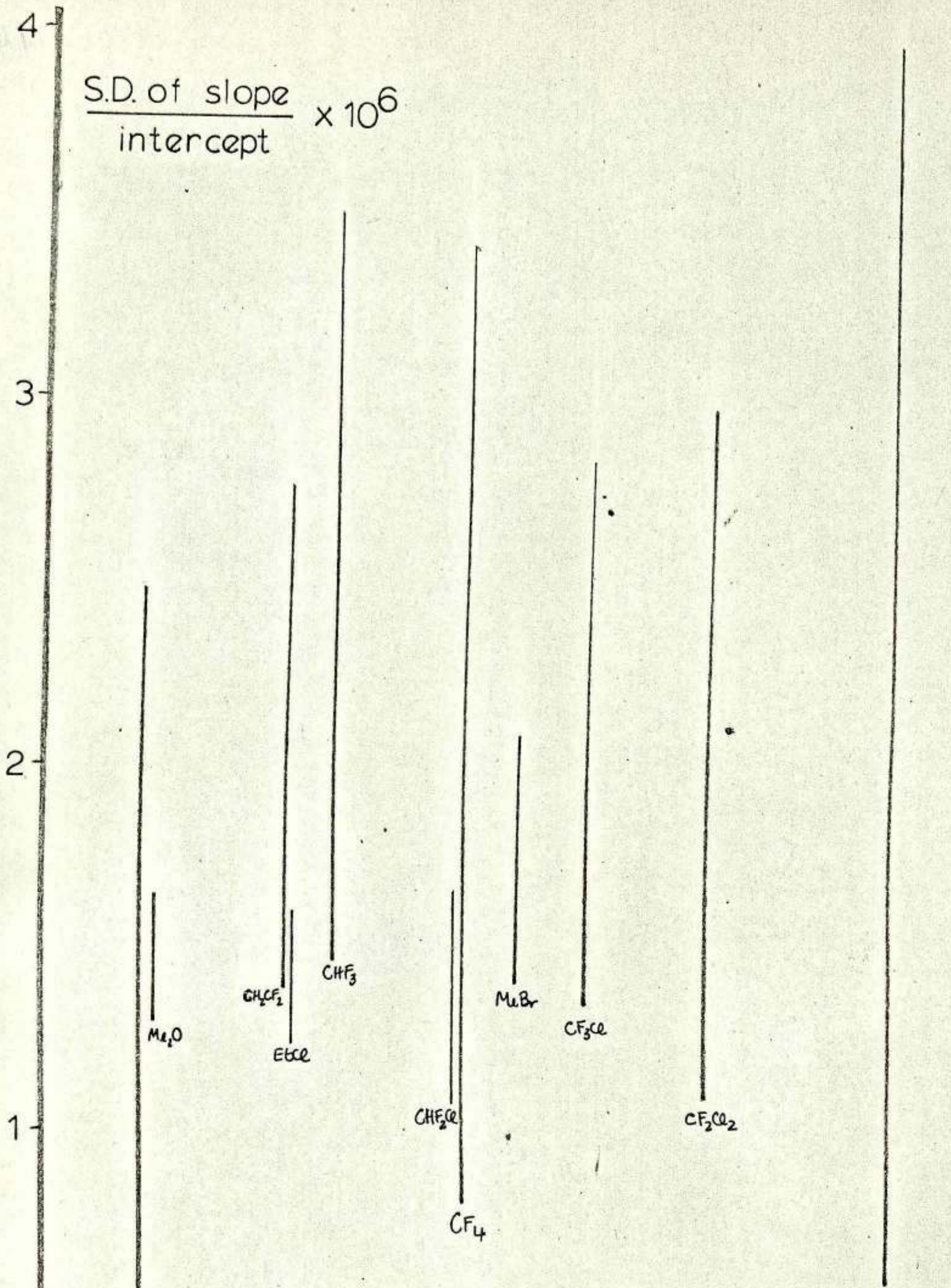


Figure (VII.10) Plot against molecular weight of the ratio of the standard deviation of the slope to the intercept for the p/i' plots

$$\frac{\delta(p/i')}{(p/i')} = \delta p/p + \delta i'/i' \qquad (VII.1)$$

The standard deviation of the slope of the p/i' plot is related to $\delta(p/i')$ and the intercept is approximately equal to p/i', thus Figure (VII.10) shows some function of the relative error in p and the relative error in i'. Pressures are measured over the same range for all gases, but the range of current values is larger for the gases of higher molecular weight because of their larger absolute densities. Therefore if the errors δp and $\delta i'$ do not depend on the values p and i' being measured, the values of the standard deviation of the slope divided by the intercept will be constant if $\delta i'/i'$ is negligible, but otherwise will tend to smaller values at higher molecular weight if $\delta p/p$ is negligible. It can be seen from the plot that the former is more nearly the case. Before assigning the major error to the pressure readings, the effect of a proportional error in the current measurements, which would give rise to the same behaviour as an absolute error in the pressure measurements, must be considered.

From 1. above, the maximum error in i' is 0.001% or 10 micro-volt whichever is the greater. Such an error in i' may be shown to give rise to an effect of about ¼ to ½ those observed, for the conditions under which the experimental runs were made. Therefore, the major source of error in the measurements of p/i' is probably in the pressure measurements.

3. The likely sources of error in the pressure measurements are now considered. The differences in successive values of p/i' at the same balancing pressure imply, if the major error is in the pressure, a reproducibility of reading pressure of better than 0.001cm Hg, provided the meniscus did not move. When the meniscus did move, the reproducibility was about 0.001cm Hg, which indicates some error associated with the conversion of meniscus heights to capillary depressions. Although the manometer tubes had been thoroughly cleaned, the mercury-glass contact line was frequently sloped, and always in the same sense. When there was less than about 10 eyepiece divisions (0.01cm) difference in the positions of the contact line on either side of the tube, an average value was taken, and otherwise the mercury was run up the tube slightly to form a new surface and contact line. However, if there were significant traces of dirt in the tubes, as these observations implied, the correlation of meniscus height with capillary depression might be expected to differ unpredictably from the published results,[108] assuming that these were obtained for absolutely clean glass surfaces. There would then be a likelihood of error from this source. The effect would be increased by the relatively small diameter of the manometer tubes (11.5mm) which were used because of their

ready availability, since the capillary depression is greater in smaller tubes. However the error introduced is small (probably about 0.001cm Hg), and can be tolerated in the present apparatus.

4. The accuracy of the pressure measurements can be judged from the plots of p/i' versus p, assuming that they give rise to the major part of the error in p/i'. This will actually give an assessment of the irregular derivations from linearity of the measured pressures as a function of true pressure rather than their absolute accuracy. When the measured pressure is directly proportional to the absolute pressure, and the proportionality constant differs by only a small amount from unity, no significant error will be introduced in calculating the second virial coefficient by taking the ratio of slope to intercept of the p/i' plot. The deviation of individual points from the best straight line was seldom more than would be produced by errors of 0.002cm Hg. The increase of this figure over the reproducibility of reading a given pressure (about 0.001cm Hg) could be due to errors in the glass scale calibration, refraction errors or errors introduced by the microscope assembly. The latter could be caused by the microscope being held at different, near-normal angles to the scale and meniscus in different parts of the manometer. A check with an accurate spirit level mounted on the microscope carriage showed no significant

	MANOMETER	DENSITY BALANCE	
	(cm Hg)	$(gm.cm^{-3})$	(gm)
Range	0 to 50	0 to $4x10^{-3}$	0 to $6x10^{-2}$
Resolution	0.0002	$2x10^{-9}$	$3x10^{-8}$
Reproducibility	0.001	$2x10^{-8}$	$3x10^{-7}$
Linearity	0.002	$2x10^{-8}$	$3x10^{-7}$

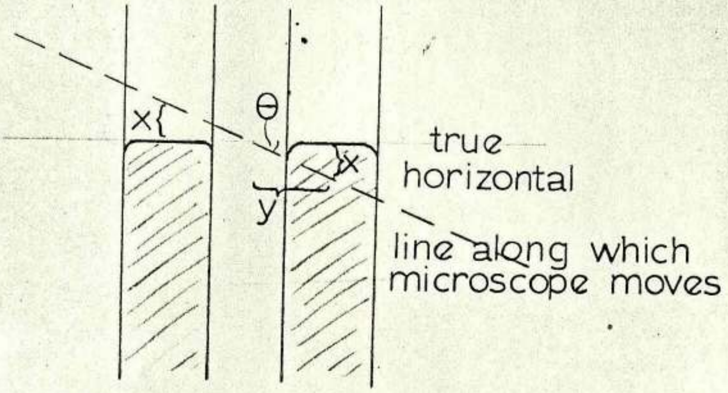
Table (VII.3) The performance of the manometer and density balance.

changes in level in the two relevant planes; refraction errors are minimised by the use of thin wall manometer tubing (0.03cm), and other workers have found no significant error with tubes of similar wall thickness.[48] The glass scale calibration therefore seems to be the most likely cause of the limitation on the linearity of the pressure readings. The method which was used for this calibration could certainly give rise to errors of the size noticed (and significantly larger ones), but this was dictated by the design of the comparator used, which allowed only one end of the scale to lie on the viewing bed. The calibration was transferred from this end to the rest of the scale using the manometer microscope, by measuring the number of eyepiece divisions to each scale division, and this could be done only to ±0.0005cm (½ eyepiece division) per scale division, largely because of the irregularity of the scale lines.

The performance deduced for the manometer and density balance are summarised in Table (VII.3), where the figures must only be regarded as likely ones, because of the lack of complete certainty in separating the individual errors of the manometer, density balance and potentiometer. The linearities quoted are those obtained after the application of all appropriate corrections. The manometer performance includes that of the separator. There was no difference in the range of values of the ratio of the standard deviation of the slope of the p/i' plot to the intercept before and after incorporating the separator which therefore has an error of less than 0.001 cm Hg (¼ of a meter scale division) provided that the zero shift is corrected for and the calibration against the manometer is used.

It must also be borne in mind that the scatter of the p/i' plot may be affected not only by errors in the pressure and current readings, but also by changes in the molecular weight of the gas from point to point. In only one or two cases is there any indication of this having occurred, and even then the values of the standard deviation of the slope divided by the intercept for the plot lie within the range of values from other runs where there is no indication of molecular weight changes. There was no evidence of significant contamination of one gas by the previous one at any time, so that evacuating the apparatus overnight seems an adequate precaution against this. Greaseless stopcocks and elastomer 'O' ring seals which are used throughout in place of greased taps and seals may be a contributing factor.

The corrections which are applied to the pressure and current readings include those for the zero error of the manometer and the zero drift of the balance respectively. While it is relatively easy to incorporate both of these factors, it is of interest to know the constancy of the former and the magnitude of the latter.



For apparently higher pressure on the right side, the correction is taken to be positive and the error negative.

$$\text{Zero error} = -2x = -2y.\tan\theta$$

Figure (VII.11) The origin of the manometer zero error

Figure (VII.12) Stability of balance zero

The manometer zero error has had values of zero, -0.007 and -0.010cm Hg. The spirit level indicated that these arose from a lean of the manometer in the plane of the tubes. The way in which this introduces an error can be seen by reference to Figure (VII.11). When the microscope moves along the broken line, the indicated pressure with zero actual pressure difference between the two sides will be $-2x$ or $-2y.\tan\theta$ where $2y$ is the distance between the axes of the tubes, provided that the glass scale is also tilted, as happens with the arrangement used. If y is about 1cm, a lean of 1° is required to produce a zero error of 0.010cm Hg. As mentioned earlier, the suspected cause of the alteration of the zero error was the bolted-up manometer stand, and this was replaced by a welded-up one before the last few measurements. No information is yet available to confirm whether this has in fact improved the constancy of zero.

The long term zero stability of the density balance is best seen from Figure (VII.12). (a) shows the variation with the original rounded hooks supporting the magnet; (b) shows the drift after these had been reformed into 'V'shaped hooks, and presumably arises from slow ageing of the quartz; (c) shows the behaviour about 3½ months after the 'V' hooks were introduced, and gives some indication of the improvement obtained.

When considering the long term drift, it is important to remember that this includes effects from the drift of the resistance in the control box across which the potential difference is measured. The change of the value of this resistance with temperature (the control box is lagged but not thermostatted) and the drift of the potentiometer is also included. Over periods of a month the latter is unlikely to be a large effect if the proper correction for the standard cell temperature is made (the standard cell is lagged and corrections are made assuming the value at 20°C as calibrated by the makers, and a temperature coefficient of -40micro-volt per °C).

It can be seen that for the later measurements the zero point was stable to ±35 micro-volt ≡ ±1 micro-gram over two weeks. The constancy during one day was about ±20micro-volt on average, and the zero readings seldom differed by more than ±10micro-volt (about 0.3micro-gram) before and after each reading, that is over periods of about 1½ hours. The last value is the one quoted as the reproducibility of the density balance.

The temperature coefficient of the density balance vacuum reading was about 130micro-volt per °C over the range 25° to 55°C, the large value probably arising from the fact that parts of the balance case were not entirely non-magnetic. The expansion of the metal case with increased temperature will change the relative position of the magnet and these parts of the case, and because the magnet is hung on a long quartz fibre there will also be an effect from this. An alteration to the position of neighbouring magnetic material will alter the constant force on the magnet from temperature to temperature. There is also a second order effect on the proportionality constant relating i' to density which changes by 1 part in 15,000 per °C, and which may arise from many sources, for example, volume changes of the flotation bulb with temperature, expansion of the solenoid altering the current-force proportionality, etc. However, with short term thermostatting to about 0.01°C, both effects are negligibly small.

One further difficulty is the necessity of applying a correction for the contraction of the bulb with pressure increase. Because the value for this is determined by doing a run for a standard gas, instead of by direct measurement, the uncertainty in this correction is a source of further error in the virial coefficients obtained. This detracts from the performance of the apparatus as a whole. It will be discussed further in the next section.

POSSIBLE IMPROVEMENTS OF THE PRESENT APPARATUS

This section discusses detailed alterations that might be made to improve the performance of the existing apparatus as a result of the considerations of the previous section.

Manometer: Improvements directed to reducing the deviations from linearity to bring them closer to the resolution would include replacing the existing manometer tubes with ones of larger diameter and attempting a better calibration of the glass scale, or, preferably, replacing it with a more accurate one. These replacements might be expected to reduce nonlinearity errors to less than 0.001cm Hg, and so make it possible to measure second virial coefficients with the existing balance with probable errors of about $\pm 4\text{cm}^3\text{mole}^{-1}$.

Density balance: The alteration which would most simply improve the accuracy with which virial coefficients could be determined would be the elimination of the pressure dependent correction. The contraction of the bulb is probably the major, if not the only significant, contributor to this effect. A sufficiently thick walled bulb could be used to eliminate this, if the additional mass did not overload the suspension fibres. From the expression in Appendix II, such a bulb could weigh 1.5gm (the present bulb weighs 0.7gm) but selection from a batch would be necessary to ensure the use of one which did not have thin spots causing contraction much larger than the theoretical value.

An alternative approach would be to attempt to measure the volume change which occurs. For the bulb used in this series of experiments, the volume changes by about 0.02cm^3, if the contraction of the bulb is the only pressure dependent effect, for an increase of external pressure of 50cm Hg. Such a change in volume causes an error of about 50cm^{3}mole^{-1} in the measured second virial coefficient, so it would have to be measured to about one part in 50, that is, to 0.0004cm^3, so that no significant error could be introduced in the correction factor. This might be done before the bulb was sealed, by altering either external or internal pressure and measuring the change in volume by the displacement of a fluid along a capillary, using a suitable arrangement. Such a method could also be used to preselect a bulb with appropriate small volume dependence on pressure.

Whether there were other significant sources of pressure-related effects could be ascertained only if a bulb of known volume/pressure dependence were used and the results for a standard gas were shown to be in error by more than the correction due to the change in the bulb volume. If there were such an effect, its cause would require identifying and eradicating. It is possible that if, as suggested earlier, the expansion of the casing causes a significant error by altering the magnet-solenoid separation at null, alteration of the position of the solenoid might be made to minimise the effect, or even make the sense opposite to that of the bulb contraction and so to counteract the latter effect.

It follows that if the pressure dependent error could be eliminated or separately calibrated, and the manometer improvements detailed above made, it should be possible to measure the second compressibility virial coefficient with an accuracy of better than $\pm 2\mathrm{cm}^3\mathrm{mole}^{-1}$. A standard gas would then be required only in order to give the relation between i' and absolute density so that molecular weights could be determined.

Two further modifications to the balance assembly might be made relatively easily. The present magnet used for the electromagnetic compensation has a pole strength of about 20 unit poles. Such a strong magnet was required originally because solenoid current was to be supplied by lead-acid accumulators, and so had to be made as small as possible. The original solenoid also had a larger diameter, and so gave a smaller field for a given current and number of turns. It would now be advantageous to reduce the magnet pole strength and increase the number of layers on the solenoid and possible also the solenoid current. The former would be preferable because it would involve a smaller increase in heating effect for a given increase in solenoid field strength, but it should be possible to reduce the pole strength and weight of the magnet to about one third of its present value. A reduced pole strength would make the balance less susceptible to stray external magnetic fields; the reduction in weight of the magnet (by 0.8gm to about 0.4gm) would enable a suitable heavier bulb to be used, as described above, without increasing the load on the pivoting fibres.

The other modification suggested is the incorporation of additional resistors in the control box, for the measurement of the solenoid current, the arrangement effectively providing a range switch. Thus the potentiometer could be used approximately over its full range for each gas studied. The values of the resistors could be calibrated with the potentiometer, but provided that during a run on one gas only one combination were used, no calibration would be required in order to obtain values of the virial coefficient, although it would be needed for intercomparison of runs done on different ranges to obtain values of molecular weights.

USE OF THE DENSITY BALANCE FOR MEASUREMENTS ON MIXTURES

The second compressibility virial coefficient, B_x, of a binary mixture has contributions from three different interactions (molecule type 1 with type 1, type 2 with type 2 and type 1 with type 2), weighted according to the likelihood of their occurrence:

$$B_x = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22} \qquad \text{(VII.2)}$$

where x represents the mole fraction, and the subscripts have the obvious significance.

The determination of B_{12}, the cross interaction virial coefficient is the aim of measurements on mixtures.

For density balance investigations, two (or more) component mixtures in which there is at least one 'sticky' gas present the additional problem of increased uncertainty in the molecular weight which can alter by partition effects. This is a parallel problem to that encountered in the conventional PV methods of uncertainty about the validity of assumptions concerning the number of molecules in the gas phase.

Various methods have been used for the study of mixtures containing 'sticky' components including the Boyle's Law[131-135] method, various differential methods,[124-126,136] measurement of the pressure exerted by a known weight of gas in a known volume[137] and density balances.[41,43] Adsorption corrections may be applied.[136] For accurate work on mixtures where adsorption is unlikely to introduce large errors, and so may be corrected for, the Burnett method has been used.[57,138] There are three further approaches which may be used for the determination of the interaction virial coefficient, and which have no equivalents in the determination of virial coefficients for pure gases. The volume change on mixing the two components at constant pressure[139-143] or the pressure change on mixing the two components at constant volume[144-146] are both related by simple expressions to the excess virial coefficient, E, defined by equation (V11.3).

$$E = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) \qquad \text{(VII.3)}$$

These methods have usually been used for series of mixtures of such gases as nitrogen, oxygen, carbon dioxide, carbon monoxide, ethylene, argon, hydrogen, helium at temperatures near room temperature, but have been used also for the fifteen binary mixtures of normal alkanes from methane to hexane at 25°, 50°, 75° and 100°C.[144]

Gas-liquid chromatography offers another method for the determination of the interaction virial coefficient.[147-151] It has been used for the study of the interaction between many different hydrocarbons and simple molecules such as nitrogen, carbon dioxide, argon etc. It appears to offer a very useful method for a mixture of a relatively non-volatile component and one sufficiently volatile to be used as a carrier gas.

The increase in vapour pressure of a relatively involatile component, in the liquid[152] or solid phase[153,154] caused by increased pressure of a very much more volatile component, may be related to the second and higher interaction virial coefficients. This method has not been widely used. The phenomenon is important in some industrial systems, for example, it is responsible for the deposition of silica or sodium chloride on turbine blades[153] and the enhanced vapour pressure of lubricating oil in compressed ethylene.[155]

The volume change or pressure change on mixing two components has not been widely used for gases where adsorption could be significant. Nevertheless it might be a very useful method for such gases. It would be possible to arrange the surface and volume of the gas containers to give a first order correction for adsorption, that is, to give zero error, if the mass adsorbed is directly proportional to area and pressure and if the adsorption is reversible and rapid. If such corrections were inadequate, the excess virial coefficient obtained would depend on the starting pressure, so that a series of runs with different starting pressures would enable an extrapolation to be made to zero pressure and so give a value free from adsorption error. Such a procedure would be better than an attempt to extrapolate to zero surface to volume ration because it does not involve different surfaces and the problem of differing ratios of real to apparent surface for different specimens of the same material does not arise.

It would obviously be advantageous to have an entirely different method for measuring the interaction virial coefficient for two component mixtures including 'sticky' gases. Accordingly, some consideration has been given to possible methods of making such measurements with the density balance and manometer, without a major modification to the existing apparatus. Four different methods are suggested:

1. A mixture of the two components could be used in the same way as the pure gases, using a large reservoir of small surface to volume ratio, filling the balance case with a fresh sample for each reading and either removing the sample to a third vessel (for salvage) after each reading, or discarding it. If such a procedure enables the set of samples to be obtained with adequate constancy of composition, a straight line plot of p/i' against p will be obtained with no more scatter than for the pure gases. The value of B_x may be obtained as for pure gases (see Chapter II), and the intercept will give the molecular weight of the mixture, from which the composition may be calculated with adequate accuracy to obtain the interaction virial coefficient, (B_{12}), from the virial coefficient of the mixture, B_x, using equation (VII.2) and taking values for the two components from the literature or previous measurements.

2. The balance case could be filled from separate containers for each different pressure. The containers would have surfact to volume ratios equal to that of the balance case, and volumes such that when each container was filled to the same initial pressure, opening the containers to the balance case would give a series of suitable pressures. The separate containers would be

connected to each other for filling, and to allow the composition of the mixture to become the same in each. This interconnection would be made using greaseless taps, which would be closed prior to the run. It can be shown that if the same materials are used for the reservoirs and balance case such an arrangement would give first order correction for composition changes caused by adsorption on the walls of the balance case (partition) and so might give better constancy of composition than 1. The interaction virial coefficient would be obtained as above.

3. The balance now has a sufficiently stable zero to enable a series of measurements to be made between vacuum readings. Advantage would be taken of this by either of the following proposals. The balance case would be filled with a mixture to the highest pressure to be used. Two (or more) vessels, which could be evacuated, made from the same material as, and having the same surface to volume ratio as, the balance case would be provided, into which the gas in the balance case would be expanded successively to give a series of suitable pressures. The interaction virial coefficient would be obtained as above. The principal drawback to this method is that composition changes would not be immediately obvious from the p/i' plot, and so there would be the possibility of deducing incorrect virial coefficients without warning if such changes occurred.

4. The mixture, or a series of mixtures, might be made up actually in the balance case. The case would be filled first with one component and the null current and pressure read; the second component would then be added and null current and pressure again read after mixing was completed. The null current values can be used to find the mole fractions of the components actually in the gas phase by the relationship:

$$x_1 = d_1 M_2 / M_1 d_x - d_1(M_1 - M_2) \qquad \text{(VII.4)}$$

in the obvious notation. Thus, if the molecular weights of the two components are known the molecular weight of the mixture may be calculated, and its virial coefficient, B_x, can then be obtained from M_x, p_x and d_x according to the simple balance expression, equation (VII.7).

If a series of readings are taken by adding successive amounts of the second component, then the reliance on knowledge of the molecular weights of the two components can be eliminated.

From the virial expansion of density in powers of the pressure, taking terms to the second:

$$d_x = \frac{M_x p_x}{RT + B_x p_x} \qquad \text{(VII.5)}$$

and by definition:

$$x_1 = d_1 M_x / d_x M_1 \qquad \text{(VII.6)}$$

From equation (VII.5):

$$B_x = M_x/d_x - RT/p_x \qquad (VII.7)$$

Substituting from equation (VII.6) into (VII.7):

$$B_x = x_1M_1/d_1 - RT/p_x \qquad (VII.8)$$

From the definition of the excess virial coefficient, E, in equation (VII.3):

$$B_x = - 2x_1^2E + 2x_1(B_{12} - B_{22}) + B_{22} \qquad (VII.9)$$

And substituting equation (VII.9) into equation (VII.8) gives on rearrangement:

$$\frac{1}{x_1}\left[\frac{RT}{p_x} + B_{22}\right] = M_1/d_1 - 2(B_{12} - B_{22}) + 2Ex_1 \quad (VII.10)$$

Therefore, B_{12} can be obtained from the slope of a plot of $\frac{1}{x_1}\left[\frac{RT}{p_x} + B_{22}\right]$ versus x_1. The successful use of this method would depend on there being complete mixing in a relatively short time, on the volume of sytem remaining constant and on the constancy of the number of molecules of the first component in the gas phase. The last fact means that if only one of the two component is a 'sticky' gas it should be used as the second gas; if both are 'sticky' then some considerable time would be required for the first component to attain adsorption equilibrium.

The relative practical merits of these four possibilities could only be satisfactorily assessed experimentally. There has not been time to try such a programme, but it would seem to be worthwhile to have some information about any of these four methods for measuring interaction virial coefficients in mixtures involving 'sticky' components.

POSSIBLE FUTURE DEVELOPMENTS

With the detail improvements suggested earlier, the density balance should provide a method for obtaining second compressibility virial coefficients accurate to 1 or 2$cm^3 mole^{-1}$ from measurements in the pressure range 10 to 50cm Hg.

The first objective in the development of the apparatus should be to enable measurements to be made over a much wider temperature range. The importance of having experimental results for the second virial coefficient at low and high temperatures has been pointed out in a number of papers[36,55,56] and emphasised recently by Klein and Hanley.[156] They stress that within the range $2 < T_r < 10$, where $T_r = kT/\varepsilon$, and ε is the value obtained from a fit to the Lennard-Jones 12-6 potential, one can learn little about the relative merits of different potential functions by fitting to to the experimental data. The accurate determination of the second virial coefficient at low reduced temperatures is complicated both by adsorption and the reduced pressure range available.[55-57] The density balance, however, is particularly suitable for operation under these conditions, so the obvious development would be to extend the temperature range available to lower temperatures. This is not to preclude the use of a density balance at higher temperatures; intrinsically there is nothing to prevent the use of a suitable electromagnetic balance at temperatures up to the limit imposed by the constructional materials. However, the extension of the range of the present apparatus to lower temperatures would be more easily accomplished, and it might even be possible to do this simply by using a suitable low temperature thermostatted supply tank in place of the present water supply tank.

If such a development were to be made it would be valuable to increase the accuracy of the method further for a given pressure range, or to enable the presently available accuracy to be obtained from measurements over a smaller pressure range. The major source of error at present is in the pressure measurements. This could be improved by an order of magnitude, with the probability of increasing the accuracy of the measured virial coefficient by the same amount, by replacing the existing manometric arrangement with one similar to that described by Weir et al.[56] which uses mercury columns of much larger cross section, thus eliminating significant capillary depression, and has a more accurate optical method for determining the mercury level. Alternatively, a density balance in conjunction with a separator might be used for measuring pressure, by using a gas of known virial coefficient. This could also offer a means for automating the pressure readings. Such a method has been used with a commercial recording vacuum microbalance[81] with lower accuracy than that required in this context. A density balance similar to the one described in this thesis could be used, but would probably not be the best design for this specialised application. A balance for measuring pressure would be used at or near room temperature with a gas which would not be adsorbed to a significant extent. A galvanometer type of electromagnetic compensation with its greater insensitivity to level changes and external stray magnetic fields would probably have advantages over the magnet in solenoid arrangement. It might be possible to alter one of the commercial balances[96,100-102] to give the range required while retaining the automatic nulling.

If an automatic pressure reading device were available, and if it were possible to make the density balance automatically nulling, readings on the 'stickier' gases would be more readily made. For these gases there may be a considerable delay after the introduction of the gas before the pressure is stable enough for measurement, even by the technique outlined in Chapter V. With automatic nulling equipment, and a suitable recording device it would be possible to read off the measured density and pressure at the same instant. The ratio p/i'

should become constant after attainment of thermal equilibrium (and this could be followed) and so the time necessary for a measurement would be considerably reduced.

There would also be incidental advantages: operator fatigue and reading error would be eliminated (a major consideration); more points could be conveniently obtained for the p/i' plot and the line better defined; with mixtures the rate of mixing, or any composition change with time, depending on how the mixture was investigated, could be readily observed.

So far, the density balance has been considered as operating in the pressure range where the second virial coefficient is the only significant one, that is, at pressures up to 1 atmosphere. In many cases it would be possible to measure the second and higher virial coefficients with a balance operating over a wider pressure range. Where this is possible the values of the second virial coefficient obtained from a suitable polynomial fit to the data should be more accurate, if the ratio of accuracy to range remains constant. Alternatively, a balance of relatively lower accuracy could give a second virial coefficient of the same accuracy. One such all-metal balance which could operate at pressures up to about 37 atmospheres has been described,[52] but this seems to be the only one reported.

A particular application of such a balance would be an extension of an earlier method for the measurement of the second dielectric virial coefficient. Buckingham and Raab[34] attempted to use a deflection density balance of relatively low sensitivity for the measurement of gas density at the same time as its total polarisation was measured and so to obtain the second dielectric virial coefficient from equation (VII.11).

$$ {}_{T}P = \frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{M}{d} = \mathcal{A} + \mathcal{B}\frac{d}{M} + \mathcal{C}\left(\frac{d}{M}\right)^{2} + \ldots\ldots \qquad \text{(VII.11)} $$

where ε is the static dielectric constant of the gas. The accuracy of their results was, however, diminished by the low precision of their balance.

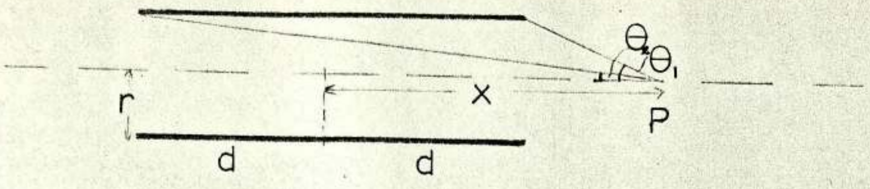
By using a more sensitive balance able to measure the density of gases at pressures up to a few atmospheres, and a gas dielectric constant measuring side similar to that of Barnes[44] or Cole and co-workers,[40,157-160] it should be possible to obtain meaningful dielectric virial coefficients for the 'stickier' gases. The limitations might then be imposed by adsorption on the plates of the dielectric cell causing errors in the measured dielectric constant of the gas. This could probably be overcome by using a cell with two sets of plates each having different plate separations. It would then be possible to eliminate the effect due to the adsorbed layer from separate readings for the two sets, effectively by extrapolation to infinite plate separation.

Finally, it may be recalled that the electromagnetic balance which is used here for the comparison of densities is very similar in capacity and sensitivity to balances used for sorption, magnetic susceptibility and other studies. However, it has a range which, relative to its sensitivity, is larger by one or more orders of magnitude. It seems likely, therefore, that among the applications of such a balance are various studies in these and related fields.[62]

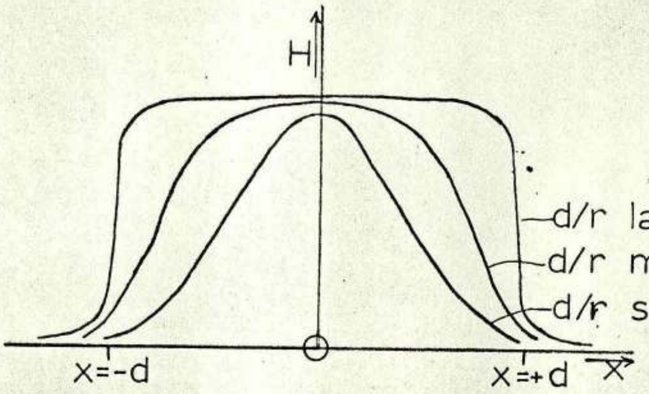
ADVANTAGES AND DISADVANTAGES OF THE DENSITY BALANCE METHOD

The single major advantage of the density balance over the conventional PV methods for the precise evaluation of gas densities is that adsorption effects can be eliminated. The major disadvantage is the dependence on either accurate knowledge of molecular weights or at least on considerably greater constancy of molecular weight than is necessary for the PV methods. A lesser disadvantage is that there is as yet no practicable differential density balance for determining directly and accurately the difference in or ratio of the densities of two gases. The limitations which this imposes are less important because of the availability of the stable wide-range balance described in this thesis.

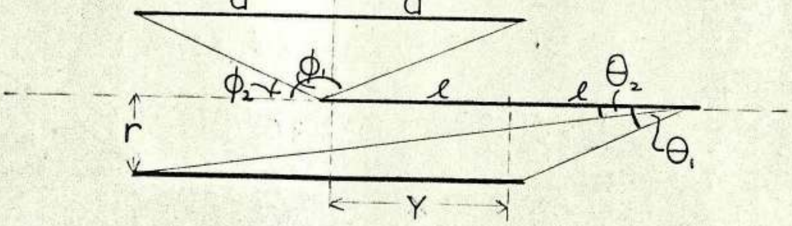
(a)


θ_2
θ_1
r
x
P
d
d

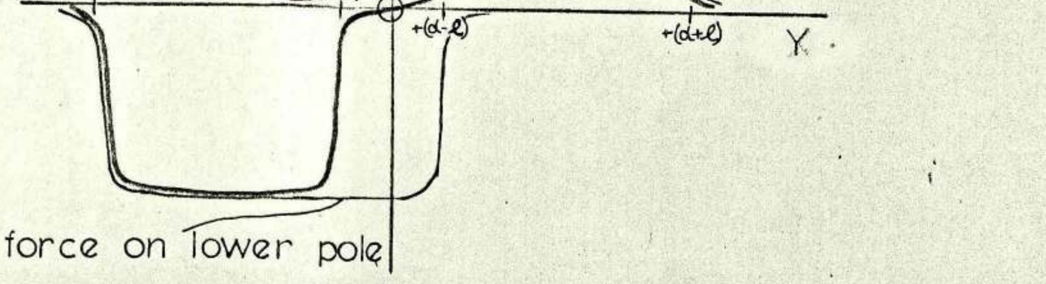
(b)


H
d/r large
d/r medium
d/r small
O
x=-d
x=+d
x

(c)


d
d
ϕ_1
ϕ_2
ℓ
ℓ
θ_2
θ_1
r
Y

(d)


F
force on top pole
resultant force
-(d+ℓ)
-(d-ℓ)
O
+(d-ℓ)
+(d+ℓ)
Y
force on lower pole

APPENDIX I

THE INTERACTION OF MAGNET AND SOLENOID

The field at a point P on the axis of a solenoid and distance x from the centre of the solenoid is given by:[109]

$$H = \frac{2\pi nI}{10}(\cos\theta_2 - \cos\theta_1)$$

where the angles are defined in figure (a), H is in oersteds, I is in amps, and n is turns/cm. The form of this function is shown in figure (b) for different ratios of solenoid length to radius.

The force on a magnet lying along the axis of a solenoid is then given by:

$$F = \frac{m2\pi nI}{10}(\cos\phi_2 - \cos\phi_1 - \cos\theta_2 + \cos\theta_1)$$

where the angles are defined in figure (c), F is in dynes, m is the pole strength in unit poles, the length of the magnet is 2ℓ and of the solenoid 2d, and y is the distance between the centres of the magnet and solenoid.

There are two requirements for the satisfactory performance of the electromagnetic compensation:

1. The force on the magnet should be directly proportional to the current flowing in the solenoid.

2. For the deflection sensitivity of the balance to be independent of the current in the solenoid, the force on the magnet for a given current in the solenoid should be independent of small displacements of the magnet along the solenoid axis.

The first requirement is seen to be met if the geometry of the system, the magnet pole strength and the number of turns per centimetre of the solenoid are constant.

The conditions under which the second requirement is met are best seen from figure (d), by considering the total force on the magnet as the sum of the forces on the two poles. It can be seen that the regions of approximately constant forces are for $-(d+\ell) < y < -(d-\ell)$ and $(d-\ell) < y < (d+\ell)$. From figure (b) it can be seen for the field in the centre of a solenoid to be as constant as possible, that d/r should be large. Furthermore, from figure (d), ℓ should have a value near the value of d to make the plateau as long and hence as flat as possible. The dimensions used were $2r = 0.75$cm, $2\ell = 5$cm, $2d = 6.5$cm. Calculation showed that at the position of the maximum force and for the largest currents used, the force changed by 1 part in 20,000 per 0.1cm of displacement. As a result of this the deflection sensitivity of the balance changes by about 10% over the current range used, that is from 50micro-volt per eyepiece division at zero current to 55micro-volt per eyepiece division at the highest current.

APPENDIX II

CONTRACTION OF A THIN SPHERICAL BULB WITH INCREASING PRESSURE

The radial strain, ϵ_r, at a point distant r from the centre of a spherical shell of internal radius a and external radius b ($a < r < b$) due to an internal pressure of p_0 and external pressure p_1 is given by:

$$\epsilon_r = \frac{p_0\frac{a^3}{b^3} - p_1}{(3\lambda_e + 2\mu_e)\left(1 - \frac{a^3}{b^3}\right)} + \frac{(p_0 - p_1)\,a^3}{4\mu_e\left(1 - \frac{a^3}{b^3}\right)} \cdot \frac{1}{r^3}$$

where $\lambda_e = \frac{E\nu}{(1+\nu)(1-2\nu)}$ and $\mu_e = \frac{E}{2(1+\nu)}$, E = Younge modulus
ν = Poissons ratio

(see, for example, Eringen, Mechanics of Continua, p215
Wiley & Sons, New York, 1967.)

For a thin spherical shell of thickness t(=b-a) this reduces to:

$$\epsilon_r = \frac{(p_0 - p_1)(1-\nu)\,r}{2Et}$$

and so the volumetric strain of the enclosed volume, ϵ_v, is:

$$\epsilon_v = 3\epsilon_r = 3\,\frac{(p_0 - p_1)(1-\nu)\,r}{2Et}$$

The values of E and ν for fused quartz were taken as 10.1×10^6 psi and 0.17 respectively (Thermal Syndicate Ltd. Catalogue, 1958), t was calculated from the weight of the bulb, 0.68gm, less 10% for the weight of the hook, using $2.2\,\mathrm{gm.cm^{-3}}$ for the density of fused quartz, and found to be about 0.01cm. With these values the change of volume with pressure is:

$$\frac{dV}{dp} = -5\times10^{-5}\text{cm}^3 \text{ per cm.Hg}$$

The value of the pressure dependent correction which has to be applied to obtain literature values for the second virial coefficient is about $-43\text{cm}^3\text{mole}^{-1}$ at 40°C. This correction factor may be shown to be equal to $\frac{RT}{V}\frac{dV}{dp}$, and therefore experimentally,

$$\frac{dV}{dp} = -31\times10^{-5}\text{cm}^3 \text{ per cm Hg}$$

The discrepancy of less than one order of magnitude between the theoretical and experimental values may be insignificant, or may arise from an additional pressure dependent effect from some other source.

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