PHYSIC~~I~~AL MEASUREMENTS ON (i) SOME BORON-CONTAINING COMPOUNDS AND (ii) SOME AQUEOUS INORGANIC IONS

A thesis submitted by Peter John Gardner in candidature for
the degree of Doctor of Philosophy of the University of London .

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ABSTRACT (PART I)

The synthesis and stability of dioxaborepan systems have been investigated. These heterocycles are considerably less stable than the dioxaborinan and dioxaborolan analogues. The thermal stability of some bisdichloroborinates and derived esters has been studied and a mechanism for the disproportionation is discussed. The association in the solution phase of some inan and olan heterocycles was investigated cryoscopically. Associative models are proposed and discussed. B-chloro derivatives of the above systems have been studied thermochemically in solution and relevant enthalpies of formation and hydrolysis derived. Data on the heat of solution of some diols is also reported.

The accuracy of the calorimetric procedure was checked by the measurement of the heat of solution of an ionic thermochemical standard. This type of measurement was extended to other ionic systems and other thermodynamic functions derived. This investigation comprises Part II of this thesis.

ABSTRACT (PART II)

This section is concerned with the determination of lattice energies and related thermodynamic functions of some simple ionic salts of the main groups I and II. Lattice energies are derived principally via the use of empirical correlations between (i) lyotropic number and hydration enthalpy and (ii) anion radius and hydration enthalpy. Interpolated hydration enthalpies are introduced into a simple Born-Haber cycle involving the heat of solution of the salts. The accepted data of Latimer et al. is used for Group I salts and the recent data of Noyes extended to include Group II salts. When sufficient data is available determinations are checked by simple calculation of lattice energy by the method of Kapustinkii. Integral heats of solution for the Group II chlorates have been determined to complete the series of soluble salts of the type $M^{I}XO_3$ and $M^{II}(XO_3)_2$ where X = halogen. An attempt was made to correlate the "effective crystal radius" of non-spherically symmetrical ions with an easily accessible property of the ion (e.g. Pauling radius, partial molal volume).

ACKNOWLEDGEMENTS.

The author wishes to express his indebtedness to the late Dr. A.G. Foster and to Dr. K. Singer who continued as official supervisor to the investigation.

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PART I

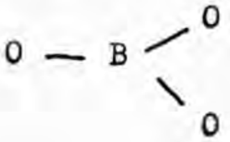
ORGANO-BORON COMPOUNDS

INTRODUCTION

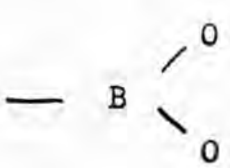
Several reviews exist on organo-boron chemistry; Lappert [1] surveys the literature up to 1956, Gerrard and Lappert [2] (1958) review the action of boron trichoride with organic compounds. These are now superseded by Gerrard's [3] comprehensive book, "The Organic Chemistry of Boron" (1961). One year later Maitlis [4] reviews heterocyclic organo-boron derivatives. It is with the physical properties of simple heterocyclic systems that this thesis is principally conerned.

The nomenclature used here to identify the cyclic systems is : seven-membered rings are epans, six-membered rings are inans and five-membered rings are olans. In American literature[5] these terms are suffixed with an "e" i.e. epane, inane and olane. The nomenclature for acyclic systems is:-

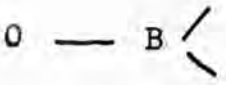
Compounds containing the nucleus



are designated BORATES,



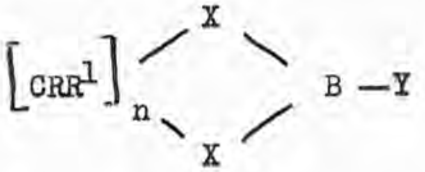
are designated BORONATES,



are designated BORINATES,

The ground state of the boron atom is $1s^22s^22p$ and normally exhibits a trigonal configuration. Because of the vacant $2p_z$ orbital in this state, transformation to the tetrahedral configuration occurs readily. This means that in simple boron-containing compounds where the boron is trigonal, the structure is susceptible to nucleophilic attack or will act as a Lewis acid. The electron deficiency on the boron atom may be internally satisfied as in the mesomeric stabilization of boric acid and tri-alkyl borates[6]. The Lewis acidity of the boron is reduced to such an extent in alkyl borates that only tri-methyl borate forms stable amine complexes;[59] in the higher homologues the steric factor outweighs the remaining Lewis acid strength. Triaryl borates, however, complex[64] readily because of the interaction of the π- electrons with the oxygen lone pairs. As would be expected, tri-alkyl boranes are less stable[7] than the corresponding borates and complex easily with Lewis bases. The qualitative assessment of the lability of a boron atom in terms of its immediate electron density and its steric environment (by no means independent factors) is further complicated if the boron is a hetero-atom in a cyclic system. One must now also consider the reactivity of the boron atom in terms of ring-strain (or cyclisation energy). This thesis is primarily concerned with putting this assessment on a quantitative basis.

The heterocycles considered were of the following general formula

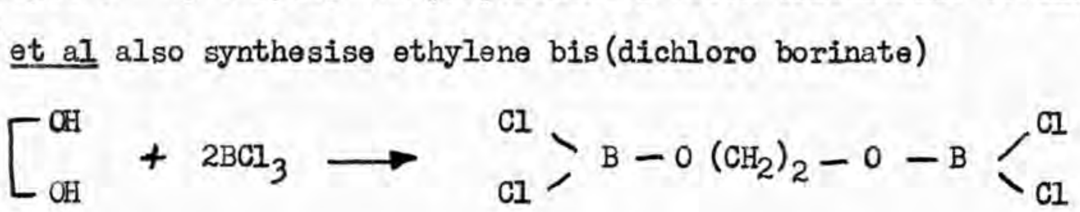


n = 2, 3, 4
X = O, S
R,R^1 = H or Me
Y = Cl, ϕ, O alkyl

The first systematic study of the chloroborolan nucleus (n = 2, X = O, Y = Cl) was undertaken by Blau[8,9] et al. The compound, 2-chloro-1,3,2 dioxaborolan, synthesised by condensing equimolar proportions of ethan 1,2 diol and boron trichloride, has markedly different properties from its acyclic analogue, methyl chlorboronate[10]. Whereas the acyclic compound is a volatile, unstable mobile liquid disproportionating readily via the reaction

$$3(Meo)_2BCl \rightleftharpoons 2(RO)_3B + BCl_3$$

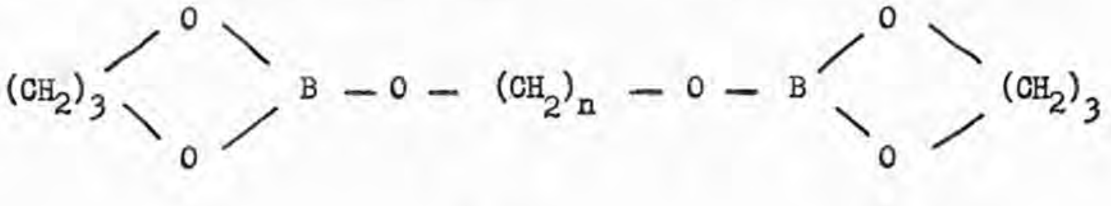
the cyclic system is a high boiling, relatively stable syrup. It is remarkable that such drastic changes in physical properties derive from such a minor change in structure. The chlorine in the heterocycle has the normal reactivity associated with the B - Cl link and readily undergoes alcoholysis. By varying the proportion of boron trichloride to diol Blau[9] et al also synthesise ethylene bis(dichloro borinate)



$$(CH_2OH)_2 + 2BCl_3 \longrightarrow Cl_2B-O(CH_2)_2-O-BCl_2$$

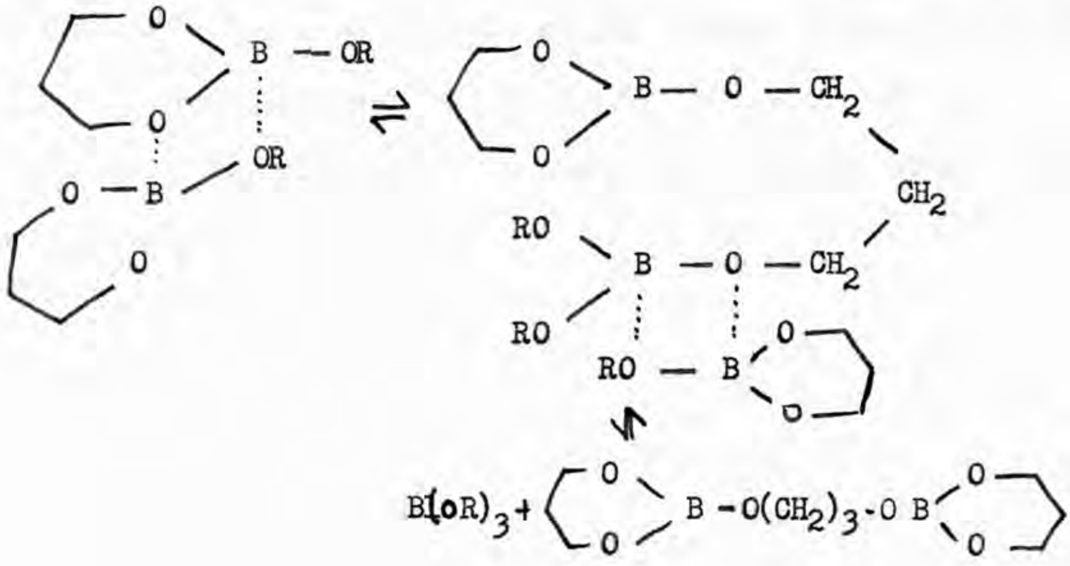
and derived esters. The stability of this class of compound will be discussed later.

The corresponding inan analogue 2-chloro-1,3,2 dioxaborinan was synthesised and characterised by Finch[11] et al. This compound is unstable compared with olan, darkening rapidly at room temperature. However it is considerably easier to handle due to its fluidity. The mechanism of the pyrolysis was studied by the above authors and several derivatives including tris (diol) diborates prepared

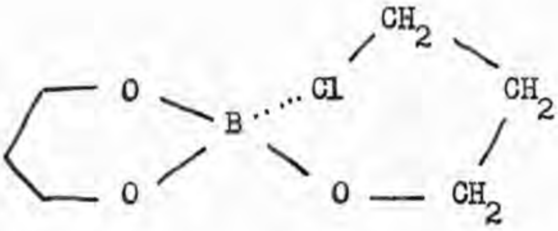


$n = 2, 3$

Cyclic systems containing the BCl link are often characterised by formation of the cyclic ester (containing $\rangle B - OR$). The stability of the esters shows marked dependence on the nature of the alkyl group. For example, if the synthesis of 2-methoxy-1,3,2 dioxaborinan is attempted, on distillation the ester disproportionates into tris(1,3 diol) diborate and trimethyl borate[12]. It is suggested that the disproportionation proceeds via a B—O four centre interaction, the initial four centre approach always being between an endo-cyclic and an exo-cyclic B – O bond,



The stability of the ester towards disproportionation bears a direct relationship to the bulk of the alkoxy substituent, the sequence being $Me < Et < Pr < Bu^n < Cl.(CH_2)_2 < Cl(CH_2)_3$, in increasing order of stability. The last two cases are interesting and it is proposed that this enhanced stability is due to back-co-ordination of the chlorine atom[13]



The boron atom in this structure is tetrahedrally coördinated and therefore reluctant to form part of a four-centre complex. This point is mentioned because when attempts to synthesise a new cyclic series (the epans), by the usual procedure, failed, the 2-chloroethyl esters might be expected to prove stable.

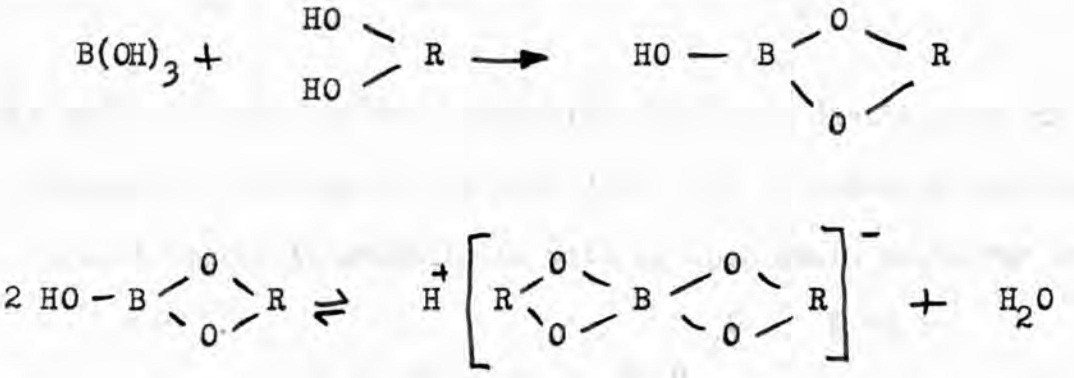
Brotherton and McCloskey[14] have synthesised several olan and inan heterocycles and report molecular weight data obtained cryoscopically in benzene. They also note the highly viscous nature of 2-chloro-1,3,2 dioxa-borolan and propose that it is highly associated in the pure phase. The degree of association of the compounds they studied are presented in the table below.

TABLE I : MOLECULAR WEIGHT DATA OF SOME OLANS AND INANS IN BENZENE

Compound	Concn.	Degree of assn.
	(moles/litre based on monomer)	
2-chloro-1,3,2 dioxaborinan	0.27	1.03
2-n butoxy-1,3,2 dioxaborinan	0.14	1.03
2-chloro-1,3,2 dioxaborolan	0.36	1.96
2-n-butoxy-1,3,2 dioxaborolan	0.17	1.27
2-dimethylamino-1,3,2 dioxaborolan	0.33	1.01

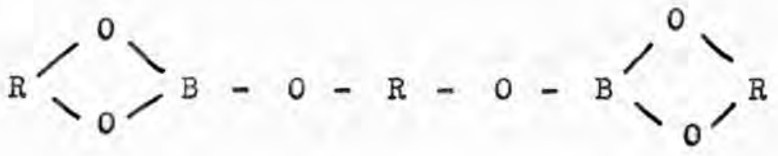
These data, although useful, are quoted at isolated concentrations and do not yield a full picture of the physical state of the compounds in solution.

In 1949 Böeseken[15] reported the effect of the addition of certain diols on the conductivity of boric acid solutions. He found, in general, that 1,2 diols had little effect on the conductivity whereas 1,3 diols increase the conductivity appreciably. This forms the basis of the usual method for estimating boric acid volumetrically. Rippere and La Mer[16] propose the following reaction scheme

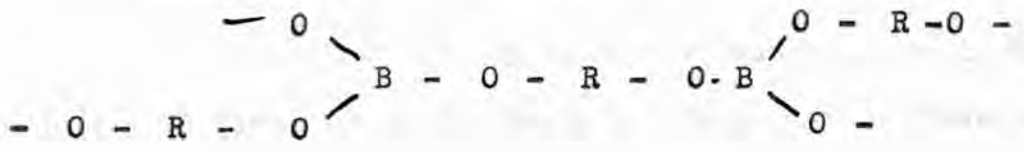


The work of Boeseken initiated a systematic study by Dale et al.[17]

on the relative stabilities of boric esters of 1,2 and 1,3 diols. The stability of the cyclic system is studied by obtaining an estimate of the Lewis acidity of the boron atom by measuring the heat of complexing of the heterocycle with a Lewis base (in this case, benzylamine and pyrrolidine). They find that the heat of complexing for olan rings is, in general, an order of magnitude higher than that for inan rings. This is interpreted as evidence of an inherent strain in a five-membered ring containing a trigonal boron. By implication, it is deduced that in a six-membered ring there is little or no change in strain on the transposition of a trigonal boron to the tetrahedral configuration. This is confirmed by a competitive cyclisation reaction. A mixture of one mole of ethan 1,2 diol and one mole of propan 1,3 diol was esterified with boric acid. It was found that the mixed ester of propan 1,3 diol formed preferentially. Evidence for differences in ring strain in the diborate structure was also outlined. Tris (1,3 diol) diborates are easily distillable stable liquids and are assigned the structure



The corresponding 1,2 diol diborates are often distillable but become viscous or glass-like on condensation. It is probable that the cyclic structure exists in equilibrium with an open chain polymeric structure

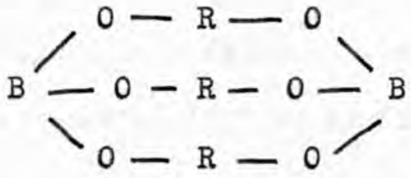


Several diborates were synthesised by Dale and is co-workers, the physical state being dependent, in the olan system, on the extent of substitution in the parent diol.

TABLE II : PHYSICAL STATE OF SOME TRIS DIOL DIBORATES

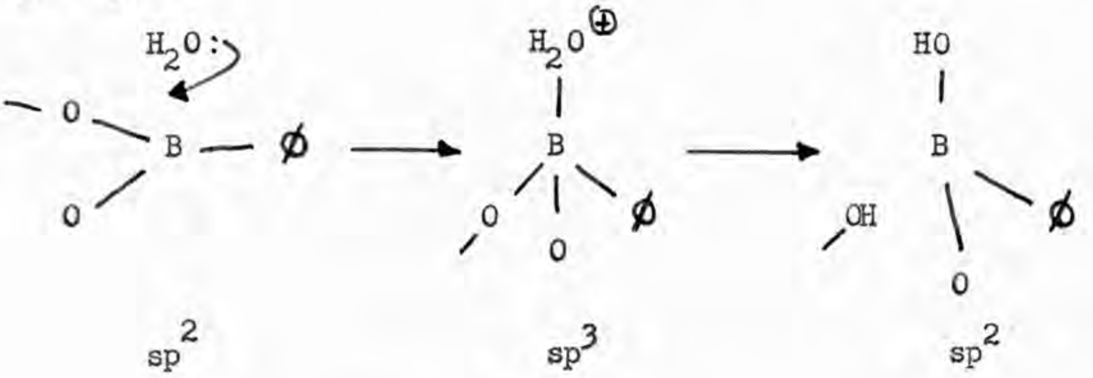
Parent diol	State
HO $(CH_2)_3$ OH	Liquid
HO $(CH_2)_2$ OH	Glass
HO CHMe CH_2O H	Gelatinous liquid
HO CHMe CHMe OH (meso)	Very viscous liquid.

It is interesting to observe that these workers were unable to isolate simple mixed 1,4 diol esters or tris (1,4 diol) diborates. They also reject the cage structure of Dupire[18] for diborates



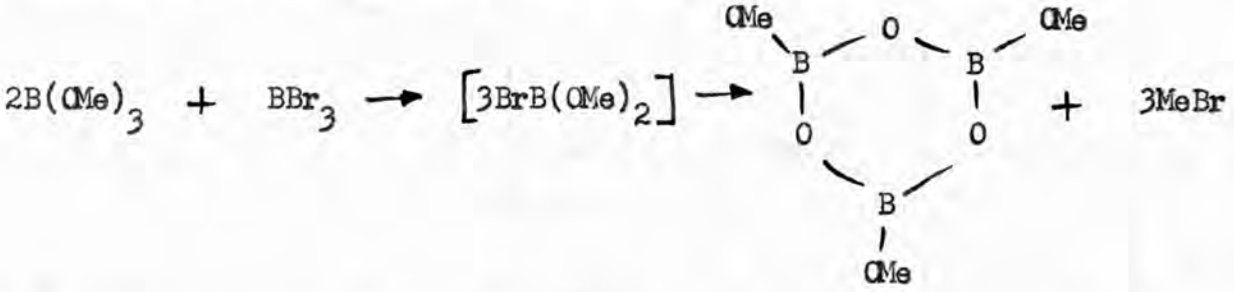
This structure is impossible for 1,2 and 1,3 diol diborates on steric grounds and unlikely for 1,4 diol diborates. Their attempted synthesis of the simple 1,4 diol derivatives presumably resulted in the open chain polymeric structure illustrated above.

The enhancement of stability with respect to polymerisation of the diborate structures by successive substitution in the parent diol has been studied recently by Bowie and Musgrave[43]. These authors investigate the stability towards hydrolysis of a series of phenyl boronates derived from (1, n) diols (n = 2,3,4,5,6). In general, phenyl boronates are more stable compounds than the corresponding "alkoxy boronates" (i.e. borates) possibly due to $p_z - \pi$ overlap. For example 2-phenyl-1,3,2 dioxaborepan is an established compound[60]. Musgrave finds that phenyl boronates containing 8- or 9- membered rings (derived from pentan 1,5 diol and hexan 1,6 diol respectively) could not be characterised. They probably exist in the polymeric form suggested by Dale[17]. The stability of the other phenyl boronates was measured by the rate at which they absorb water from moisture-saturated air at constant temperature (the fact that the liberated diol is itself hygroscopic was accounted for by a series of control experiments). The rate at which the derivatives absorb moisture depends both on the size of the heterocyclic ring and the extent of substitution in the aliphatic part of the ring. For example, 2-phenyl-1,3,2 dioxa borolan is hydrolysed rapidly but on methyl substitution of the ring, hydrolysis falls to the extent that the $3,3^1,4$-trimethyl and $3,3^1,44^1$-tetramethyl derivatives are completely stable to aqueous hydrolysis. The inan phenylboronates are far more resistant to hydrolysis, the simplest homologue, 2-phenyl-1,3,2, dioxaborinan, being the only structure which absorbs moisture to any extent. The seven-membered heterocycles are all hydrolysed rapidly; the $4,4^1,7,7^1$ tetramethyl derivative having a slower moisture uptake than the butan 1,4 diol derivative but not appreciably stabilized by ring substitution. The explanation of these observations is based on the opposing effects of the relief of strain in the ring and induced steric interaction during conversion of the boron atom from sp^2 to sp^3, this being the precursor to hydrolysis



In the case of the olan system the inherent strain in the ring is relieved by coördination of water to the boron atom. Because of this change in configuration at the boron atom, the steric interaction between the C - H bonds and the oxygen lone-pairs increases. The energy lost by virtue of this increased steric hindrance is, however, less than that gained by loss of ring-strain as the boron becomes tetrahedral. The introduction of methyl groups to the ring causes, via a combination of increased steric interaction between C - CH_3 bonds with the oxygen lone-pairs and an inductive effect stabilizing the B - O bond, the energy gained on relief of ring strain to be a secondary factor. Therefore these substituted systems are resistant to hydrolysis. Coordination of water to the boron in the strain-free inan-skeleton is hindered by the axial interaction of the oxygen lone pairs with the phenyl group. These phenyl boronates hydrolyse slowly and the introduction of one methyl group into rings induces complete hydrolytic stability. Because of the flexibility of the epan skeleton there is little obstruction to coördination of water and little resulting steric interaction so, in general, these systems hydrolyse readily.

In 1955 Goubeau[19] et al. report attempts to synthesise methyl esters of mono- and di-bromo boric acid. Although they were unable to isolate these esters, their general comments on the stability of halogenated esters, in terms of associated forms, proves interesting. Attempts to synthesise methyl bromoborinate yielded a substance with the composition B_3O_4Br (structure uncertain), methyl bromide and hydrogen bromide. It is possible that methyl bromoboronate exists at low temperatures, but at ambient temperature the following decomposition was observed:



Of the corresponding halogen compounds, methyl chloroborinate and chloroboronate may be prepared although they disproportionate on distillation.

$$2BCl_3 + B(OMe)_3 \longrightarrow 3Cl_2BOMe$$

$$2Cl_2BOMe \rightleftharpoons ClB(OMe)_2 + BCl_3$$

$$3ClB(OMe)_2 \rightleftharpoons 2B(OMe)_3 + BCl_3$$

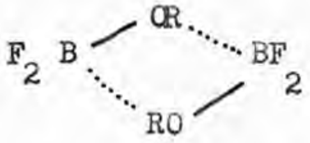
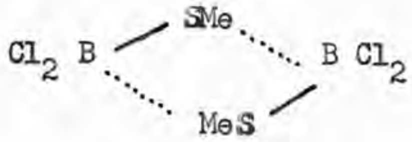
and methyl fluoro borinate is a stable compound although methyl fluoroboronate disproportionates readily.

$$2FB(OMe)_2 \rightleftharpoons F_2B(OMe) + B(OMe)_3$$

Goubeau compares the stability of compounds of the type (halogen)$_2$B(XR$_n$) where X = O,N,S with the electronegativity difference between X and the halogen (electronegativities on a Pauling scale). This is shown in the table below.

TABLE III : DIMERISATION, STABILITY AND ELECTRONEGATIVITY DIFFERENCE IN (XR$_n$)B(Hal.)$_2$

Halogen / XR$_n$	F	CI	Br	I
- OMe	+ 0.5 dimer	- 0.5 monomer	- 0.7 unstable	- 1.0
- NMe$_2$	+ 1.0 dimer	0.0 dimer	- 0.2	- 0.5
- SCH$_3$	+ 1.5	0.5 dimer	+ 0.3	0.0

From the table it may be seen, in a very general way, that as the electronegativity difference (defined by $\Delta x = x_x - x_{hal.}$) becomes more positive compounds increase in thermal stability and are more likely to exist in dimeric form. As Δ x becomes negative the compounds are not usually isolable at ambient temperature. Also when dimeric forms exist, the more electropositive component acts as the bridging group eg.  and 

Between 1952 and 1955, Skinner[20-24] et al. published a series of papers on the thermochemistry of simple organo-boron compounds. The compounds studied were of the type $(RO)_3B$, $Bu^n{}_3B$, $Bu^n_2\ BX$ (X = Cl,Br,I), $B(NMe_2)_n\ Cl_{3-n}$, and $B(OEt)_n\ Cl_{3n}$ (n=1,2,3). The final two groups of compounds were studied to investigate the extent to which different groups "back-coördinate" to boron. In the case of the trialkyl borates the standard heats of solution (in water) and formation of the hydrolysis products (i.e. H_3BO_3 and ROH) are known so it is possible to derive the heats of formation of the trialkyl borates. They also attempt to evaluate the mean bond dissociation energy of the boron-oxygen bond in these systems. This function is given by

$$\bar{D}\ (B-O) = 1/3\left[D_1 + D_2 + D_3\right]$$

where D_1, D_2 and D_3 are the individual bond dissociation energies of the processes

$$\left.\begin{aligned} B(OR)_3 &\longrightarrow B(OR)_2 + OR & \Delta H_1 &= D_1 \\ B(OR)_2 &\longrightarrow B(OR) + OR & \Delta H_2 &= D_2 \\ B(OR) &\longrightarrow B + OR & \Delta H_3 &= D_3 \end{aligned}\right)\ \text{All components in the gas phase}$$

$$\therefore\ D_1 + D_2 + D_3 = \Delta H^o_f\ B\ (g) + 3\Delta H^o_f\ OR(g) - \Delta H^o_f\ R_3BO_3(g)$$

The term ΔH_f^o OR(g) was estimated from the bond dissociation energies in alcohols and from thermal data on the decomposition of alkyl nitrates and nitrites,

$$R = Bu^t; \qquad ROH(g) \longrightarrow RO(g) + H(g) \qquad \Delta H = D\ (RO - H)$$

$$R = Et, Me \quad \left(\begin{array}{l} RO.NO(g) \longrightarrow RO(g) + NO(g) \\ \\ RO.NO_2(g) \longrightarrow RO(g) + NO_2(g) \end{array} \right.$$

The estimation is only accurate to a few kilocalories and the final estimate of the B - O bond dissociation energies in trialkyl borates is 110 ± 5 kcal/mole. In this calculation Skinner et al use the value for ΔH_f^o B(g) quoted by N.B.S. Circ. 500[25] of 97.2 kcal/mole. A more recent (1957) value for this figure of 139 kcal/mole[26] raises Skinner's estimate for $\bar{D}$ (B - O) to 124 ± 5 kcal/mole. However the heat of sublimation of boron can still not be regarded as unequivocably assigned.

The di-n-butyl boron halides were prepared via

$$B\ Bu_3^n + HX \longrightarrow B\ Bu_2^n\ X + n - C_4H_{10}$$

and all except the iodide were obtained pure (the iodide has a similar volatility to Bu_3B and could only be separated 90 - 95% pure). This reaction was studied thermochemically and the heat of hydrolysis of the product also measured:

$$Bu_2\ BX\ (liq) + (n+1)H_2O\ (liq) \longrightarrow Bu_2\ BOH\ (liq) + HX.nH_2O\ (soln.)$$

Dibutyl boronic acid is a sparingly soluble oil which undergoes aerial oxidation - these reactions are therefore carried out under an inert atmosphere. Assuming that the dissociation energy D (Bu_2B - Cl) is the same as the mean bond dissociation energy, $\bar{D}$ (B - Cl), in

BCl_3, combination of the enthalpy changes in the above reactions with standard data yields

$$D\ (Bu_2B - OH) = 132 \qquad D\ (Bu_2B - Cl) = 108$$

$$D\ (Bu_2B - Br) = 89 \qquad D\ (Bu_2B - I) = 70$$

(all values in kcal./mole and corrected for the new value of

$\Delta H^{o}_{f}\ B(g)$)

Although the absolute values of these bond dissociation energies depend on the initial assumption, the bond energy differences are established. By studying the acid hydrolysis of tris dimethylaminoborine thermochemically

$$B(NMe_2)_3 + 3HCl + 3H_2O \longrightarrow H_3BO_3 + 3Me_2\overset{+}{N}H_2\overset{-}{Cl}$$

and assuming $\Delta H^{o}_{f}\ NMe_2(g)$ may be deduced from data on $D(H - NMe_2)$, Skinner is able to estimate $\bar{D}\ (B - NMe_2)$. He then compares values of bond dissociation energies for the coördinate and covalent B - X linkage; for example $\bar{D}\ (B - NMe_2)$ in $B(NMe_2)_3$ and $D(Me_3B \longleftarrow NHMe_2)$. In general for both X = O and N the covalent linkage is an order of magnitude greater than the corresponding dative link.

It is, in effect, the thermoneutrality assumption which Skinner investigates in the final two papers of the series. This assumption is that the enthalpy change in a redistribution reaction is zero. A redistribution reaction is one in which bonds may change their relative position but not their total number or formal character. It is this assumption which is implicit in applying a bond dissociation energy from one molecule to another of similar formal structure. For example in the series $B(NMe_2)_n Cl_{3-n}$ the bond dissociation energies of B - N and B - Cl should remain constant within the series. By investigating the heat of hydrolysis of this series of compounds and the similar series $B(OEt)_n Cl_{3-n}$, Skinner shows that this assumption is not upheld. This is ascribed to different degrees of back coördination of nitrogen, oxygen and chlorine to the boron atom, i.e. the superimposition of π-bonding to the vacant $2p_z$ orbital on the boron over the normal B - X σ-bonding. By establishing the standard enthalpies of formation of the compounds comprising the two series in the gas phase the enthalpy changes involved in the redistribution reactions may be deduced, e.g. Skinner finds

$$2/_3 \ BCl_3(g) + 1/_3 \ B(OEt)_3(g) \longrightarrow BCl_2OEt(g) \quad \Delta Hr = -4.8$$

$$1/_3 \ BCl_3(g) + 2/_3 \ B(OEt)_3(g) \longrightarrow BCl(OEt)_2(g) \quad \Delta Hr = -4.0$$

The stabilization energy derived from π -bonding is also derived from a molecular orbital treatment of six electrons extending over four atoms in a plane. The localized reference system is when the $2p_z$ boron orbital is vacant and the P_z^2 pairs are localized on the nitrogen and/or chlorine atoms (in the case of the series $B(NMe_2)_n Cl_{3-n}$). The stabilization obtained on delocalizing the three pairs of P_z^2 electrons is derived by standard M.O. methods beyond the scope of this thesis. Skinner finds that the order of effectiveness of back-coördination is

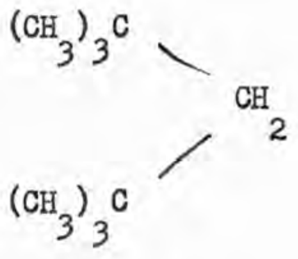
$$N > O \gg Cl$$

This order is correlated with the strengths of the coördinate links between BF_3 and Lewis bases containing the above atoms.

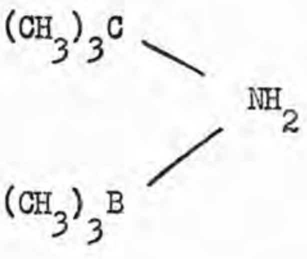
$D(Me_3N \rightarrow BF_3)$ is approx. 28 kcal/mole,

$D(Et_2O \rightarrow BF_3)$ is approx. 12 kcal/mole, and alkyl chlorides show no tendency to complex with BF_3 at all. It is important to realize that this treatment of redistribution energies assumes that the energy is attributed entirely to back-coördination and this is clearly an over-simplication of the problem because it ignores all steric factors (between, for example, the $-NMe_2$ groups in $ClB(NMe_2)_2$).

The influence of steric factors on the stability of Lewis acid-base complexes has been extensively investigated by Brown and his collaborators. Brown[27] has synthesised a series of complexes of the type $Me_3B.RNH_2$ (where R = H, Me, Et, i-Pr, s-Bu, t-Bu) and assessed by stability of the complexes by measuring the rate of change of vapour pressure above the complex at constant temperature in a high vacuum line. In this way the strain inherent in a particular structure may be deduced and this strain is then ascribed to similar organic structures (homomorphs) e.g. the difference in heat of dissociation between $nBuNH_2.BMe_3$ and $t\text{-}BuNH_2.BMe_3$ is 5.4 kcal - because of the similar formal structure of the t.Bu complex (I) with di-t-butyl methane (II), a strain of 5.4 kcal/mole is assigned to this structure

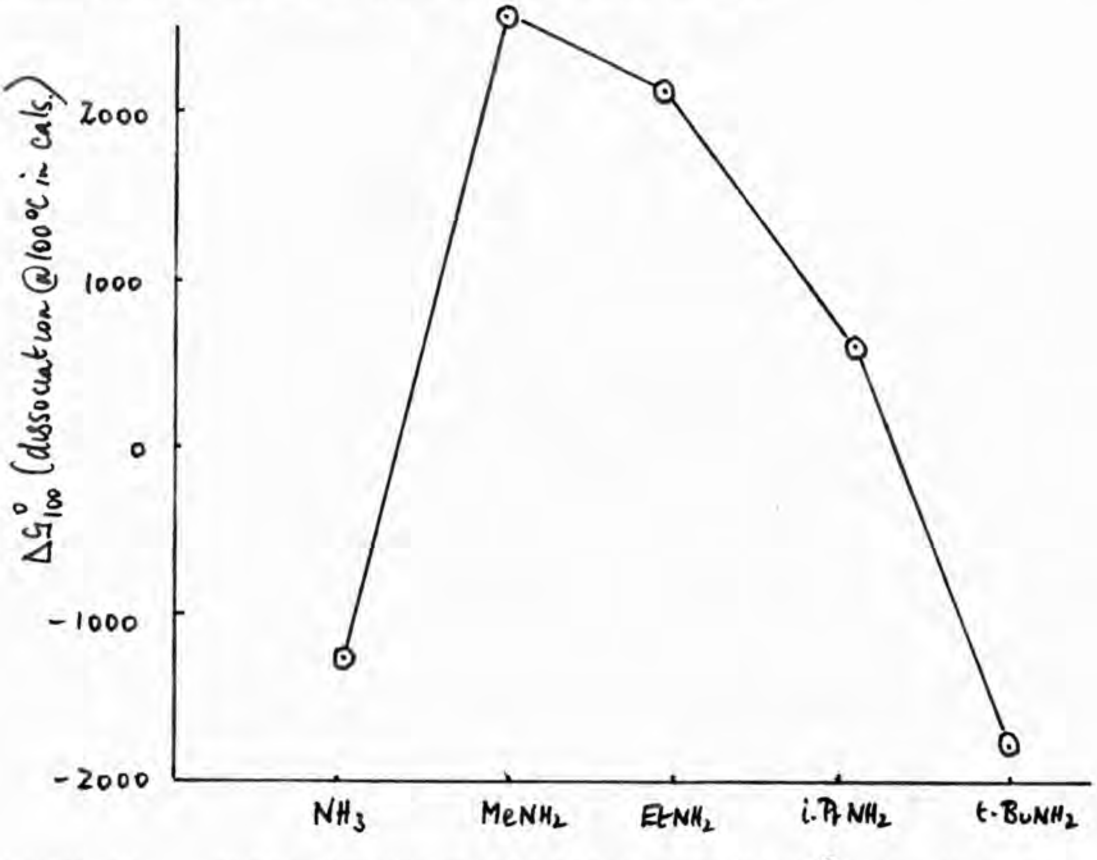


II



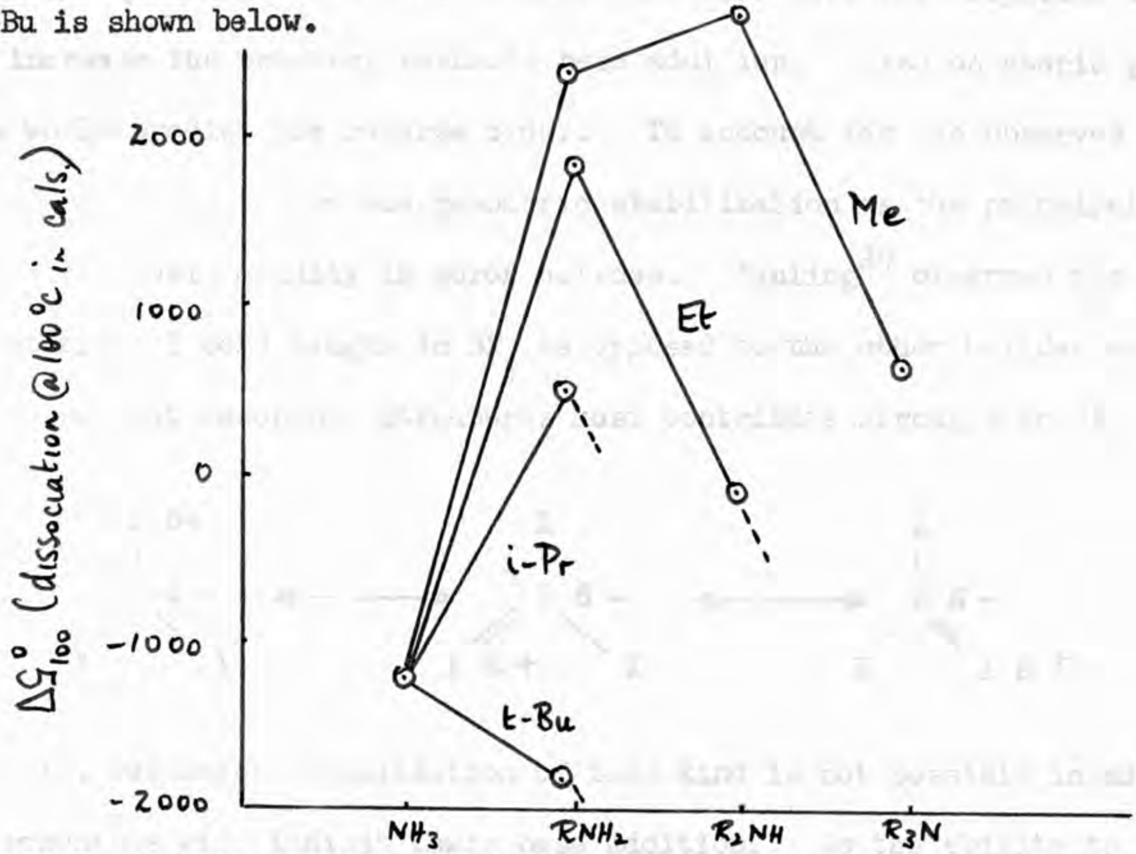
I

Other homomorphs of $t\text{-}BuNH_2.BMe_3$ would be di-t-butyl ether, di-t-butylamine etc. The change in free energy of dissodation of $RNH_2.BMe_3$ with increasing chain-branching is illustrated below.



GRAPH I : FREE ENERGY OF DISSOCIATION AT 100°C OF $RNH_2.BMe_3$

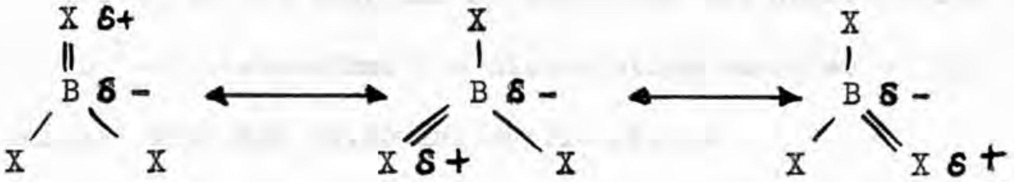
One can observe here the operation of two conflicting effects - substitution of one methyl group in ammonia causes a stabilization of the complex due to the methyl inductive effect - further substitution causes the steric effect to outweigh the combined inductive effect. The free energy of dissociation for the amine series Me, Et, i-Pr, t-Bu is shown below.



GRAPH 2 : FREE ENERGIES OF DISSOCIATION OF BMe_3 WITH DIFFERENT AMINES

Brown and Holmes[28] measure the enthalpies of reaction between certain Lewis bases and BX_3 (X = Cl, Br, I) to establish a sequence of acceptor properties of the boron halides. The heat of reaction of the halides with pyridine in nitrobenzene solution at 25°C. is

$- 25.0 \pm 1.0$ (BF_3); $- 30.8 \pm 0.2$ (BCl_3) and $- 32.0 \pm .2$(BBr_3) kcal/mole. These data imply that the Lewis acid strength of the halides increases in the order $BF_3 < BCl_3 < BBr_3$. From electronegativity considerations one would expect the opposite sequence, for high electronegativity would tend to make the boron more electrophilic and so increase its tendency to Lewis base addition. Also on steric grounds one would predict the reverse order. To account for the observed sequence it is necessary to propose mesomeric stabilization as the principal factor affecting Lewis acidity in boron halides. Pauling[29] observed the marked shortening of bond length in BF_3 as opposed to the other halides and proposed that resonance structures must contribute strongly to BF_3



Clearly, resonance stabilization of this kind is not possible in adducts so resonance will inhibit Lewis base addition. As the ability to form double bonds appears to decrease sharply among the heavier elements resonance stabilization will decrease along the series F > Cl > I.

The work of Brown[27] on amine complexes with trimethyl boron as reference acid illustrates some of the concepts of the "FBI" strain theory[30, 31]. Strain is defined in terms of the dissociation reaction

A.B $\longrightarrow$ A + B. If either or both of A and B contain bulky groups there will be some release of compression forces [i.e "frontal" (F) strain] as the complex dissociates. The strain that results from the crowding together of the groups on A or B individually is designated "back" (B) strain. Internal (I) strain is a special case of B-strain applied to cyclic systems. The increasing basicity of the amines R_3N (-R = HorMe) (see graph 2) followed by the sharp decrease at the tertiary amine illustrates the effect of F-strain i.e. $NH_3 < MeNH_2 < Me_2NH > Me_3N$ in order of increasing base strength. Using a bulkier reference acid (R = Hort-Bu) the sequence is reversed

$$NH_3 > tBuNH_2 > (t\text{-}Bu)_2NH > (t\text{-}Bu)_3N$$

The effect of I-strain on stability was demonstrated by Brown and Gerstein[32] who determined the dissociation energies of the trimethyl boron complex with the following cyclic amines

aziridine

azetidine

pyrrolidine

piperidine

They found the following stability order in terms of ring size: 4 > 5 > 6 > 3. This order was explained on the basis of two opposing effects : F and I-strain. F-strain arises from the interaction between B - Me and α -methylene hydrogens in the cyclic base and would tend to increase with increasing ring size. I-strain derives from the change in configuration at the nitrogen on complexing coupled with the change in bond angle and should decrease with ring size, i.e.

if $F \gg I$, stability order is $6 < 5 < 4 < 3$
and $F \ll I$, " " " $6 > 5 > 4 > 3$.

It appears from the experimental order observed that F-strain is the controlling factor except in the case of the three-membered ring where the strain induced in transposing the preferred tetrahedral bond angle ($109\frac{1}{2}^\circ$) to that defined by the geometry of the ring (60°) out-weighs the F-strain component.

Also in a recent paper, McLaughlin et al[33] repeat the work of Brown described above using the N-methyl derivatives of the cyclic amines and find the complete reversal of the 3-membered ring in the stability order, i.e. $3 > 4 > 5 > 6$.
This implies that because of the bulky methyl substituent (relative to H) on the nitrogen $F > I$ throughout the series.

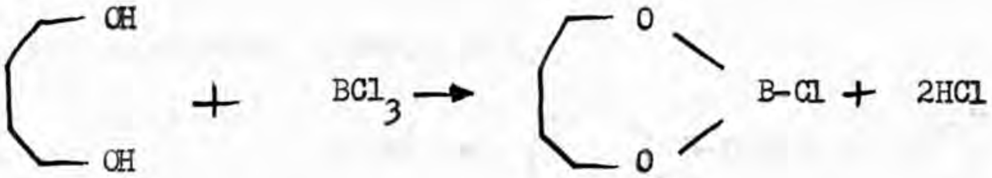
Finally, in a recent paper Aubrey et al.[65] investigate steric effect on the replacement reaction between boron trichloride and compounds of the type $(R_2N)_3B$. They find that if the alkyl group (R) is branched in α -position, replacement proceeds only as far as $(R_2N)_2BCl$. This illustrates the limitations of Skinner's treatment of back coördination where all steric effects are ignored.

DISCUSSION AND RESULTS

SECTION 1 : SYNTHESIS OF CYCLIC SYSTEMS

(a) Epans

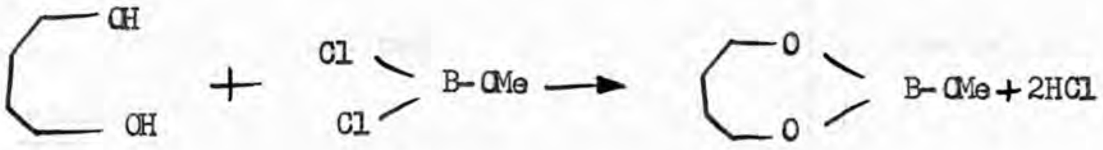
It is desirable to synthesise 2-chloro-1,3,2 dioxaborepan to compare its physical properties and chemical stability with the established inan and olan analogues. The preparation of this compound was attempted by Standard procedures[8,9]:- by mixing equimolar proportions of butan 1,4 diol with boron trichloride at -80°C. in methylene chloride solvent. The reaction is carried out under a -80°C. reflux condenser to prevent loss of boron trichloride (condensation reactions of this type are usually exothermic) :



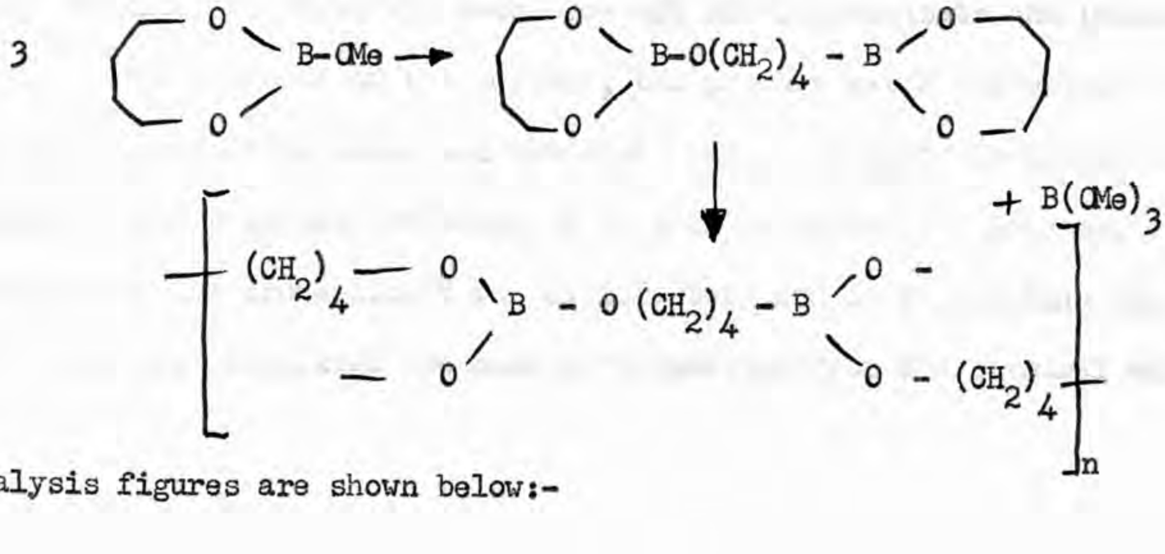
Butan 1,4 diol solidifies at 16°C. so periodically the reaction flask was warmed; however the solvent helps to disperse the diol. This preparation was attempted several times but on each occasion, after removal of solvent, a brown syrup remained which darkened on standing at ambient temperature. Distillation of this residue was unsuccessful.

Next, the synthesis of 2-methoxy-1,3,2- dioxaborepan was attempted via the reactions

$$MeOH + BCl_3 \longrightarrow MeOBCl_2 + HCl$$



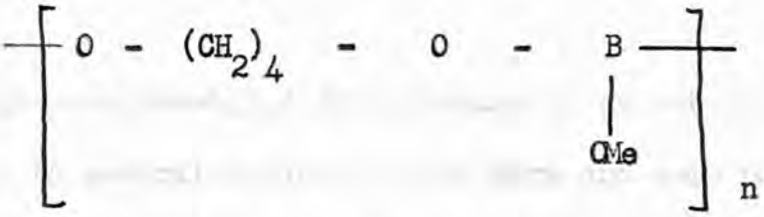
The first stage was performed using a similar procedure as described for the attempted preparation of the B-chloro derivative (94% of the stoichiometric hydrogen chloride was obtained). The product was used directly in the methylene chloride in which it was prepared as these compounds are known to disproportionate on distillation. The compound obtained from stage two, after removal of solvent, was a pale yellow glass. Distillation was again unsuccessful. This synthesis was attempted before either Dale's or Musgrave's work on 1,4 diol derivatives was published. It seems probable, therefore, that if the methoxy ester was formed at all on distillation it was converted to the diborate which polymerises subsequently



Analysis figures are shown below:-

Compound	% B	
2 methoxy-1,3,2 dioxaborepan	8.33	theoretical
diborate or polymer	7.6	
trimethyl borate	10.4	
"glass-like" residue	8.3	

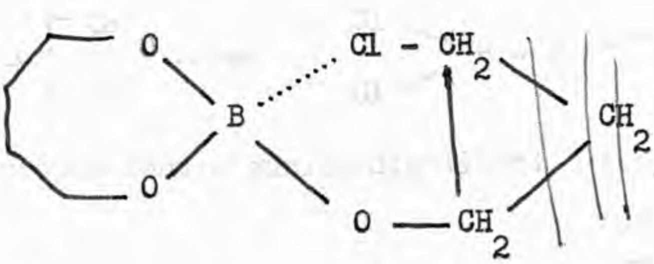
Full analysis figures for the glass were consistent with formation of the heterocycle. It appears then that either the epan heterocycle may be synthesised but not distilled or that it exists in the form of an open-chain polymer



$$\left[- O - (CH_2)_4 - O - \underset{\displaystyle OMe}{\underset{|}{B}} - \right]_n$$

The very low solubility of the glass in benzene would indicate a polymeric form is likely.

The same procedure was used to synthesise 2(2'-chloroethoxy) 1,3,2 dioxaborepan i.e. via 2-chloroethyl dichloroborinate and butane 1,4 diol. After removal of the solvent, the product was a colourless viscous liquid. Again this ester was not distillable, attempts to distil it under reduced pressure, reducing it to a black residue. However, a full analysis of the crude liquid was satisfactory and it is possible that this ester is stabilized via back-co-ordination from the terminal chlorine.

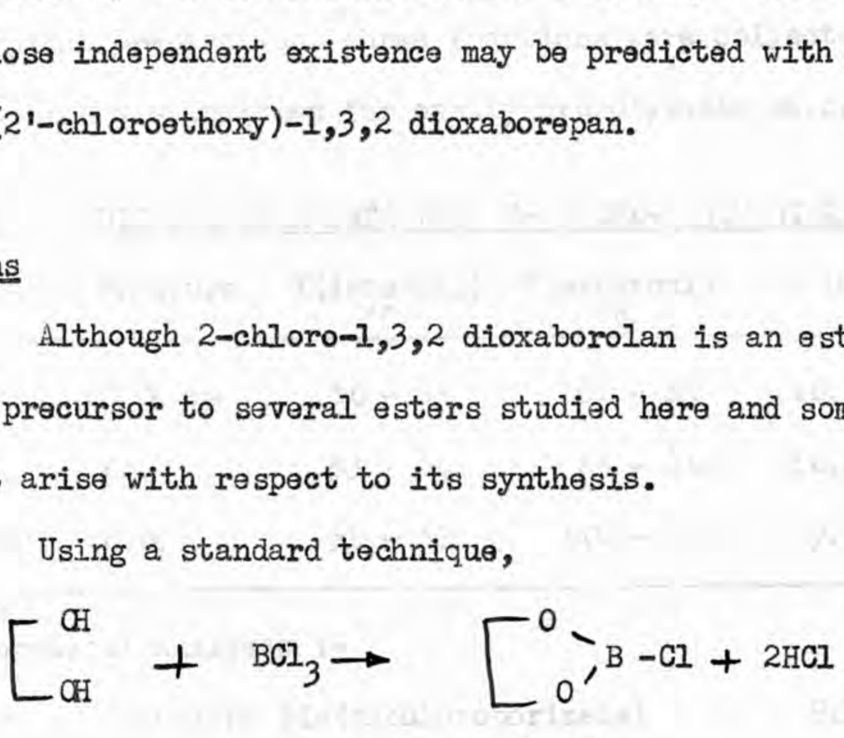


To summarize, the B-chloro derivative of the epan system is not preparable, the derived esters are thermally unstable and the only ester whose independent existence may be predicted with any confidence being 2(2'-chloroethoxy)-1,3,2 dioxaborepan.

(b) Clans

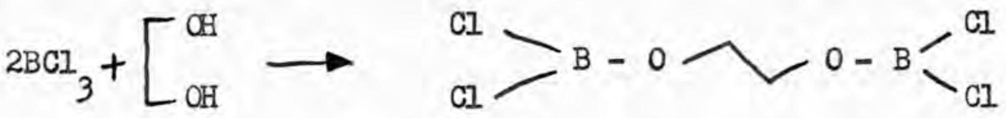
Although 2-chloro-1,3,2 dioxaborolan is an established compound[8] it is a precursor to several esters studied here and some points of interest arise with respect to its synthesis.

Using a standard technique,

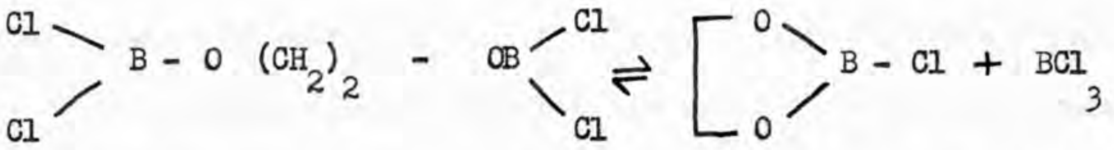


Solvent : CH_2Cl_2

Efficient stirring of the reaction mixture is necessary as the diol is viscous and local concentration of the diol causes the formation of diborate. To avoid any diborate formation this synthesis was first performed using a 5% excess of boron trichloride. It was thought that the ethylene bis (dichloroborinate) formed by virtue of this excess



would disproportionate during distillation to yield the B-chloro-olan



In a typical preparation, three fractions were collected on distillation. Each fraction was analysed for easily hydrolysable chlorine and boron.

TABLE IV : DISTILLATION DATA FOR 2-CHLORO-1,3,2 DIOXABOROLAN

Fraction	Pressure	T(internal) °C	T(external) °C	% B	% Cl
I	0.04 mm	50 - 53	60 - 83	10.14	42.5
II	0.04	53 - 54	83 - 100	10.13	41.3
III	0.04	51 - 53	100 - 120	9.97	39.8

Theoretical analyses :-

Ethylene bis(dichloroborinate)	9.7	63.6
2-chloro-1,3,2 dioxa-borolan	10.18	33.3

The first two fractions were less viscous than the third. Observing the trend in analysis figures for successive fractions and comparing with the calculated figures, it appears that the ethylene bis(dichloroborinate) is distilling in conjunction with the heterocycle.

(A rough calculation on the basis of the chlorine analysis figures indicates the final fraction contains ~ 10% dichlorborinate). As the bis(dichloroborinate) has sufficient thermal stability to be partially distilled all subsequent preparations of the heterocycle were performed with a 5% excess of diol to guarantee some diborate formation in the reaction mixture. The diborate is not distillable and probably polymerises on heating. Whenever 2-chloro-1,3,2 dioxaborolan was prepared it always distilled over a wide range of temperature : 40 - 80°C./ 0.02 mm. Literature reports on the boiling point of this compound vary and are tabulated below.

TABLE V : COMPARISON OF REPORTED BOILING POINT OF 2-CHLORO-1,3,2 DIOXABOROLAN

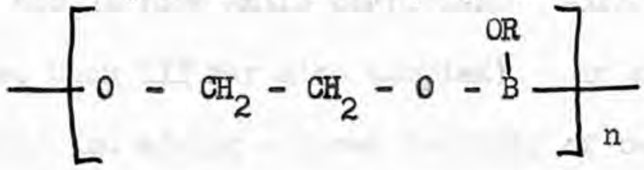
Source	Boiling point °C./mm.Hg.
Blau et al[8]	70 - 74°/ 1 mm.
V.Buls (Shell Development Co.)	74° / 20 mm.
Chainani[35]	42 - 43° / 1.5 mm.
Hyams[36]	35 - 40° / 0.5 mm.
This work	40 - 80° / 0.02 mm.

The B-chloro-olan is undoubtedly highly associated in the pure phase and its wide boiling range is probably due to different degrees of association existing in the vapour phase during the distillation.

Boiling point cannot be considered a criterion of purity for this compound.

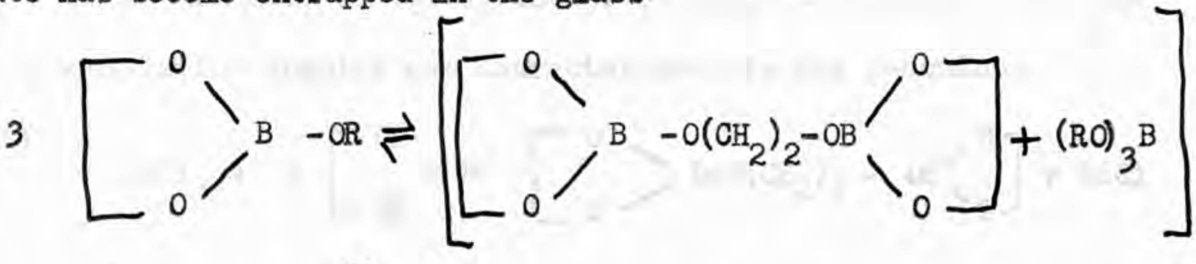
Blau et al.[8] report that 2-ethoxy-1,3,2 dioxborolan is a stable distillable liquid (b.p. 38°C./0.1). It was attempted to repeat this synthesis and also the synthesis of the 2-methoxy derivative. In both cases, the product, after removal of solvent, was a non-distillable transparent glass. The boron analysis in each case was satisfactory and the product contained no easily hydrolysable chlorine. It would appear that, in these syntheses, either

(i) the compounds exist in polymeric form



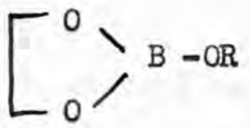
$$-\left[O - CH_2 - CH_2 - O - \overset{OR}{\underset{}{B}} \right]_n-$$

or (ii) the compounds have disproportionated and the trialkyl borate has become entrapped in the glass



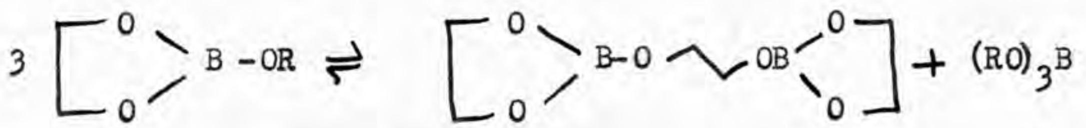
It has been established[12], in the case of the corresponding inan systems, that the derived esters are thermally stable if the volatility of the trialkyl borate is less than that of the ester itself. If the tri-alkyl borate is of higher volatility then disproportionation occurs as in (ii).

It is possible that compounds of the type



R = Me,Et,Pr ^{n}

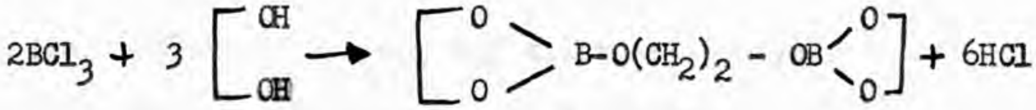
are partially disproportionated and it was decided to investigate the extent of the disproportionation by making use of the fact that in the reaction



I II III

Only components I and II form amine complexes[8,9] with benzylamine (except possibly if R = Me, then III may also complex). By making a solution of the glass-like solid and adding a known quantity of benzylamine, comparison of the amount of complex formed with that predicted for 100% cyclic form will yield an estimate of the extent of disproportionation. The diborate-benzylamine complex was characterised via the reactions

(i)



(ii) $\text{diborate} + n\,\phi CH_2NH_2 \longrightarrow [\text{diborate}].\ n\,\phi CH_2NH_2$

The product obtained from reaction (i) was a white solid, with physical data in accord with that of Blau, and insoluble in some thirty organic solvents. This precluded the formation of an amine complex in the solution phase so diborate was refluxed with excess benzylamine at 180° for ca. 3 hrs. [the diborate melts at ~160° and benzylamine boils at

185°C.]. On cooling, a white solid separated which was filtered off, washed with methylene chloride and analysed for boron. The stability of the complex was estimated by treating three aliquots as follows:-

	% B
1) Maintain at 50°C. in an inert atmosphere for ca. 15 mins.	5.11
2) Pump at ambient temperature and 0.05 mm. Hg for ca. 20 mins.	5.14
3) Not treated	5.13
Theoretical for 1:2 complex	5.19

The complex (mp. 49-52°C.) is of the form $\left[\text{diborate}\right].2\,\phi CH_2NH_2$ and has reasonable thermal stability. At this stage the project was abandoned for the following reasons:-

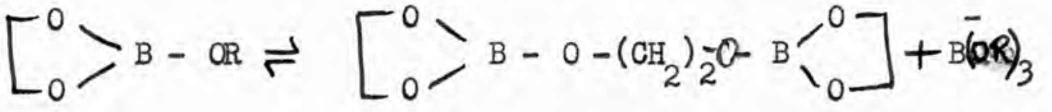
(a) the diborate may exist in open-chain polymeric form (c.f. Dale[17] and its insolubility in organic solvent)

(b) the "heterocycle", if formed, may exist as a polymer

(c) the complex between the "heterocycle" and benzylamine may not be stable (Dale[17] mentions that a complex between 2-n-butoxy-1,3,2 dioxa borolan was too unstable to be crystallised without decomposition).

2(2'chloroethoxy)1,3,2 dioxa-borolan was synthesised by condensing 2-chloroethanol with the B-chloro-olan and proved to be a stable viscous liquid. It was subsequently investigated cryoscopically.

In addition the n-butoxy ester was synthesised (this may be, in part, disproportionated). In general for cyclic esters of the type,



I II III

if B represents the boiling point and R = alkyl, when

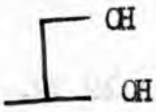
$B_I \gg B_{III}$, ester is probably polymeric

$B_I \sim B_{III}$, ester is stable but disproportionates on distillation (i.e. thermally unstable)

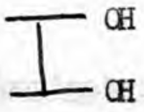
$B_I \ll B_{III}$, probably stable.

If, however, $R = -(CH_2)_nCl$ (n = 2 or 3) the ester is normally stable to distillation.

The chloroborolans derived from the following glycols

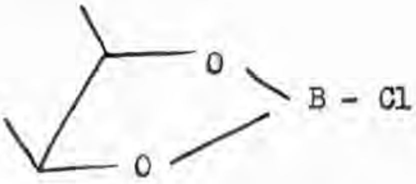


propan 1,2 diol

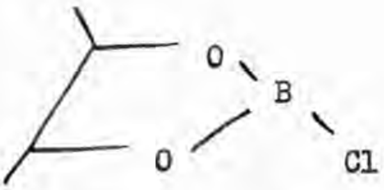


butan 2,3 diol

were also synthesised by the normal procedures[37]. A progressive decrease in viscosity of the product is observed on successive substitution of the ring. Because butan 2,3 diol contains two asymmetric carbon atoms it exists in three forms, a meso-form and a pair of enantiomorphs (racemate). It is important to know which form is used because on condensation the configuration of the methyl groups is different, dependent on whether the heterocycle was synthesised from the meso-form or the racemate.



meso-form



racemate.

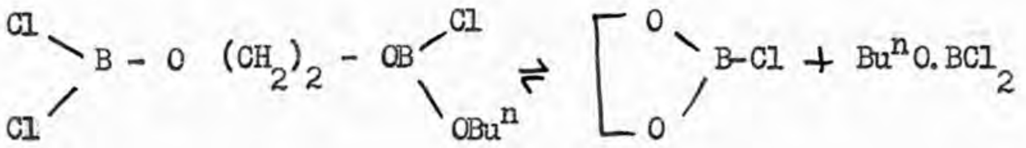
From the refractive index data supplied by Dale for the two isomeric forms it appears that B.D.H. Technical Grade Butane 2,3 diol is $>$ 95% meso-form.

(c) Inans.

Several inan heterocycles were synthesised during the course of this work and the details are recorded fully elsewhere[37].

SECTION 2 : Stability of some bis(dichloroborinates)

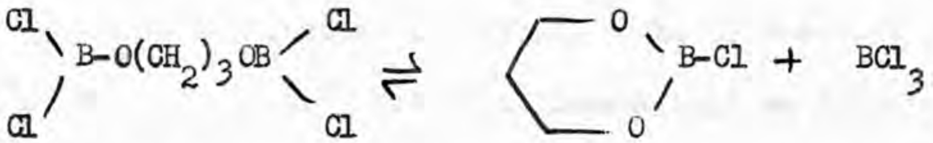
Blau et al[9] synthesise and characterise ethylene bis(dichloroborinate). The compound possesses considerable thermal stability, only slight decomposition occurring after refluxing at 110°C. for ca. 2 hr. Further heating in conjunction with pumping (5 mm. Hg) causes decomposition to 2-chloro-1,3,2 dioxaborolan and boron trichloride. Replacement of the chlorine atoms with four moles. of butan-1-ol yielded ethylene bis (di-n-butyl borate), a stable distillable compound. Replacement of one chlorine by butanol yielded a compound which was stable to pumping but disproportionates on distillation



When the corresponding trimethylene derivatives were synthesised a striking difference in thermal stability was observed. When the synthesis of trimethylene bis(dichloroborinate) was attempted by the normal procedure,

$$BCl_3 + HO(CH_2)_3OH \longrightarrow Cl_2B{-}O(CH_2)_3{-}OBCl_2.$$

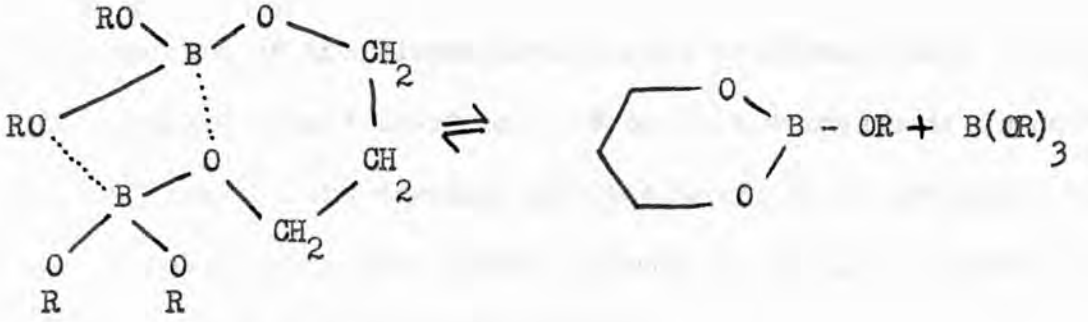
After removal of solvent a compound with a boron to chlorine ratio of one was isolated (for $C_3H_6O_2B_2Cl_4$ this ratio is two). The reaction was then attempted on a small (tenth molar) scale in the absence of solvent. This yielded the required product, a straw-yellow non-distillable fuming liquid. Even on standing at ambient temperatures for ca. 2 hrs. considerable decomposition occurs.



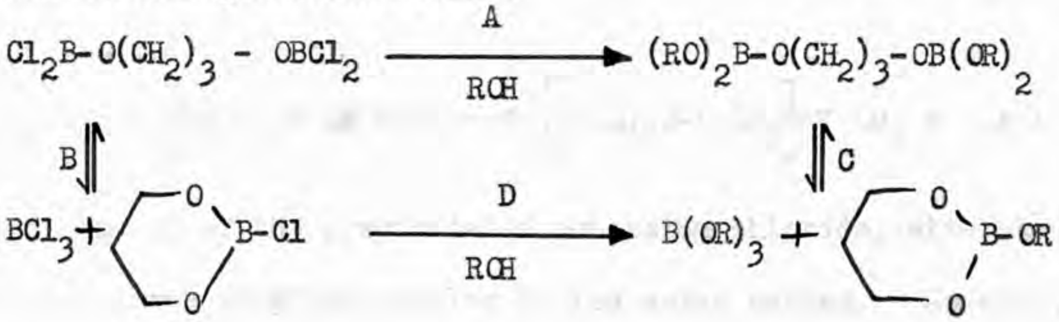
That the bis(dichloroborinate) was a discrete compound and not simply a stoichiometric mixture of inan and boron trichloride (which would yield correct analysis data) was shown by comparing the infra-red spectrum of the acyclic derivative with the superimposed spectra of boron trichloride (gas phase) and 2-chloro-1,3,2 dioxaborinan. In the rock-salt region there were intensity changes and frequency shifts in the regions 780, 1025 and 1100 cm.$^{-1}$. The preparation of an ester derivative was attempted by the reaction

$$[Cl_2BOCH_2]_2 CH_2 + 4ROH \longrightarrow [(RO)_2BOCH_2]_2 CH_2 + 4HCl.$$

Substitution was via 2-chloro ethanol in view of the stable derivatives normally derivable from this alcohol. Estimation of the evolved hydrogen chloride confirmed stoichiometric replacement of chlorine. A boron analysis was performed before distillation (the preparation being performed in the absence of solvent) and the result was indicative of ester formation. The product was then distilled under reduced pressure and fractions were collected over the range 25 to 75° / 0.1 mm. Successive distillation of any fraction invariably led to distillates boiling over approximately the same range. The synthesis was repeated and the crude product distilled into three fractions. The two end fractions were re-distilled into six further fractions. The process was repeated with extreme end fractions. The final lowest boiling fraction was identified as 2(2'-chloroethoxy) 1,3,2 dioxaborinan by analysis and comparison of the infra-red spectrum with that of an authentic sample. The final highest boiling fraction was similarly identified as tris(2-chloroethyl) borate. It is possible that the ester is thermally unstable and disproportionates on distillation.



The same result was afforded by the attempted synthesis of trimethylene bis(di-n-butyl borate), separation being effected into 2(n-butoxy) 1,3,2 dioxaborinan and tri-n-butyl borate. It is possible that the crude product did not contain the bis(di-ester) as a discrete entity but contains a stoichiometric mixture of the disproportionation products formed as a result of the decomposition of the bis(dichloro) compound i.e. disproportionation may proceed via (A + C) or (B + D) in the following reaction scheme



Accordingly a 0.125 M solution of the crude product was compared spectrometrically with a similar solution of a stoichiometric mixture of the disproportionation products. The infra-red spectrum of the first solution was quantitatively similar to the second. Also a superimposition of the spectra of the disproportionation products yielded a spectrum similar to the crude specimen spectrum. From this evidence it is possible to say that the trimethylene acyclic esters either (i) do not exist or (ii) they exist in equilibrium with their disproportionation products, the position of the equilibrium being indeterminate.

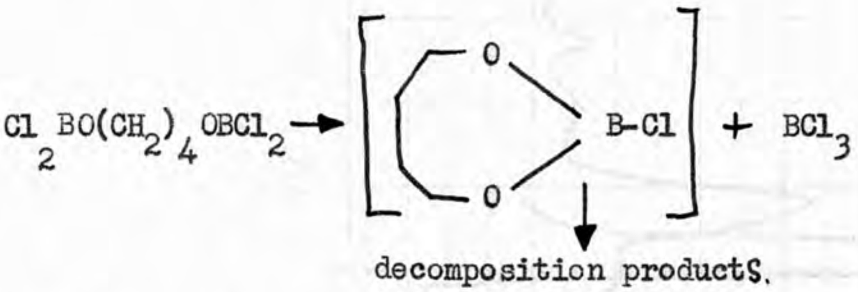
It is possible that the thermal stability of the bis(diesters) is a function of chain length (cf. Blau's stable ethylene ester), so the preparation of ethylene bis(di[2-chloroethyl] borate) was attempted via alcoholysis of ethylene bis(dichloroborinate). However on distillation the compound exhibits the same properties as the trimethylene derivatives, the 2(2'-chlorethoxy) 1,3,2 dioxaborolan being identified by a synthesis of the heterocycle by an independent method. In addition to the above synthesis, the preparation of trimethylene bis(di-iso-thiocyanato borinate) was attempted

$$\left[Cl_2B.O\,CH_2\right]_2 CH_2 + 4K\,NCS \longrightarrow \left[(NCS)_2B\text{-}O\text{-}CH_2\right]_2 CH_2 + 4KCl$$

After removal of the precipitated potassium chloride, attempted distillation caused disproportiation similar to the ester series. However, in this case only one disproportionation product (2-isothiocyanato-1,3,2 dioxaborinan) was identified. Boron tri-isothiocyanate was only described some time after the conclusion of the project.

Tetramethylene bis(dichloroborinate) was also prepared by condensing boron trichloride (2 moles) with butan 1,4 diol (1 mole).

Two moles of hydrogen chloride were evolved and the product, a white amorphous solid darkening rapidly at room temperature, analysed satisfactorily. Presumably thermal decomposition proceeds via



The stability of the compound was estimated by pumping for ca. 2 hrs. at 0.05 mm. Hg. and re-analysing. The decomposition, after this time, estimated on the basis of easily hydrolysable chlorine, was ~ 18%. Derivatives of the compound were not prepared because

(a) they are probably unstable

and (b) as the product is a solid and may not be prepared in solvent, heterogeneous formation is inevitable.

Some representative infra-red spectra (Rock salt region) are illustrated subsequently:-

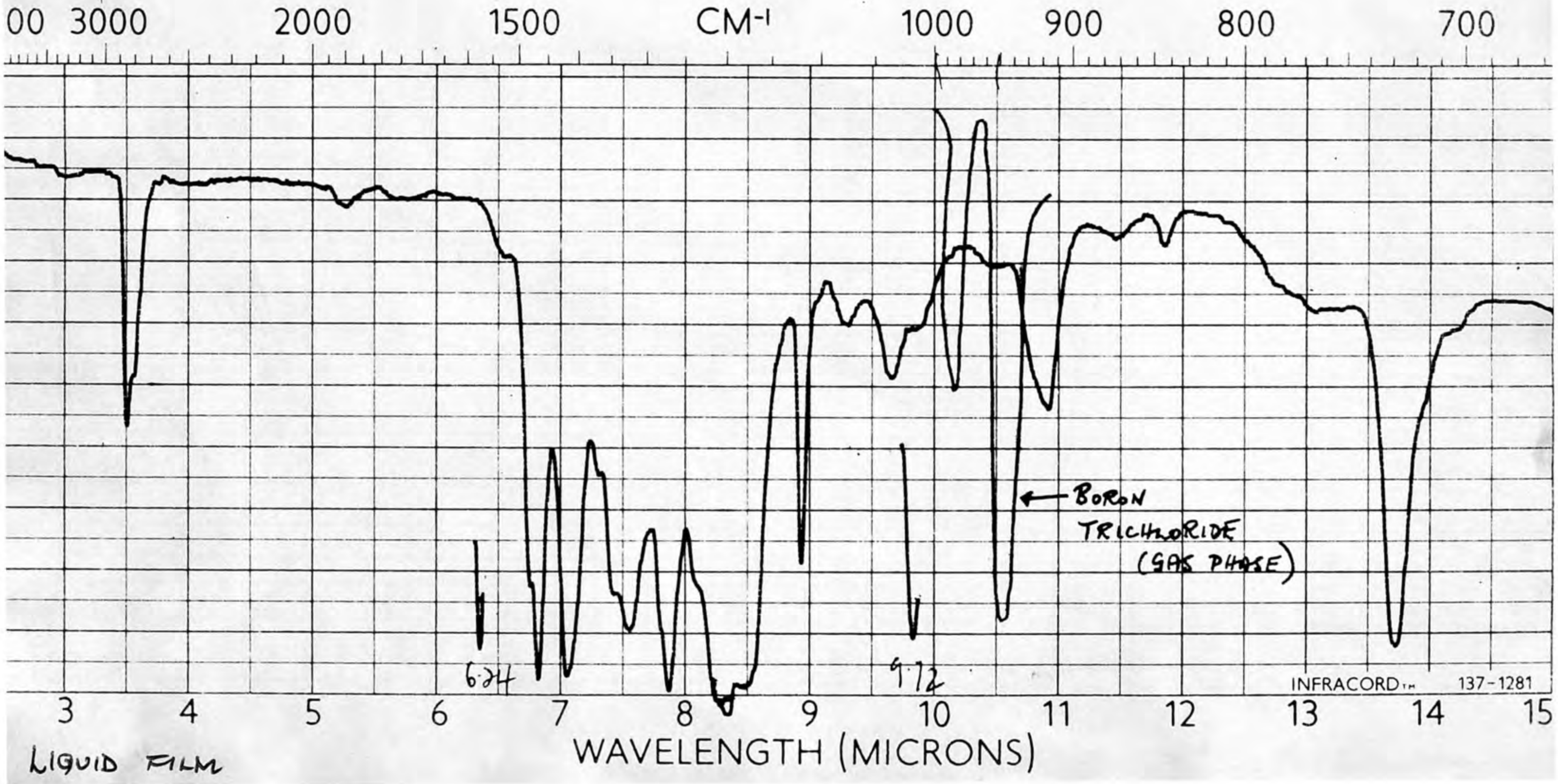
Spectrum A : 2-chloro-1,3,2 dioxaborinan with superimposed boron trichloride (gas phase)

B : Trimethylene bis (dichloroborinate)

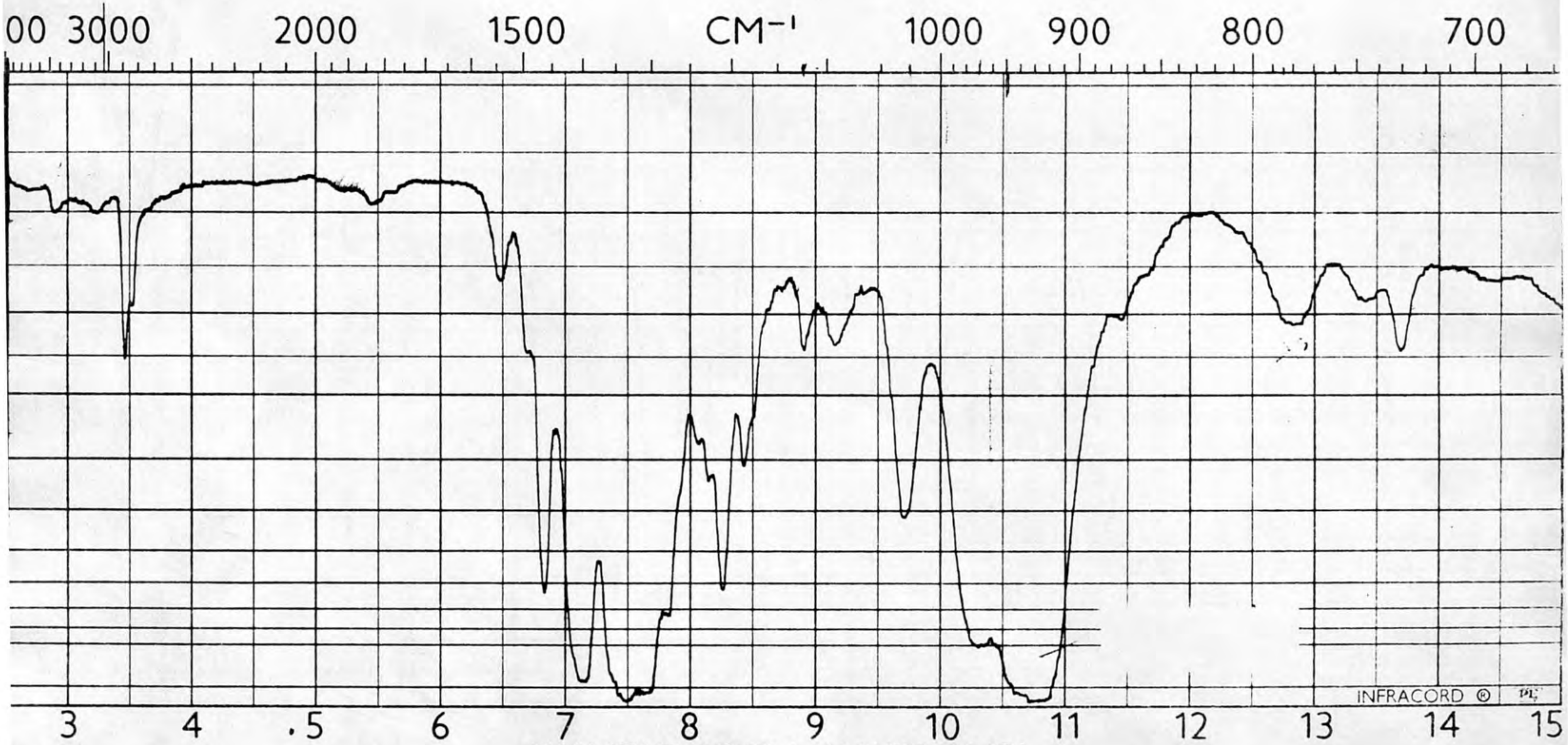
C : Final high-boiling fraction of the successive distillation of the trimethylene bis(di 2-chloroethyl borate) prep. [mostly tris-ester]

38A

SPECTRUM A : 2-CHLORO-1,3,2 DIOXABORINAN with superimposed spectrum of BORON TRICHLORIDE (gas phase)



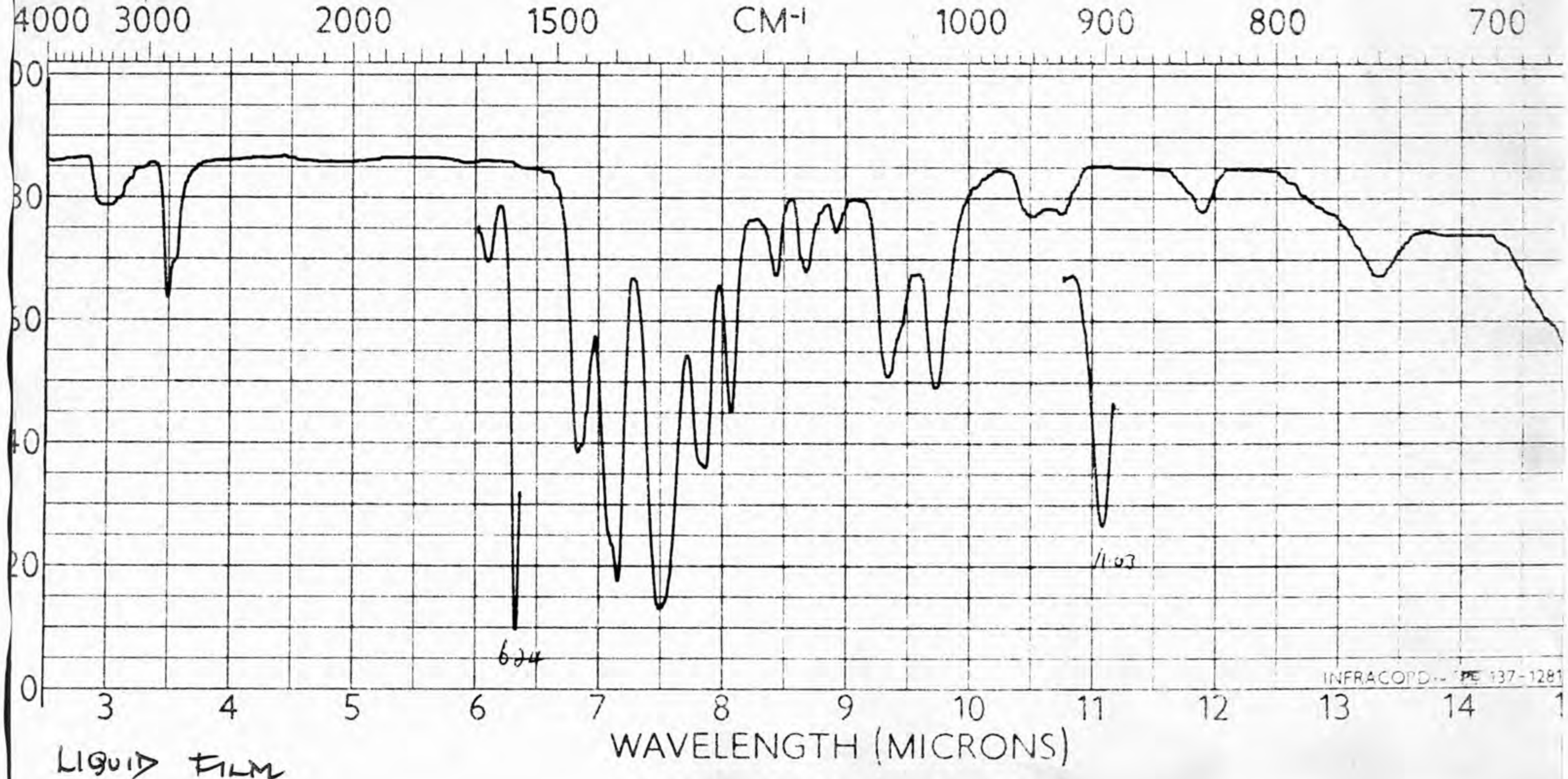
SPECTRUM B : TRIMETHYLENE BIS (DICHLOROBORINATE)



LIQUID FILM

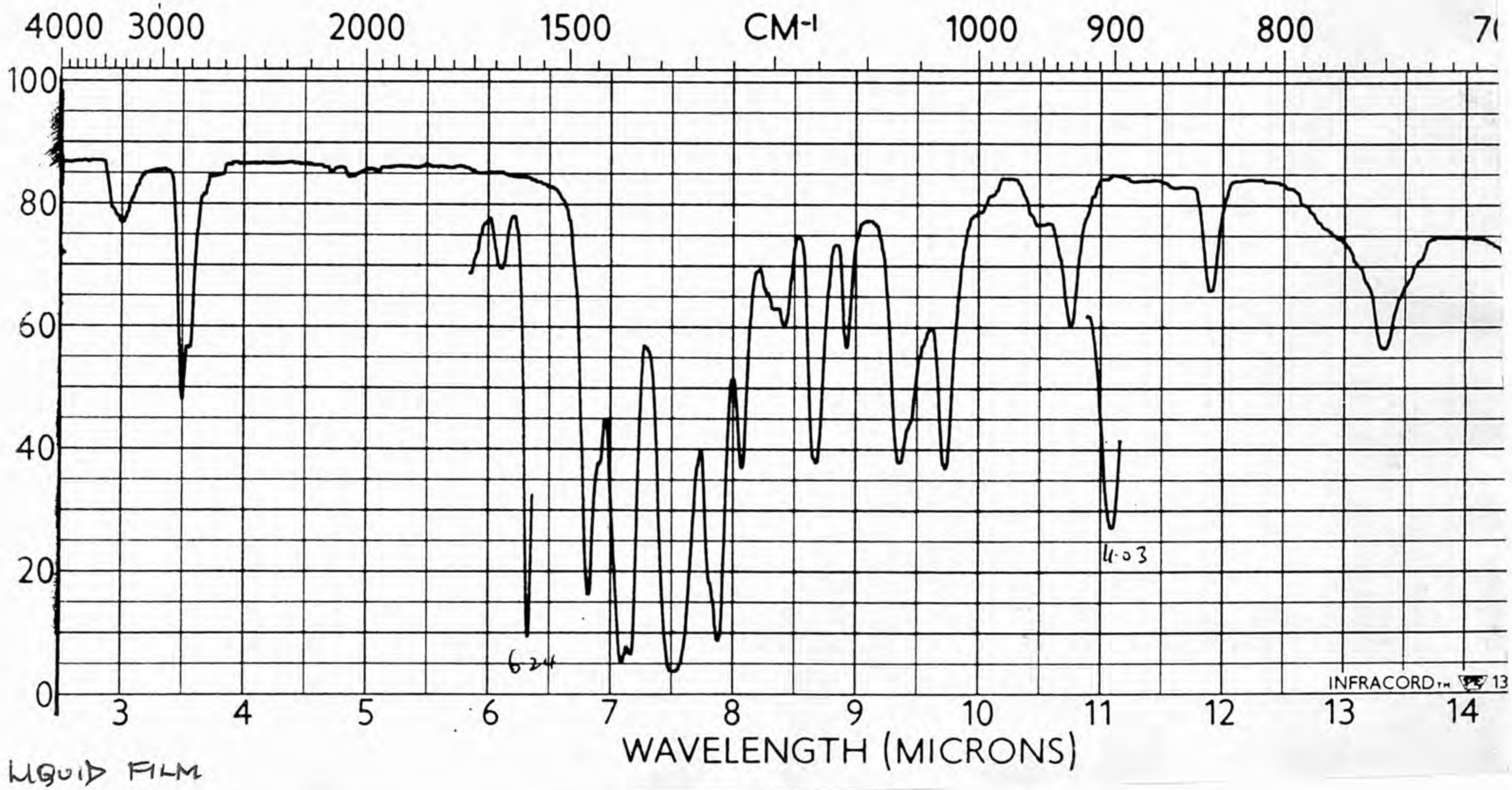
38C

SPECTRUM C: Final high-boiling fraction from successive distillation of $[(Cl.CH_2CH_2O)_2B{-}O{-}CH_2]_2CH_2$ preparation (mostly $(Cl.CH_2CH_2O)_3B$)



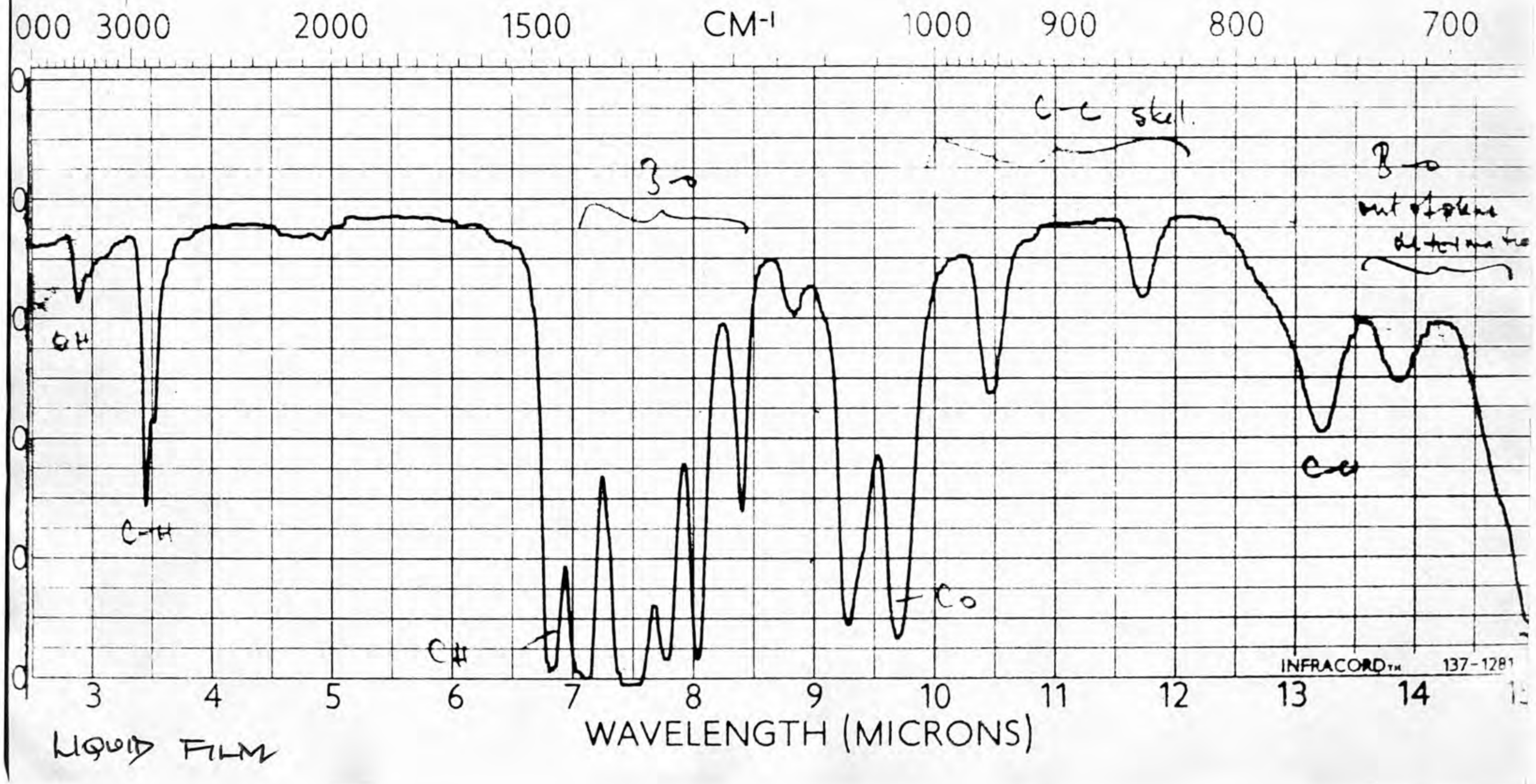
LIQUID FILM

SPECTRUM D: Final low-boiling fraction from successive distillation of $[(Cl.CH_2CH_2O)_2B{-}O{-}CH_2]_2CH_2$ preparation [mostly $\overline{O(CH_2)_3O\,B}O(CH_2)_2Cl$]



LIQUID FILM

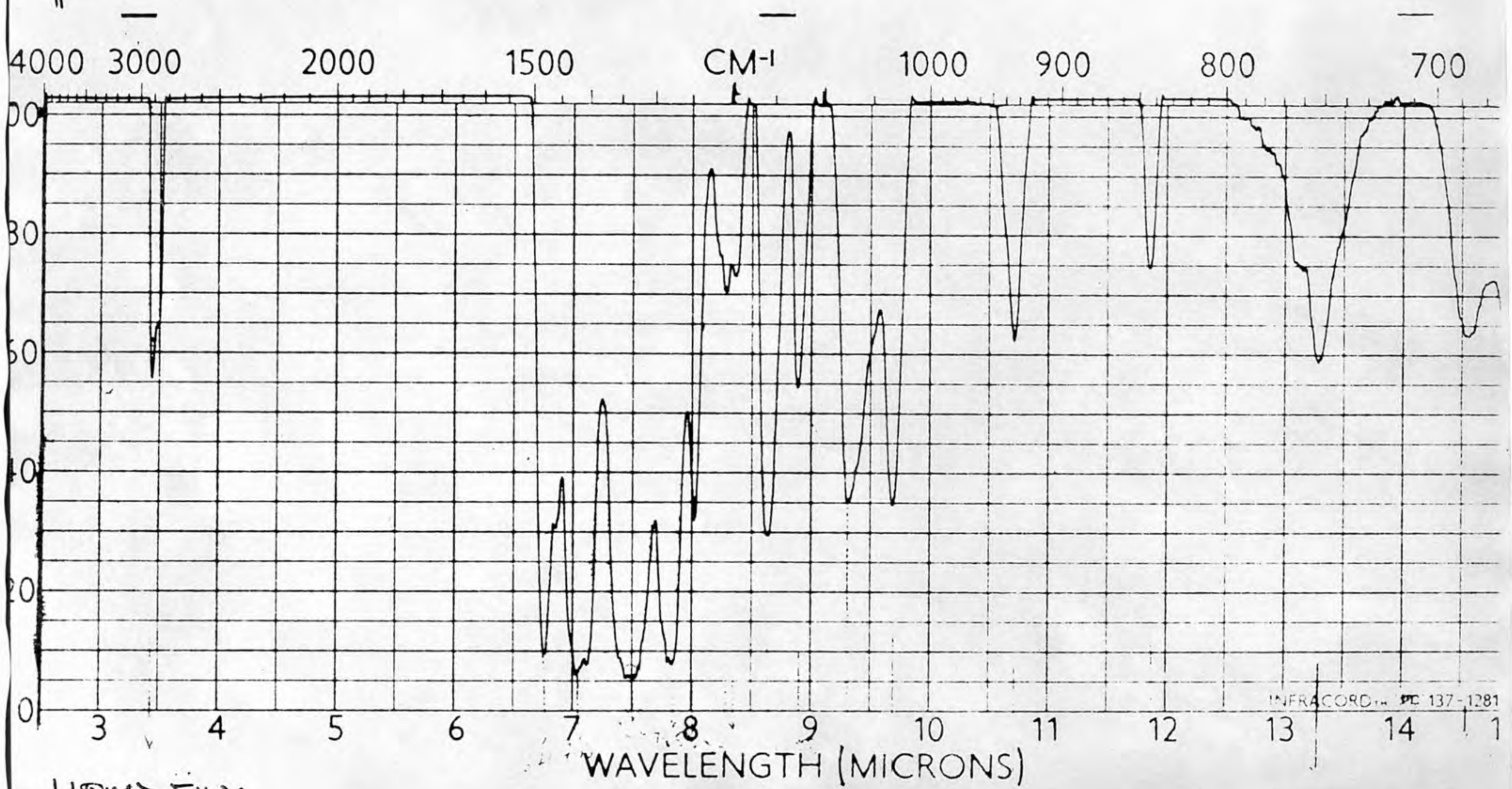
SPECTRUM E: TRI (2-CHLOROETHYL) BORATE



LIQUID FILM

38F

SPECTRUM F : 2 (2-CHLOROETHOXY) 1,3,2 DIOXABORINAN



LIQUID FILM

D : Final low-boiling fraction of the above preparation

[mostly cyclic ester].

E : Authentic tri-2-chloroethyl borate

F : Authentic 2(2'-chloroethoxy)1,3,2 dioxa borinan.

SECTION 3 : Cryoscopy.

As mentioned earlier a conspicuous feature of cyclic 1, 3, 2 - dioxaboron compounds is their strikingly different physical properties compared with their acyclic analogues. Readily available physical constants e.g. boiling point, refractive index give little insight into the reason for these divergent properties. One of the simplest and oldest methods for investigation of structure in solution is via colligative properties. Investigation via depression of freezing point was selected rather than other colligative properties because many boron heterocycles possess considerable thermal instability. Factors which must be considered in selecting a solvent for cryscopic studies are

(i) it must have a convenient freezing point preferably between -10°C. and +20°C.

(ii) it must be a good solvent for the systems under investigation and must be inert.

(iii) it should possess a reasonably high cryoscopic constant (i.e. a low latent heat of fusion).

(iv) it must remain stable over a period of time and be readily obtainable pure.

A solvent which satisfies these conditions is benzene, which may be obtained in cryoscopic grade.

An all-glass apparatus was constructed similar in design to that of Zemany[38]. Stirring was effected by a chromium plated stirrer actuated externally by a solenoid (further details are given in Experimental Section). The cryoscopic cell, when loaded, is a closed system and may be used for moisture sensitive compounds under an inert atmosphere. It is fitted with standard joints so that, if necessary, compounds may be distilled directly into the apparatus. The temperature sensitive device used is a thermistor which was calibrated as described in Part II, Experimental Section 2.

The usual equations for colligative depression are adapted as follows:-

Assuming the vapour pressure equation,

$$-\ln N_1 = \frac{\Delta H}{\underline{R}}\left[\frac{1}{T}-\frac{1}{T_o}\right]$$

ΔH = latent heat of fusion of solvent

$\underline{R}$ = gas constant

N_1 = mole fraction of species 1 (2 is considered the solute dissolved in the solvent 1).

T_o = freezing point of pure solvent

T = temperature (freezing point of solution of mole fraction N_1)

If $T_o \sim T$

The resistance/temperature relationship[39] of a thermistor is

$$R = A \exp\left[B/T\right]$$

so $$\ln\left(R/R_0\right) = B\Delta T/T_0^2$$

Where R, R_0 are the resistance values corresponding to T, T_0 and A and B are thermistor constants (determined during calibration). Substituting,

$$-\ln N_1 = \frac{\Delta H}{\underline{R}B} \ln\left(R/R_0\right)$$

Now $N_2 + N_1 = 1$ so $-\ln N_1 = -\ln(1-N_2) \sim N_2$

and $$N_2 = {}^{m_2}/_{M_2} \Big/ \frac{m_2}{M_2} + \frac{m_1}{M_1} \sim \frac{m_2 M_1}{M_2 m_1}$$

where

m_i = mass of species i

M_i = molecular weight of species i.

Therefore,

$$\frac{1}{M_2} = \frac{m_1}{M_1 m_2} \frac{\Delta H}{\underline{R}B} \ln\left(R/R_0\right)$$

Now $\frac{R}{Ro} = 1 + \frac{\Delta R}{Ro}$ if $\Delta R = R-Ro$

Substituting and expanding,

$$\frac{1}{M_2} = \frac{m_1}{M_1 m_2}\left[\frac{\Delta R}{R_0} - \frac{1}{2}\left(\frac{\Delta R}{R_0}\right)^2 + \frac{1}{3}\left(\frac{\Delta R}{R_0}\right)^3 \cdots\cdots\right]$$

ignoring square and higher terms,

$$M_2 = M_1 m_2 \underline{R}\, B\, R_o \Big/ m_1 \Delta H\, \Delta R$$

The usual experimental method for the determination of molecular weights by cryoscopic depression involves calibration using a compound of known molecular weight and applying the experimental equation

$$M_2 = \underline{k}\ \frac{m_2}{\Delta R}$$

Comparing this experimental equation with the one immediately above we have

$$\underline{k} = \frac{M_1 \underline{R}\, R_o\, B}{\Delta H\, m_1}$$

Using a specially purified sample of naphthalene (B.D.H.) values of $\underline{k}$ were determined experimentally for the solvents benzene and nitrobenzene. These were compared with values obtained using the above equation.

TABLE VI. COMPARISON OF CALCULATED AND EXPERIMENTAL CALIBRATION CONSTANTS

Solvent	k (calcd.)	k (exp.)
Nitrobenzene	6.16×10^4	6.32×10^4
Benzene	6.35×10^4	6.59×10^4

Values of k are dependent on the solvent only and approximate values (within 4%) may be calculated for any solvent - this procedure allows approximate molecular weight determinations to be performed in any solvent without first performing a calibration experiment. The cryoscopic constant (K_f) may also be evaluated in terms of the thermistor constants and well-known parameters.

From the approximate formula derived above

i.e.

$$- \ln N_1 \sim \frac{m_2 M_1}{M_2 m_1} = \frac{\Delta H \Delta T}{\underline{R} T_0^2}$$

$$M_2 = \frac{m_2}{m_1 \Delta T} \cdot \frac{\underline{R} T_0^2 M_1}{\Delta H}$$

$$= K_f \frac{m_2}{m_1 \Delta T} \qquad \left[K_f = \frac{\underline{R} T_0^2 M_1}{\Delta H} \right]$$

Comparing with the experimental equation,

$$M_2 = \underline{k}\,\frac{m_2}{\Delta R} = \underline{k}\,\frac{m_2}{\gamma \Delta T}$$

(assuming $\Delta R = \gamma \Delta T$, $\gamma =$ const.justifiable for a small temperature range),

$$K_f = \frac{m_1 \underline{K}}{\gamma}$$

A value of γ may be abstracted from a linear graphical approximation of calibration data or may be obtained as follows:-

Using $$\ln \frac{R}{R_o} = \frac{B \Delta T}{T_o^2}$$

expanding and ignoring square and higher terms

$$\frac{B \Delta T}{T_o^2} = \frac{\Delta R}{R_o}$$

Therefore as $$\Delta R = \gamma \Delta T$$

$$\gamma = \frac{R_o B}{T_o^2}$$

$$\text{and } K_f = \frac{m_1 \underline{k} T_o^2}{R_o B}$$

Values of the cryoscopic constant were calculated from this equation and compared with literature[40] data in the table below

TABLE VII : COMPARISON OF CALCULATED AND LITERATURE CRYOSCOPIC CONSTANTS.

Solvent	K_f (calcd.)	K_f (lit.)
Benzene	5.12 ± 0.1	5.12
Nitrobenzene	7.16 ± 0.1	7.20

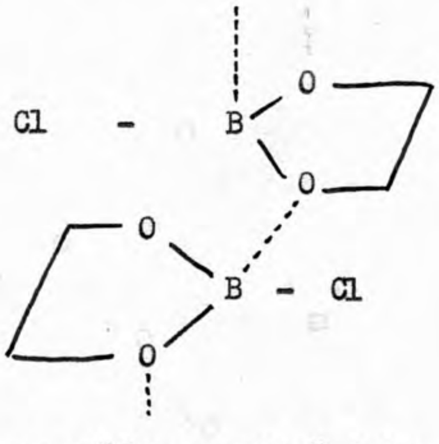
(the physical significance of K_f is that it is the depression in °C. of 1 mole of ~~solvent~~ Solute dissolved in 1000 g. of solvent).

A detailed analysis of the approximations and the errors involved in cryoscopy are presented in the experimental section. The compounds studied cryoscopically had either the olan- or inan- skeleton and will be discussed under this classification.

(a) Olans

The only reference to the molecular weight of 2-chlor-1,3,2 dioxaborolan is due to Brotherton and McCloskey[14] who quote a degree of association of 1.96 at 0.36 M (based on monomer). This compound was investigated cryoscopically in benzene (in which it is soluble in all proportions) up to one molar concentration. The degree of association increased from about 1.2 to 3.2 at 1M; at no concentration did it appear monomeric. The extent of reproducibility of results obtained with this compound is probably at its worst, the error in dilute solutions probably being of the order of ± 5%. However, even by taking into account this large error no evidence for the existence of a monomeric species in solution is found. Because of the much higher dielectric constant of nitrobenzene (15 x that of benzene) it is possible that using nitrobenzene as a cryoscopic solvent, association may not be possible. A considerable depression of the extent of association at all concentrations was observed but even at the lowest concentrations a monomer was not detected (see Graph 1). This change of the degree of association with concentration is possibly due to the following associative forms existing in solution.

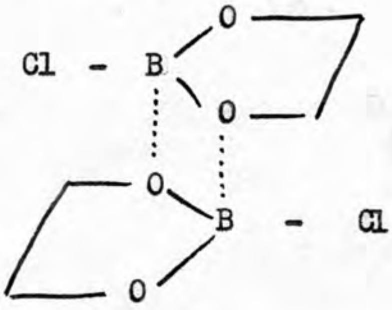
(i) <u>"loose" packing</u>



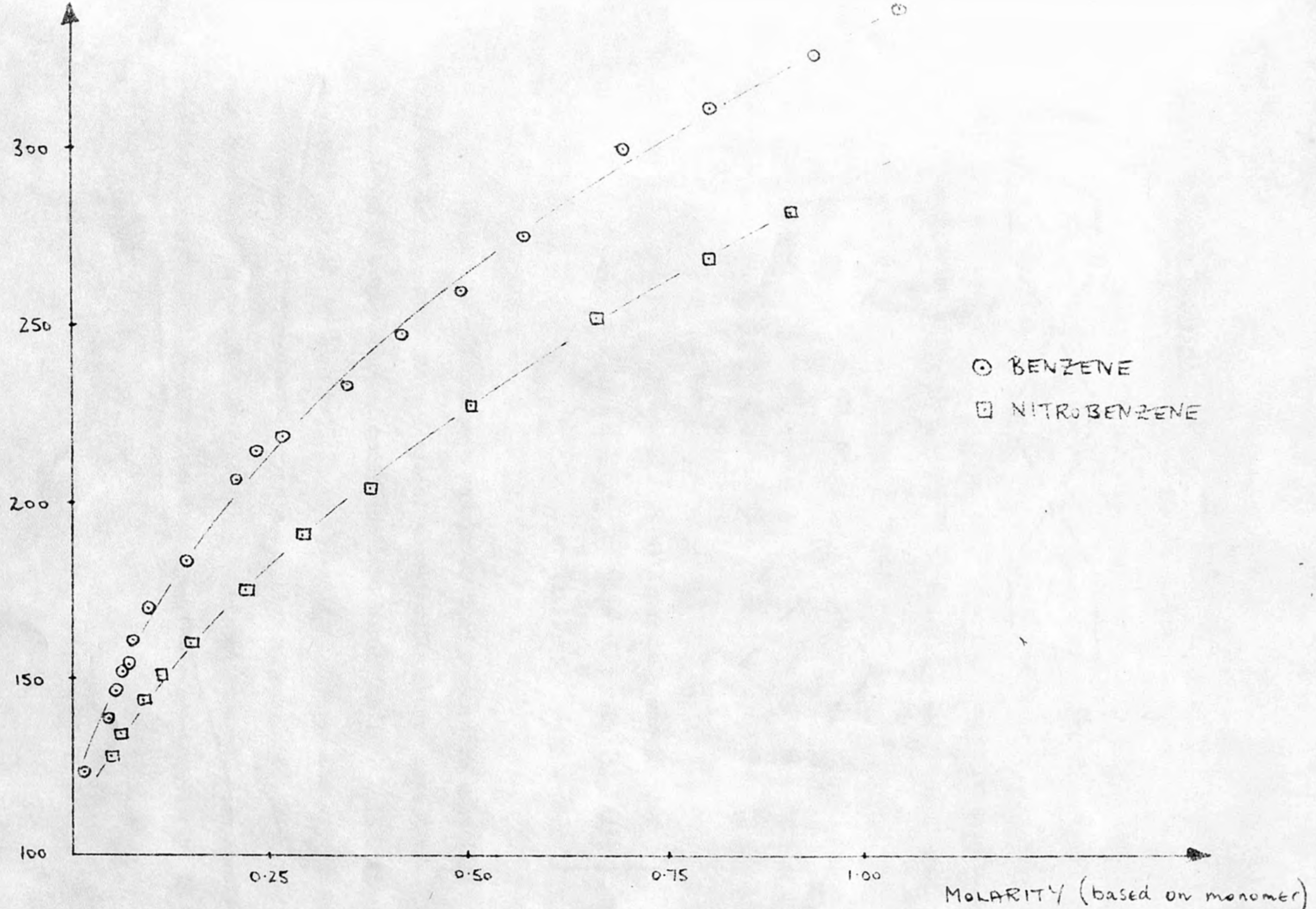
α_1 = limiting degree of association

$\alpha_L > 2$

(ii) <u>Stronger "four centre" interaction</u>

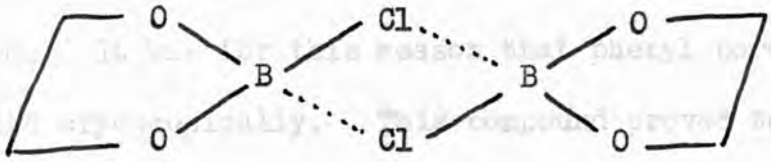


$\alpha_L = 2$



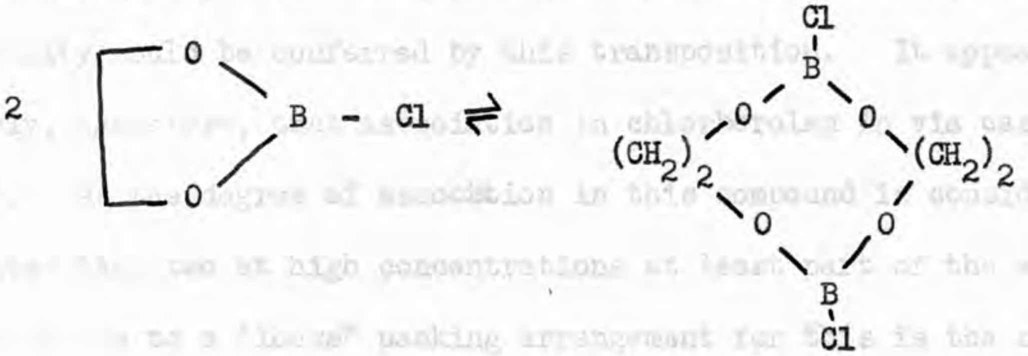
GRAPH I : MOLECULAR WEIGHT OF $\overline{\text{OCH}_2\text{CH}_2\text{O}}\text{BCl}$ IN BENZENE AND NITROBENZENE

(iii) Chlorine bridging



$\alpha_l = 2$

(iv) Equilibrium with a ten membered ring



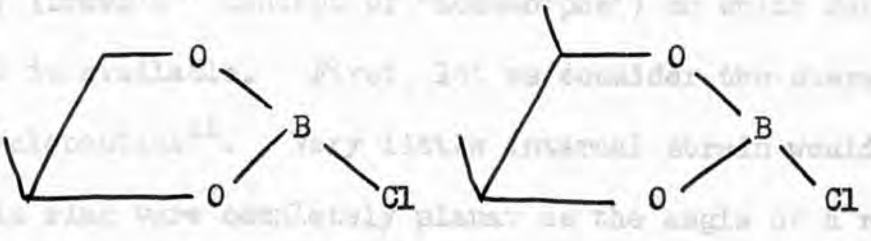
$\alpha_l = 2$

with possible combination of this ring with (i), (ii) or (iii) } $\alpha_l > 2$

Case (iv) follows as a result of bond rupture in case (ii) followed by ring expansion. All of these models except case (iv) involve the transposition of boron (sp^2) to boron (sp^3). This latter model is unlikely to be a reality as the energy required for bond fission and formation would not result from a dilution effect. The energy of weak electrostatic bonding (as in case (i)) is of the order of 5-10 k cal./mole c.f. hydrogen bonding) whereas the energy of the boron-oxygen link is ca. 120 kcal./mole.

Although no examples of stable chlorine bridging are to be found in the literature of boron chemistry this possibility cannot be ignored. It was for this reason that phenyl boron dichloride was examined cryoscopically. This compound proved to be monomeric at all concentrations up to 0.4 M. Chlorine bridging in phenyl boron dichloride would involve sp^3 hybridization and in an acyclic system no particular stability would be conferred by this transposition. It appears most likely, therefore, that association in chlorborolan is via case (i) or (ii). As the degree of association in this compound is considerably greater than two at high concentrations at least part of the association must be due to a "loose" packing arrangement for this is the only case where the limiting degree of association is greater than two.

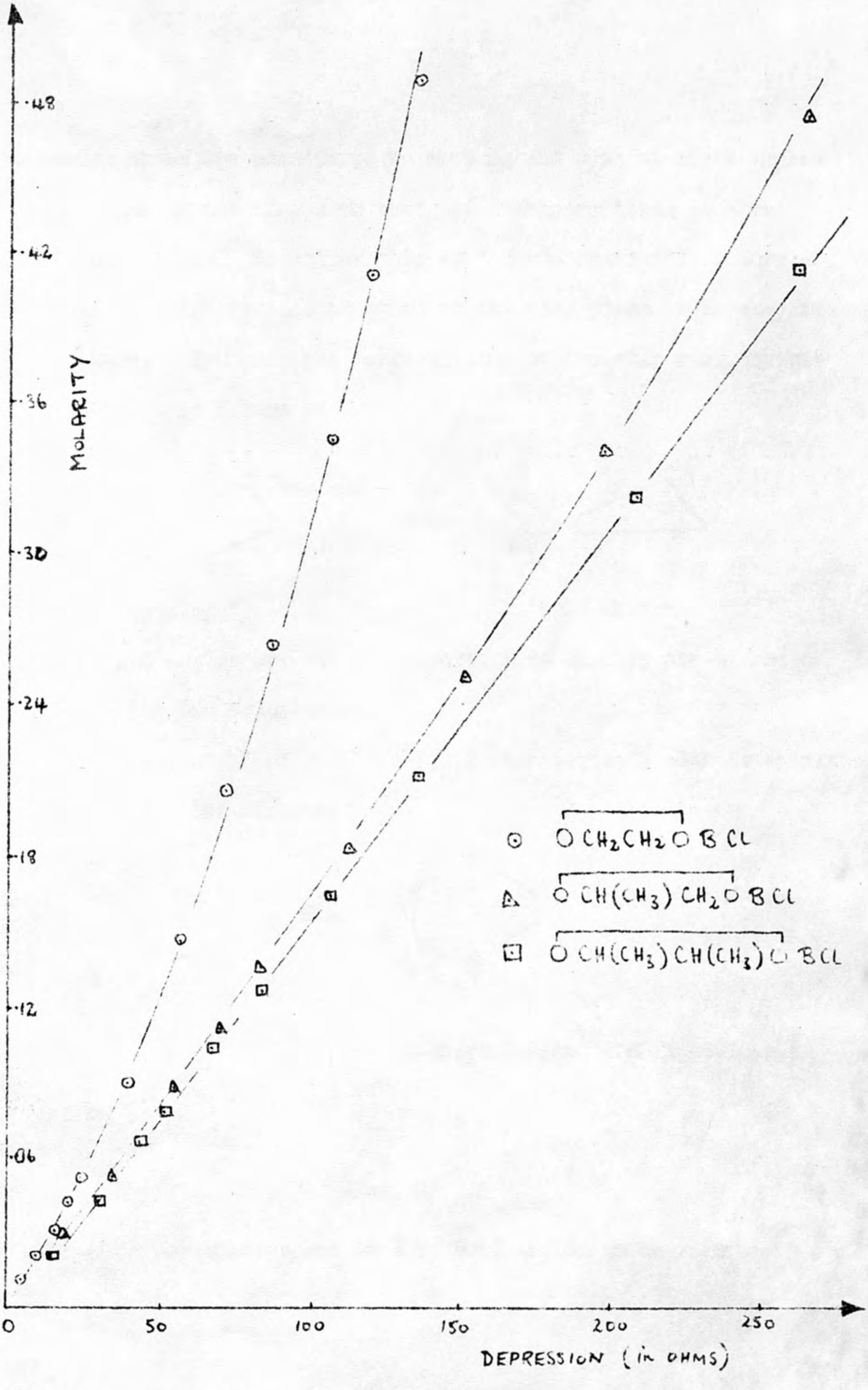
If association does take place via the stacking arrangement proposed above substitution in the ring as in the compounds



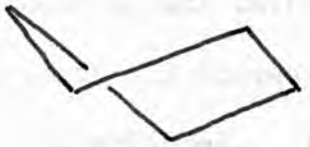
would provide considerable steric hindrance to any form of stacking (this point is clarified by the construction of molecular models). Accordingly, these compounds were synthesised by the usual methods and cryoscopic measurements performed up to 0.7 M. As predicted the extent of association in these compounds is considerably depressed.

In this case, this is best illustrated in graphs of concentration vs. depression rather than concentration vs. degree of association because the extent of association in the two derivatives differs very little. In these graphs the molecular weight at any concentration is estimated from the gradient at that concentration, linearity indicating a constant degree of association and monotonic curvature indicating a gradual change in association with increasing concentration. (see Graph 2). The derivative with the great degree of steric hindrance i.e. 2-chloro-4,5-dimethyl-1,3,2 dioxaborolan has a linear concentration/depression plot, corresponding to a constant degree of association of 1.1 over the total concentration (this point is of interest when discussing the corresponding inan heterocycle).

The validity of the proposed association forms may be considered in a qualitative manner in the light of structures possessing similar stereochemistry (Brown's[27] concept of "homomorphs") on which detailed structural data is available. First, let us consider the stereochemistry of cyclopentane[41]. Very little internal strain would be expected if this ring were completely planar as the angle of a regular pentagon (108°) is very close to the tetrahedral angle. However in this configuration the α(H - H) interaction is at its maximum as all the hydrogen atoms are eclipsed with respect to one another. A decrease in total strain (4 - 5 kcal./mole) is obtained by considering the molecule as being slightly puckered. The conformation of the ring is not constant



GRAPH 2 : DEPRESSION VS. MOLARITY FOR SUBSTITUTED OLANS and the carbon atoms are considered to move up and down at right angles to the mean plane of the ring such that the puckering tends to move round the ring (Pitzer[42] describes this as "pseudorotation"). However, the time averaged distribution of atoms in the ring gives it an essentially planar structure. Two puckered conformations of the olan ring exhibit greater symmetry than others viz.

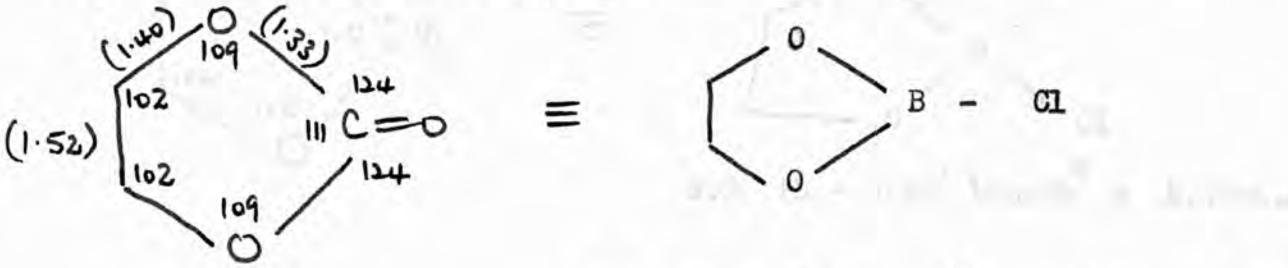


"envelope"

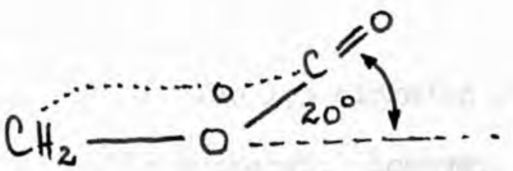
"half-chair"

(bond lengths and angles are out of proportion to clarify the minor differences in the two structures).

The "homomorph" of 2-chloro-1,3,2 dioxabor(sp^2) olan is ethylene carbonate which has the structure

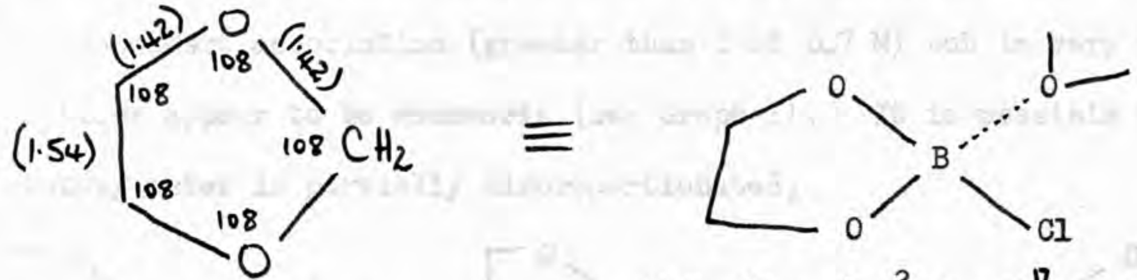


N.B. $(B-O)sp^2$ length[17] = 1.36-1.38 Å



[bond lengths in parentheses and in Å ; bond angles in degrees].

Assuming that the borolan ring (containing Sp^2B) has this "envelope" stereochemistry (the C - O and B - O bond lengths are not markedly different), the oxygen atoms are tetrahedral and the oxygen lone pairs (O.L.P.) are staggered or, at worst, gauche with respect to the ring C - H bonds. Musgrave[43] interprets the hydrolytic stability of ring substituted olans to the increase in the interaction OLP - CH to OLP - CMe, concomitant being the transposition of B(sp^2) to B(sp^3). The magnitude of the increase is only appreciable if the OLP - CX interaction is eclipsed. For this to occur the borolan ring (containing the Sp^3 boron) must exist in a planar configuration (c.f. cyclopentane). This postulate is substantiated by the conformation of the "homomorph" of 2-chloro-1,3,2 dioxabor(sp^3) olan, i.e. 1,3 dioxolan.



N.B. (B - O)sp^3 length[17] = 1.47-1.49 Å

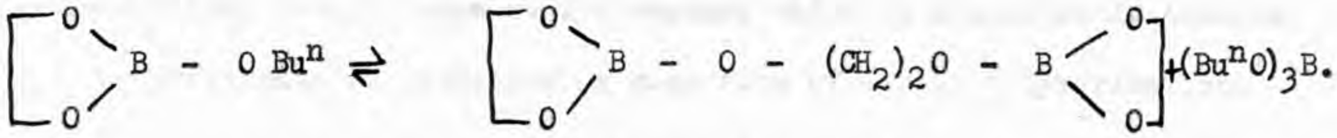
The 1,3 dioxolan ring is similar to cyclopentane in that it is slightly puckered; however, as in cyclopentane, its mean conformation is planar (certainly the preferred configuation is not "envelope". If then, by analogy, we may assume the boron (sp^3) heterocycle to be planar, stacking arrangements proposed as associative forms, will occur readily. It is realised that the idea of "homomorphic analogy" leads only to an approximation of reality but the weight of experimental evidence available

i.e. (i) that substituted borolans are hydrolytically stable

and (ii) unsubstituted borolans exhibit high association whereas the non-substituted analogues do not

indicates that bor (Sp^2) olans exist in "envelope" configuration and bor (Sp^3) olans exhibit a planar configuration.

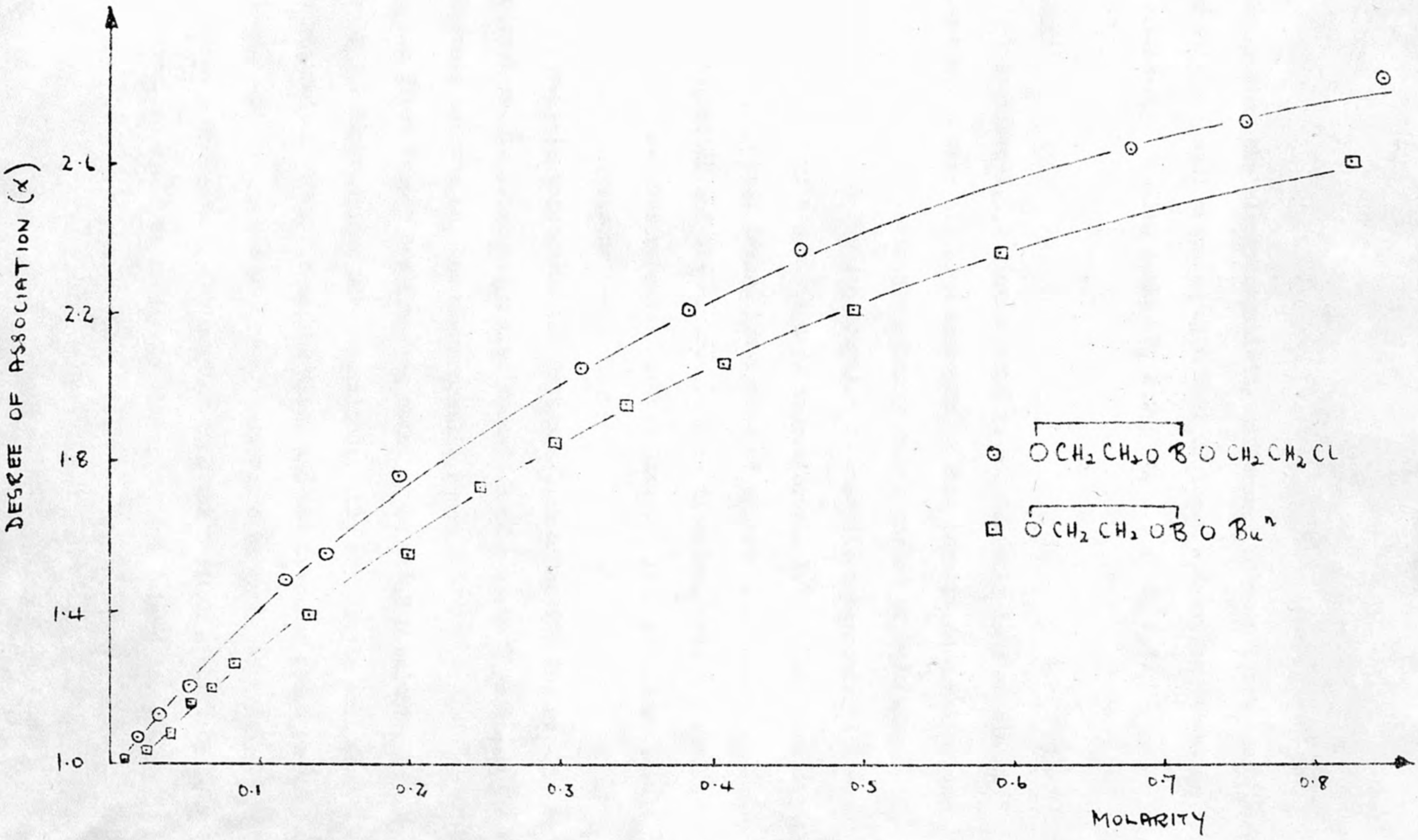
Because of the possibility of chlorine bridging contributing to the association of borolan systems, the 2-n-butoxy and 2(2'-chloroethoxy) esters of B-chloroborolan were examined. Both esters exhibit a concentration dependent association (greater than 2 at 0.7 M) but in very dilute solutions appear to be monomeric (see Graph 3). It is possible that the n-butoxy ester is partially disproportionated,



It has been suggested that the extent of disproportionation in these cyclic esters is proportional to the volatility of the cyclic system relative to the trialkyl borate. In this case, 2(n-butoxy) 1,3,2-dioxaboralan was collected over 66-68°/0.1 mm. and tri-n-butyl borate boils at approximately 48°/0.1 mm. A full analysis for the cyclic ester was satisfactory, but it is possible that the sample is a stoichiometric mixture of disproportionation products. An isolated unsuccessful attempt to assess this was made via vapour phase chromatography but the maximum column temperature was too low to obtain any separation. By a comparison with the corresponding inan-esters (where 2 n-butoxy 1,3,2-dioxaborinan disproportionates to less than 3%) it is estimated that disproportionation proceeds to less than 10%.

As mentioned earlier, chlorine bridging in these systems is impossible as a mode of association, and as maximum association is greater than two a "loose packing" arrangement must account for some proportion of the association. A further compound examined, at low concentrations only, was 2-phenyl-1,3,2 dioxaborolan; this was monomeric up to 0.2 M.

It is interesting to compare the physical properties of these cyclic systems with some thio-analogues. In direct contrast to the oxygen analogue, 2-chloro 1,3,2-dithioborolan is a colourless mobile liquid boiling at $24-25^{o}/0.1$ mm. On standing in completely dry air this compound slowly forms a scum on its surface which is insoluble in benzene; this was attributed to oxidation or some form of aerial polymerisation. Both this compound and 2 phenyl 1,3,2 dithioborolan were strictly monomeric up to 0.3 M concentration in benzene. The aqueous hydrolysis of the thio-analogues was observed qualitatively to be extremely violent compared with the corresponding oxygen compounds. An undoubtedly over-simplified explanation of the reluctance of the sulphur compounds to associate in



GRAPH 3: ASSOCIATION OF SOME BOROLAN ESTERS

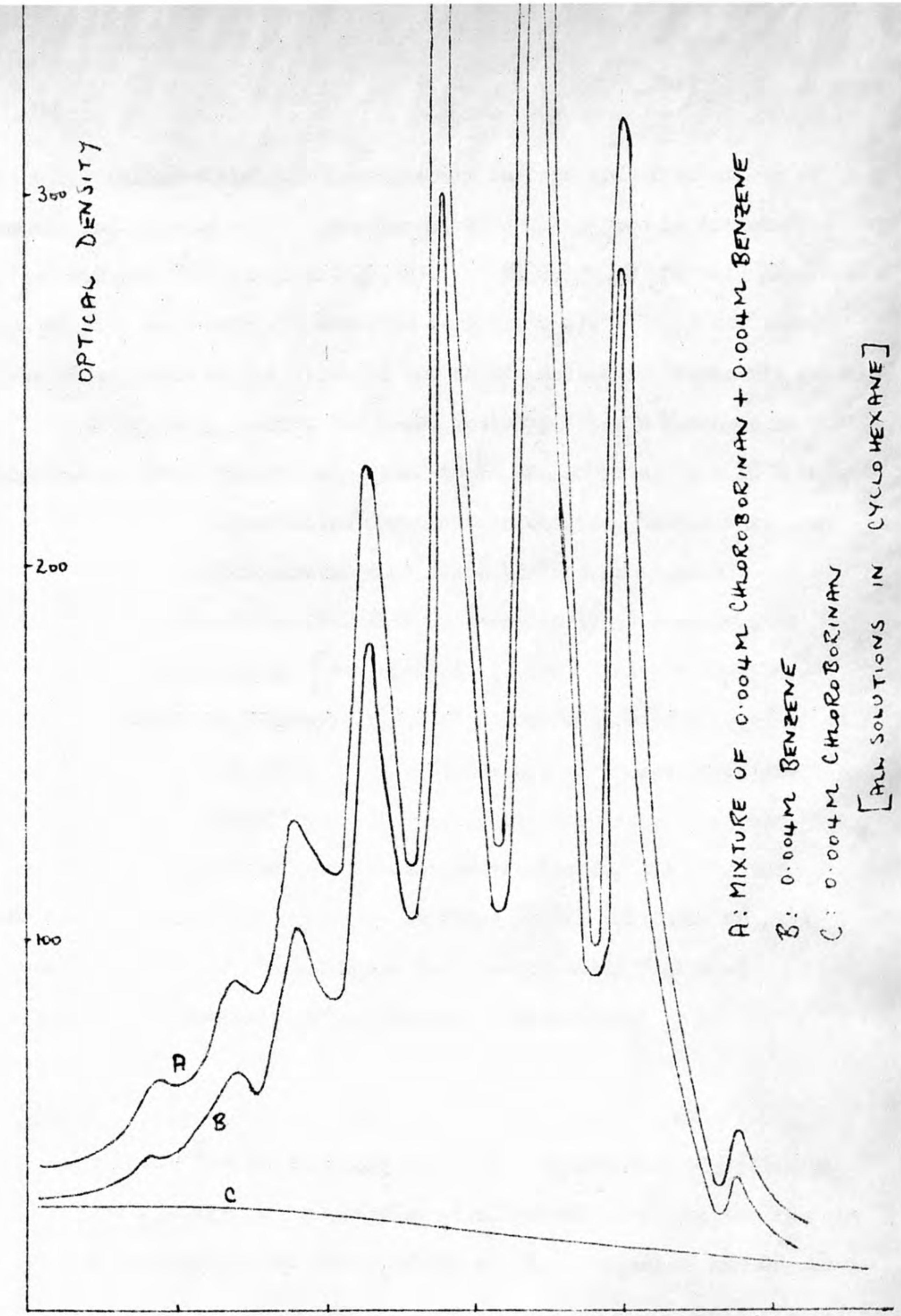
solution is that the electronegativity difference between boron and sulphur is very small compared with that of boron and oxygen (electro negativities on a Pauling scale B, 2.0 ; O, 3.5 ; S, 2.5)

(b) Inans

2-chloro-1,3,2 dioxaborinan is considerably less stable at room temperature than the olan analogue. When pure it is a colourless mobile liquid which darkens appreciably over a period of ~30 mins. In both benzene and nitro benzene solution it exhibits a concentration - independent degree of association of approximately 1.1. This association, although small, is well beyond the limits of experimental error. It is, moreover, unexpected and the cryoscopic determination, over the entire concentration range, was repeated several times. This anomalous result could be due to two reasons :-

(i) slow pyrolysis throughout the determination affecting the result, or
(ii) solvent-solute interaction i.e. formation of a weak π-complex between benzene and the electrophilic boron.

To test the first theory the freezing point of an ~ 0.2 M solution of 2-chloro 1,3,2 dioxaborinan was determined; the cryoscopic cell was then maintained at 70°C. for ca. 60 mins. and the freezing point re-determined. No change was observed. It would be expected that if benzene forms a charge-transfer complex with the borinan a shift or loss of fine structure would occur in the characteristic B-band of benzene



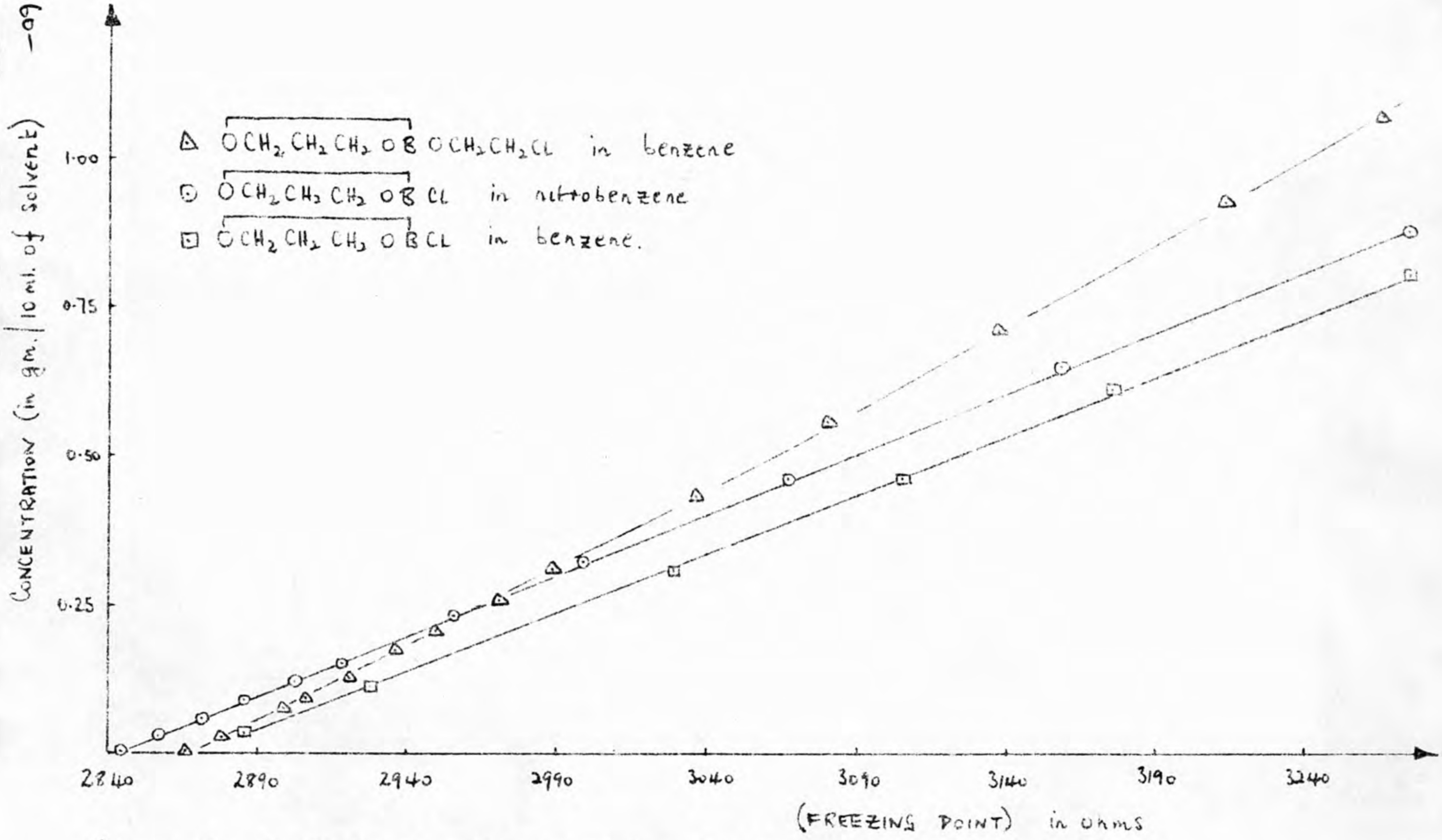
GRAPH 4: ULTRA-VIOLET SPECTRA OF CHLOROBORINAN AND BENZENE

at 255 mμ. (ultra-violet). Consequently the spectra of solutions of chloroborinan, benzene and a equimolar mixture of the two in cyclohexane were recorded over the range 220-290 mμ . No shift of the band envelope or loss of fine structure was observed (see Graph 4). It is concluded that the association of 1.1 observed for chloroborinan in benzene is genuine.

Of the inan esters, the 2-chloroethoxy ester is known to be stable. Cryoscopically, this compound was found to be monomeric up to 0.16 M then exhibiting a slight concentration dependent association beyond this concentration. This is illustrated in a graph of concentration vs. depression (also shown in similar form is 2-chloro 1,3,2 dioxaborinan in benzene and nitrobenzene) [see Graph 5 .] Two thioinans (2-chloro-1,3,2 dithioborinan and 2-phenyl- 1,3,2 dithioborinan) were also examined in benzene solution. The former exhibited a constant concentration-independent degree of association of $\sim$1.1 while the latter was monomeric at all concentrations. The detailed results for all compound studied cryoscopically are presented in Table VIII; molecular weights are quoted at 0.05, 0.2 and 0.5 M and the corresponding degree of association at these molarities are quoted in parentheses.

(c) General discussion.

From the results outlined above it is clear that there are at least two modes of association operating i.e. concentration-dependent and concentration-independent modes, which may be ascribed to any of the



GRAPH 5 : DEPRESSION VS. CONCENTRATION PLOTS FOR SOME DIOXABORINANS

TABLE VIII : MOLECULAR WEIGHTS AT THREE MOLARITIES

COMPOUND	BOILING POINT °C / mm Hg.	MOLECULAR WEIGHT			Calcd. M. Wt.
		0·05M	0·2M	0·5M	
$\overline{OCH_2CH_2OB}Cl$	/	130 (1·22)	200 (1·88)	260 (2·44)	106·3
		130 (1·22) †	168 (1·58) †	220 (2·07) †	
$\overline{OCH_2CH_2CH_2OB}Cl$	22-24 / ·05	135 (1·12)	135 (1·12)	135 (1·12)	120·3
		130 (1·08) †	130 (1·08) †	130 (1·08) †	
ϕBCl_2	66 / 18	161 (1·01)	161 (1·01)	—	158·8
$(Bu^nO)_3B$	232 / 760	226 (0·98)	226 (0·98)	—	230·2
$\overline{OCH_2CH_2CH_2OB}OCH_2CH_2Cl$	57-58 / ·05	169 (1·03)	169 (1·03)	189 (1·15)	164·4
$\overline{OCH_2CH_2OB}OBu^n$	58-60 / ·05	146 (1·01)	233 (1·62)	346 (2·40)	144·0
$\overline{OCH_2CH_2OB}OCH_2CH_2Cl$	59-60 / ·05	152 (1·01)	305 (2·03)	374 (2·49)	150·4
$\overline{SCH_2CH_2SB}Cl$	24-25 / ·05	141 (1·02)	141 (1·02)	—	138·5
$\overline{SCH_2CH_2CH_2SB}Cl$	52 / ·1	165 (1·08)	165 (1·08)	—	152·5
$\overline{SCH_2CH_2SB}\phi$	90-92 / ·05	179 (0·99)	179 (0·99)	—	180·1
$\overline{SCH_2CH_2CH_2SB}\phi$	110-111 / ·05	196 (1·01)	196 (1·01)	—	194·1
$\overline{OCH_2CH(CH_3)OB}Cl$	38 / ·1	120 (1·00)	134 (1·11)	147 (1·22)	120·3
$\overline{OCH(CH_3)CH(CH_3)OB}Cl$	26-27 / ·1	147 (1·09)	147 (1·09)	147 (1·09)	134·4

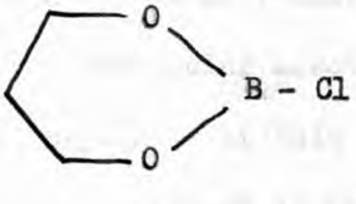
† in nitrobenzene solvent ; all others in benzene.

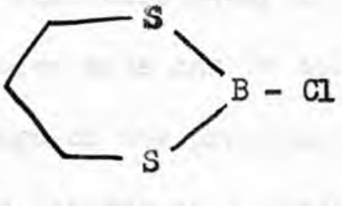
three associative models (assuming ten-membered ring formation to be unlikely). The models of association are boron-oxygen "loose packing" (B - O), boron-oxygen four centre interaction (B - O)* and chlorine bridging (B - Cl). All olan systems studied show association with the exception of the **thio** compounds and 2-phenyl-1,3,2 dioxaborolan. The boron oxygen nucleus in this latter example is probably shielded by $2p_z - \pi$ overlap to prohibit any association. From the physical state of the sulphur containing heterocycles and the fact that the boiling point increases with molecular weight (the opposite effect is apparent in the B-chlorodioxa heterocycles) we must conclude that either

(i) the small electronegativity difference of boron and sulphur precludes assocation, or

(ii) a five membered thio-heterocycle is strain free.

Accepting this fact for the moment, the only heterocycles which exhibit a concentration-independent associative mode are those containing the boron chlorine group and a six-membered skeleton or a sterically hindered skeleton (i.e. one which would preclude stacking arrangements). These heterocycles are





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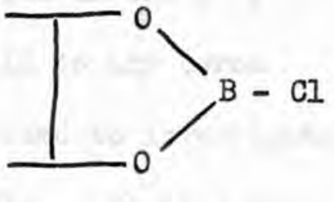


To heterocycles of this nature is ascribed a small concentration-independent associative mode; it would be presumptive to assume that this mode is, in fact, chlorine-bridging. It is worthy of mention that Köster[44] reports that 2-chloroborolan is monomeric in benzene solution. It would be interesting to have similar data for 2-chloroborinan. Many of the esters studied exhibit an association greater than two; this must be due to a combination of (B - O) and (B - O)* association or solely (B - O) association. 2-(2'chloroethoxy) dioxaborinan exhibits association only at high concentrations because the inan skeleton is relatively unstrained and the transposition of boron (Sp^2) to boron (Sp^3) via association does not lead to an energetically more stable state. A general property of the esters is that in dilute solution they are monomeric. 2-chloro-1,3,2 dioxaborolan was not monomeric at any concentration and it is possible that, in this case, the concentration-dependent association ascribed to the esters is superimposed on the concentration independent association ascribed to "chlorine-bridging". Why any form of association which, after all, is an equilibrium between monomer and multiples of monomer, should be independent of the concentration of the species is difficult to imagine. It is realised that this study is not conclusive in the respect that a particular associative mode can be ascribed at will to any boron heterocycle. At this stage of the programme it was decided to investigate the "association" in these systems on a quantitative basis. To this end a calorimetric technique was applied and is described in the following section. Detailed cryoscopic data are tabulated in Appendix III.

SECTION 4 : CALORIMETRY

The quantity most usually derivable from thermochemical measurements is the heat of formation of compounds under standard conditions of temperature and pressure. It is usually not practical to determine the heat of formation of a compound directly from its constituent elements and the normal procedure is to measure the enthalpy change of a reaction of the compound which yields products of known heat content. This forms the basis of degradative oxidation reactions, usually performed in a bomb at constant volume, for the heat contents of carbon dioxide, water etc. are accurately known. The reactions studied in this section are hydrolyses or solution reactions as opposed to oxidation reactions. A prerequisite of any reaction to be studied thermochemically is that its stoichiometry be known exactly. It is for this reason that degradative oxidation procedures are not applicable to boron compounds because the formation of the oxide is not stoichiometrically reproducible. Also, for this reason, only the B-chloro-heterocycles are studied here because these hydrolyses proceed quantitatively in aqueous solution to yield a diol, boric acid and hydrogen chloride. For these reaction products accurate enthalpy data is either available or readily determined. It would be interesting to study the hydrolyses of the esters also but for these compounds some preliminary kinetic work is necessary to establish the position of the hydrolytic equilibrium. Normal thermodynamic conventions[45] are followed in the selection of standard states for reactants; the standard state being the most stable form existing at 1 atmosphere pressure at 25°C. The standard heat of formation of the elements in their standard states is zero and an enthalpy, if heat is absorbed, is regarded as positive. Any enthalpy change recorded for reactants in their standard states is followed by a superscript o, e.g. ΔH^{o}. To be meaningful, any solution enthalpy changes must be recorded in conjunction with the mean temperature of the reaction period and the concentration of the reactant (usually expressed as the ratio of the number of moles of solvent to the number of moles of reactant).

All thermochemical reactions were carried out in an all-glass calorimeter, the temperature changes being followed with a thermistor and a miniature platinum resistance thermometer. Full details of the experimental technique and the apparatus are outlined in Part II, Experimental, Sections 2 and 3. Information on the energetics of dioxaboron heterocycles is limited to the work of Dale[17] who measured the heats of complexing of n-butyl esters of B-chloro-inans and -olans with pyrrolidine and with benzylamine in octane solution. Dale was unable to isolate the amine complexes without decomposition and it is doubtful if the complexing reactions proceeded to completion, especially in the cases where the complex remained in solution (i.e. all of the pyrrolidine complexes). As a result, Dale's data does not appear to be consistent with the data recorded here for similar structures. For the compounds studied here no steric hindrance is to be expected from the attacking nucleophile and the results should be internally consistent. In general, it is true to say that the precision and accuracy of the subsequent measurements are limited by the purity and thermal stability of the compounds and not by the apparatus or experimental technique. All heat quantities are quoted in thermochemical calories, 1 cal. = 4.1840 abs. joules.

Let us consider the reaction sequence on the hydrolysis of a hypothetical heterocycle, $\overline{\mathrm{O\ R\ O\ B}}\mathrm{.Cl}$. When the heterocycle comes into contact with the solvent (water) it hydrolyses and this is followed by the dissolution of the hydrolysis products. It is unnecessary to consider the dissolution of the heterocycle prior to hydrolysis because this step in the reaction sequence is equivalent, in all respects, to the hydrolysis stage. The observed enthalpy change on hydrolysis is, then, a combination of two factors. The observed heat of hydrolysis, ΔH obs., refers to the reaction

$$\overline{\mathrm{O\ R\ O\ B}}\ \mathrm{Cl\ (liq.)} + (n+3)\ \mathrm{H_2O\ (liq.)} \longrightarrow (\mathrm{H_3Bo_3} + \mathrm{R(OH)_2} + \mathrm{HCl})\ \mathrm{n.\ H_2O}$$

and the standard heat of hydrolysis ΔH_h^o refers to

$$\overline{\mathrm{O\ R\ O\ B}}\ \mathrm{Cl\ (liq.)} + 3\mathrm{H_2O\ (liq.)} \longrightarrow \mathrm{H_3BO_3(cryst.)} + \mathrm{R(OH)_2(liq.)} + \mathrm{HCl(g)}$$

These two functions are related by the expression

$$\Delta H\mathrm{obs} = \Delta H_h^o + \Sigma \Delta H_s^o\ \text{(reaction products)}$$

where ΔH_s^o = heat of solution at 25°C. and mole ratio N.

The standard heat of formation of the heterocycles is obtained from equations of the form

$$\Delta H_f^o \left[\overline{\mathrm{OROB}}.\mathrm{Cl},\ \mathrm{liq}\right] = \Delta H_f^o \left[\mathrm{R(OH)_2},\mathrm{liq}\right] + \Delta H_f^o \left[\mathrm{H_3BO_3},\ \mathrm{cryst.}\right] + \Delta H_f^o \left[\mathrm{HCl},\ \mathrm{g}\right] - 3\Delta H_f^o \left[\mathrm{H_2O},\ \mathrm{liq.}\right] - \Delta H_h^o$$

In using this equation the following data were taken from the National Bureau of Standards, Circular 500[25];- the standard heats of formation, solution and dilution of hydrochloric acid and the standard heat of formation and solution of ethan 1,2 diol.

The heat of solution function in the equation for ΔHobs is the <u>standard</u> heat of solution i.e. that in infinitely dilute solution when $N = \infty$. In practice this is usually determined by extra-polation of data recorded at a series of concentrations. Experimentally this is a tedious procedure and in addition heats of dilution are usually very small e.g. ΔH_s methanol, 298°A and $N = 25$ is 1.59 kcal/mole and the corresponding figure at infinite dilution is 1.75 kcal/mole. In this work the heats of solution of various diols were determined at two different concentrations (say $N = \sim 100$ and ~ 200) to confirm that the heat of dilution was very small. In general, the heat of dilution is less than the limits of accuracy obtainable with the calorimeter. Heats of solution for diols determined in this manner are recorded in the table below.

TABLE IX. HEATS OF SOLUTION AND FORMATION OF SOME DIOLS.

Diol	T(°C)	ΔH_s(exp.)	N	ΔH_s(accepted)	ΔH_f^o(liq.)
Propan 1,3	25	-2,05	105	-2.04 ± .02	-112 ± 2
	25	-2.03	206		
Propan 1,2	25.6	-2.62	145	-2.63 ± .01	-118.9 ± 1
	25.6	-2.63	235		
Butan 2,3*	26.2	-3.57	174	-3.58 ± .03	-128.7 ± 1
	30.5	-3.54	263		
	30.5	-3.62	215		
Ethan 1,2	25	†	200	-1.5 ± .05	-108.74 ±·1[46]

† NBS. Circ. 500 * this diol solidifies over the range 22-26°C.; to avoid inclusion of ΔH fusion, the dissolution was checked at 30°C.

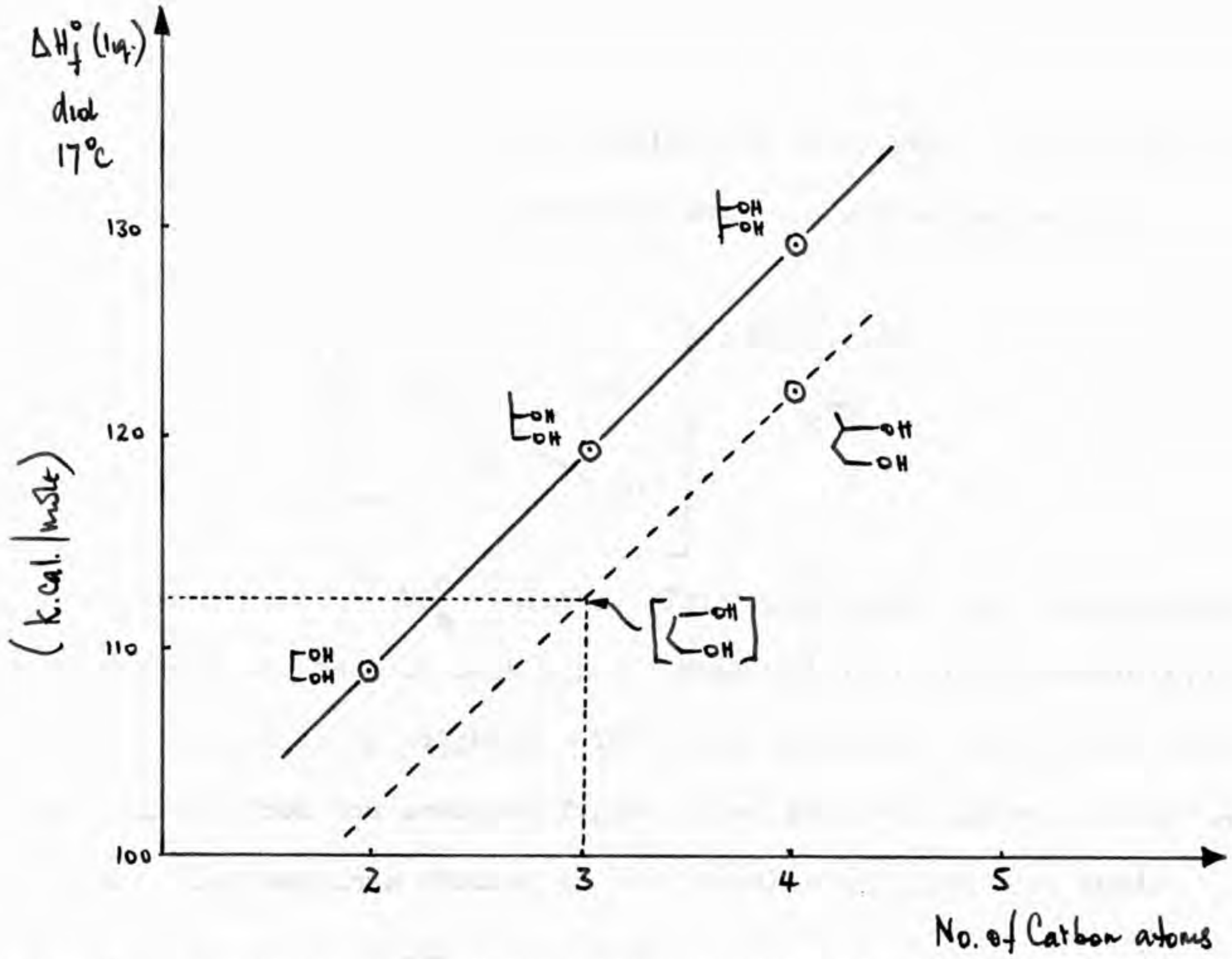
[all values in k cal./mole.] .

The heats of formation of propan 1,2 and butan 2,3 diols were taken from Moureau and Dode[47] and that of ethan 1,2 diol from Green[46]. Moreau and Dode's (1937) data is quoted at 17°C. and calculated on the basis of old values for the standard heats of formation of carbon dioxide and water. The values were corrected using the now accepted values and assigned an error of ± 1 kcal./mole. Moureau and Dode's data are quoted in the table below.

TABLE X. HEATS OF FORMATION OF SOME DIOLS AT 17°C. (taken from Moureau and Dode)[47].

Diol	ΔH_f^o (liq.) 17°C.
Ethan 1,2	107.9
Propan 1,2	118.9
Butan 1,2	124.4
Butan 1,3	122.3
2-methyl propan 1,2	128.2
Butan 2,3	128.7

The standard heats of formation of the alcohols $CH_3(CH_2)_nOH$ (n = 1,2,3 ...) vary in an approximately linear fashion with n. (this is not unexpected because for each increment in n, one C - H bond is cleaved and one CH_3 - C bond is formed). Constructing a similar graph for Moureau and Dode's data a value for the standard heat of formation of propan 1,3 diol may be interpolated

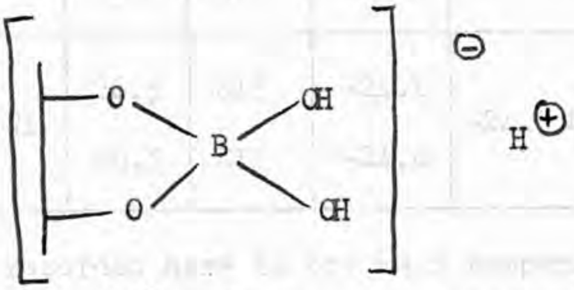


GRAPH 6 : STANDARD HEAT OF FORMATION OF DIOLS VS. CARBON CHAIN LENGTH.

The interpolation is very approximate and the value of 112 was assigned an error of ±2 k cal./mole.

The standard heat of solution of boric acid is that of Van Artsdalen[48] i.e. - 5.166 ± 0.036 k cal./mole at 298°A. and N = 1110. Davis [49] et al quote the standard heat of dilution of boric acid from N = 60 to N = 9252 as + 0.068 k cal./mole. Clearly, dilution effects may be ignored. The standard heat of formation of boric acid (crystal) is a recent value (1963) of Good et al[50] and is -261.47 k cal./mole at

298°A. In all of the hydrolyses studied the hydrolysis products included a diol and boric acid. It is possible that complexing may occur



and lead to anomalous ΔH^o_h values. This possibility was investigated by determining the heat of solution of butan 2,3 diol in saturated boric acid solution (~ 6% by weight). The value obtained, -3.40 k cal./mole differs little from the accepted figure of -3.58 k cal./mole. and may be ignored. The compounds studied and the results obtained from their hydrolyses are shown in the table below.

TABLE XI. HEATS OF HYDROLYSIS AND FORMATION OF SOME BORON HETEROCYCLES

Compound	T(°C)*	N	ΔHobs.	ΔHobs. (accepted)	ΔH^o_h †	ΔH^o_f(liq.) †
$\overline{OCH_2CH_2CH_2\ O\ B}Cl$	27.5	336	-22.2	-22.15 ± 0.4	-7.51±.5	-183.1 ±3
	25.2	329	-22.1			
$\overline{OCH_2CH_2\ O\ B}Cl$	25.5	1410	-21.2	-21.1 ± 0.5	-6.91 ± .6	-180.4 ± 1
	26.0	870	-21.7			
	25.6	2230	-20.9			
	26.0	1074	-21.2			
	26.0	1098	-20.4			

Compound	T(°C)*	N	ΔHobs.	ΔHobs. (accepted)	ΔH°_{h} †	ΔH°_{f}(liq.) †
$\overline{OCH(CH_3)CH_2O\ B}Cl$	26.2 25.2	838 1497	-22.6 -22.5	-22.5 ± .2	-7.23 ± .3	-190.3±1
$\overline{OCH(CH_3)CH(CH_3)O\ B}Cl$	26.5 26.5	845 812	-24.1 -24.8	-24.5 ± .4	-8.28 ± .5	-199.0±1.7

* the temperature recorded here is the mean temperature of the reaction period.

† errors were computed by summation of the constituent errors.

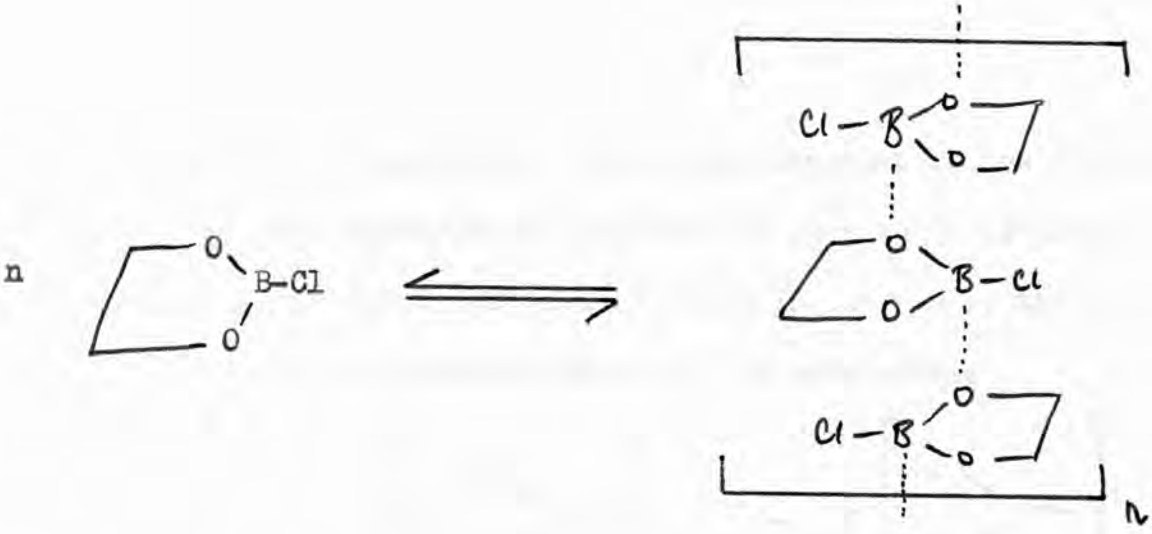
The deviation from the mean is greatest in the case of 2-chloro 1,3,2 dioxaborolan as this compound, due to its extremely viscous nature, is very difficult to load into ampoules. Because this compound is known to be less associated in solution than in the pure phase, the heat of hydrolysis of a concentrated solution of the B-chloroborolan in benzene (~40% by weight) was measured in an attempt to estimate the strength of the associative bonding. High speed stirring and a large water to benzene ratio (approx. 50 : 1) ensures abstraction of the hydrolysis products into the aqueous medium. The heat of solution of benzene in water (aqueous solubility ~ 0.08 g./100g. H_2O) was undetectable as indicated by a control experiment. The results are presented in Table XII.

TABLE XII. HEAT OF HYDROLYSIS OF A BENZENE SOLUTION OF 2-CHLORO-1,3,2 -DIOXABOROLAN

Expt.	N	T	ΔHobs	ΔHobs (accepted)	ΔH^{o}_{h}
1	356	26.6	-22.2	-21.7 ± 0.5	-7.57 ± .05
2	308	27.0	-21.3		
3	616	26.6	-21.6		
4	443	26.7	-21.7		

As is expected the mean figure is slightly more exothermic than that for the pure phase hydrolysis but the limits of uncertainty on the data preclude any assignment of the strength of associative bonding.

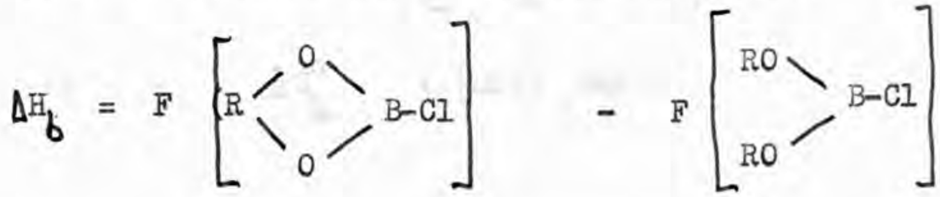
In discussing the strain present in boron heterocycles, two approaches may be considered. The strain inherent in a cyclic system may be relieved via two alternative routes; (a) conversion of the cycle to a structure of zero or reduced strain by a hybridization change about one or more atoms in ring or (b) by ring opening. The first case is illustrated by 2-chloro 1,3,2 dioxaborolan in a "loose packing" arrangement



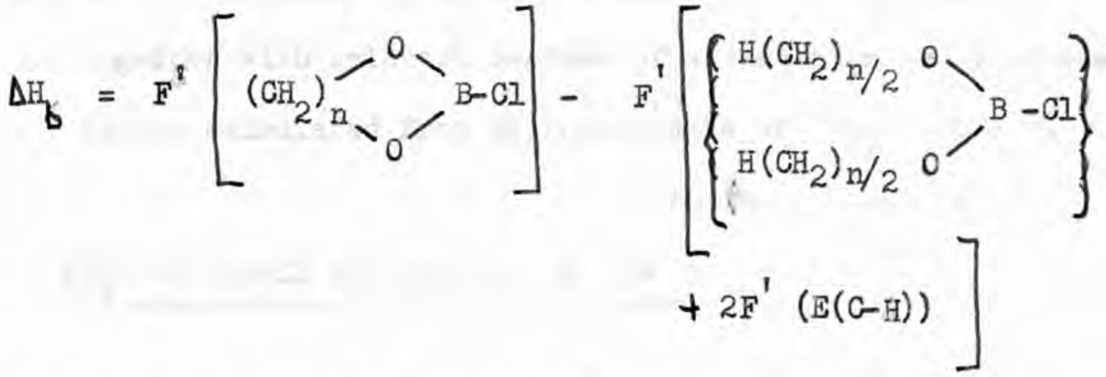
and the second by trimethylene carbonate which polymerises readily on heating[51]

Let the enthanpy changes in these two types of process be ΔH_a and ΔH_b respectively. Brown's[27] work on the free energy of dissociation of trimethyl boron amine complexes at different temperatures gives a measure of ΔH_a. This function is made up of two principal components; the adjustment energy required for the $sp^2 \rightarrow sp^3$ hybridisation change and the energy of formation of the donor-acceptor bond. As mentioned in the section on cryoscopy the detailed structure of associated forms of boron heterocycles cannot be regarded as unequivocably established. It is premature to discuss strain therefore in terms of ΔH_a and a function of the type ΔH_b is suggested. This function must be the difference between a measured parameter of the heterocycles and a similar parameter for an acyclic structure containing a similar nucleus to the heterocycle or having the same empirical formula as the heterocycle

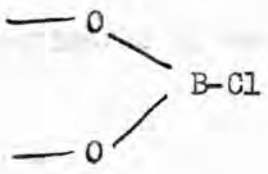
i.e.



or

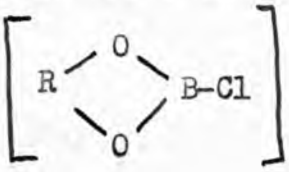


In the latter case F' depends on the number of carbon atoms in the heterocycle and the final term varies from one heterocycle to another; such a function would be the standard enthalpy of formation. Since the literature on enthalpies of formation of acyclic B-chloro compounds is limited, a function of the type F, independent of the number of carbon atoms, would be preferable. In this case the final term would depend on the nucleus of heterocyclic system only. The compounds studied here all have the nucleus



and Skinner [24] has recorded data on the compound $(Eto)_2BCl$ containing this nucleus. The function proposed for F is ΔH^o_h so

$|\Delta H_b|$ = ΔH^o_h



\- Constant

where constant = ΔH^o_h ($[EtO]_2BCl$)

ΔH_b is defined specifically by the above relationship and values of this function together with relevant degrees of association are tabulated below using a figure calculated from Skinner's date of ΔH^o_h $(EtO)_2BCl$,liq = 6.06 ± .8 k cal./mole.

TABLE XIV ΔH_b AND DEGREE OF ASSOCIATION (α)

Compound	H_6	α
$\overline{\mathrm{OCH_2CH_2CH_2\ O\ B}}\ \mathrm{Cl}$	1.4	1.1
$\overline{\mathrm{OCH_2CH_2\ O\ B}}\ \mathrm{Cl}$	0.9	>5
$\overline{\mathrm{OCH(CH_3)CH_2\ O\ B}}\ \mathrm{Cl}$	1.2	~ 2
$\overline{\mathrm{OCH(CH_3)CH(CH_3)\ O\ B}}\ \mathrm{Cl}$	2.2	1.1

The degrees of association of the compounds showing concentration-dependent association are estimated by extrapolation of the graphs to infinite molarity i.e. pure phase. It is of interest to examine the form of the function, as defined, in terms of standard heats of formation

$$\Delta H_b = \left\{ \Delta H_f^\circ \left[\overline{\text{OROB}}\text{Cl, liq.} \right] - \Delta H_f^\circ \left[\text{R(OH)}_2\text{, liq.} \right] \right\} - \left\{ \Delta H_f^\circ \left[(\text{EtO})_2\text{B Cl, liq} \right] - 2\,\Delta H_f^\circ \left[\text{EtOH, liq} \right] \right\}$$

The changing structure of the aliphatic part of the ring is compensated for by the term, $\Delta H_f^\circ \left[\text{R(OH)}_2\text{, liq} \right]$.

The extent of the ring strain is expected to be inversely proportional to the degree of association. This relationship is observed for the dioxaborolans in Table XIV. The strain of the inan system i.e. 1.4 k cals./mole is presumably less than the activation energy required for the process boron (sp^2) to boron (sp^3). This activation energy has been established for certain boron halide / amine complexes[66] as being of the order of 1-3 k cal. Confirmation of certain other predictions arises from the ΔH_b values. 2-chloro-1,3,2 dioxaborolan, which is expected stereochemically to show considerably greater strain than the analagous dioxaborinan, is apparently less strained in the pure phase. This is in accord with its highly associated state. The 4,5 dimethyl compound which exhibits little association due to the steric hindrance of the methyl groups is most highly strained. It is not possible to deduce the energy of the associative bonding present in the pure phase from the results recorded here. This point is clarified by the following cycle.

If A represents the dioxaboron hetercycle

$$\begin{tikzcd}
n\,A(g)\,\left[Sp^3B\right] \arrow[rr, "n\,E\,(B \longleftarrow O)"'] & & An\,(g) \\
n\,A(g)\,\left[Sp^2B\right] \arrow[u, "\Delta H_a"'] & & \\
n\,A\,(\text{liq}) \arrow[u, "\Delta Hr(m)"'] & & An\,(\text{liq}) \arrow[uu, "\Delta H_r(a)"'] \\
\left[\text{B, O, C, H, Cl Standard States}\right] \arrow[u, "n\,\Delta H^o_f(m)"'] \arrow[urr, "\Delta H^o_f\,(a)"'] & &
\end{tikzcd}$$

where

n = degree of association present in the pure phase

$E\,(B \longleftarrow O)$ = energy of the associative bond

$\Delta H^o_f(m)$ = standard enthalpy of formation of monomer

$\Delta Hr(m)$ = standard enthalpy of vaporisation of monomer

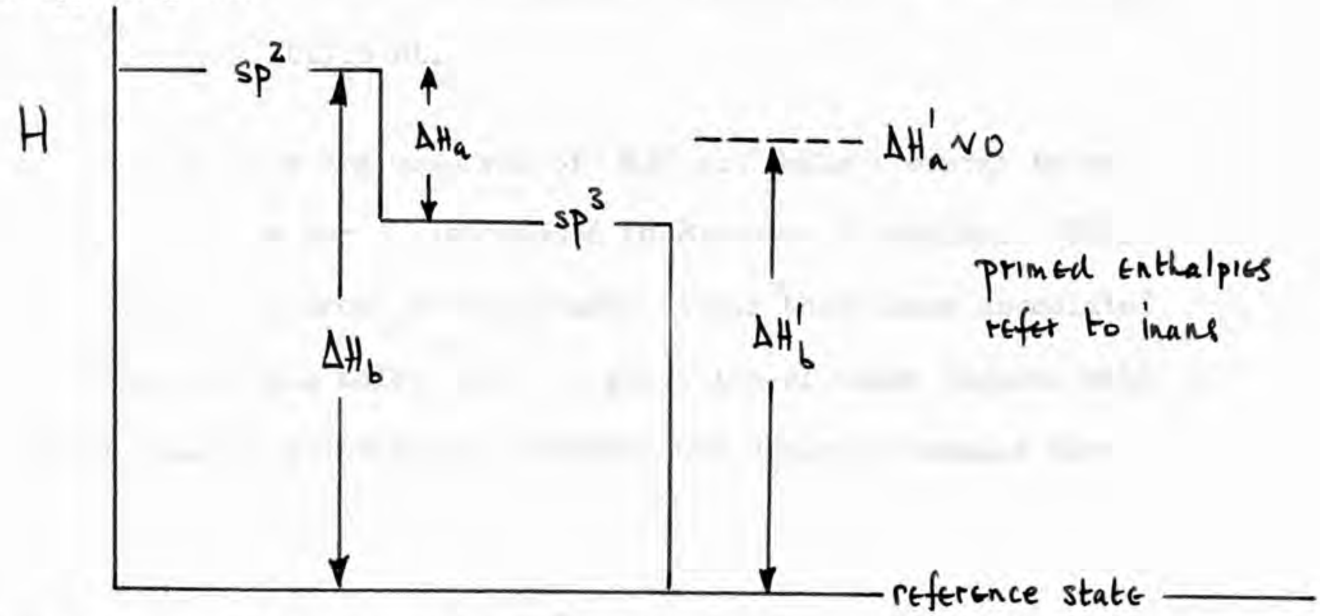
ΔH_a = enthalpy change associated with the hybridization change $B(Sp^2)$ to $B(Sp^3)$

$\Delta Hr(a)$ = standard enthalpy of vaporisation of the associated state

$\Delta H^o_f(a)$ = standard enthalpy of formation of the associated state.

The only components of this cycle obtainable from this work are $\Delta H^o_f(a)$ and estimates of n and ΔHa. The value of ΔH_b for 2-chloro-4,5 dimethyl 1,3,2 dioxaborolan may be taken, as a first approximation, as the strain inherent in the dioxaborolan ring. It is interesting to note that the difference, on this scale, between this figure and ΔH_b for the corresponding dioxaborolan is surprisingly small, of the order of one kilocalorie/mole. This is, to some extent, substantiated by recent work on the association of tri-iso propanolamine borate in benzene solution where the strength of the dipole-dipole self association is reported to be of the order of two kilocalories/mole of monomer[61]. Because the inherent strain in the inan system ($\sim$ 1.4 k cals/mole) is less than the activation energy for transposition of trigonal boron to tetrahedral boron formation of associated structures or Lewis base addition does not occur.

In view of the marked physical and chemical differences between olan and inan systems and the comparatively small enthalpy difference, the entropy change of the $Sp^2 \longrightarrow Sp^3$ transposition may be of greater significance. These conclusions are summarised in the following enthalpy diagram.



GRAPH 7 : ENTHALPY DIAGRAM FOR OLANS (————) AND INANS(-----------)

The measurements of Dale[17] on the heat of complexing (ΔH_c) of benzylamine and pyrrolidine with the n-butoxy esters of these systems is of interest and the results for pyrrolidine are listed below.

TABLE XV. HEAT OF COMPLEXING OF PYRROLIDINE N-BUTOXY ESTER OF OLANS AND INANS

Heterocycle	Δ Hc (kcal/mole)
$\overline{OCH_2\ CH_2O\ B}\ O\ Bu^n$	- 8.3
$\overline{O\ CH_2\ CH(CH_3)OB}\ O\ Bu^n$	- 10.5
$\overline{O\ CH(CH_3)\ CH(CH_3)\ O\ B}\ O\ Bu^n$	- 8.3
$(Bu^n\ O)_3\ B$ †	- 0.5

† an unstrained molecule; comparable with the reference compound $(EtO)_2B\ Cl$.

These data are measures of ΔHa and reflect energy terms associated with $B \leftarrow N$ as opposed to $B \leftarrow O$ bonding. These energies are, of an order of magnitude, larger than those associated with self-associating molecules. A gradation of these figures with successive ring substitution is probably not observed because the addition reactions were performed completely in the solution phase and probably did not proceed to completion.

In conclusion, it is fair to say, that in general the results obtained from calorimetry confirm those of cryoscopy but neither yield a conclusive physical picture of the association in dioxaboron heterocycles.

EXPERIMENTAL

SECTION 1 : General techniques

(a) Handling

Many of the compounds studied are readily hydrolysable in moist air. When adding samples to the cryoscopic cell a stream of dry nitrogen, issuing from a large fitted funnel directed towards the cell, was used to prevent hydrolysis. When loading ampoules for the calorimeter, hydrolysis was avoided by loading in a dry-box full of nitrogen.

The most successful method for transferring the extremely viscous 2-chloro-1,3,2 dioxaborolan was to condense the compound on a large cold finger maintained at -196°C. ; then allow it to melt slowly by warming the condenser and fall into liquid nitrogen in a dry box. In this way small pellets could be transferred into thin glass ampoules used for calorimetry without the compound adhering to the neck of the ampoule. Also handling at this low temperature will completely quench any pyrolytic decomposition.

When derivatives were stable and liquid they were purified by distillation in an all-glass apparatus equipped with ground glass joints. The majority of distillations were performed under vacuum using a rotary oil-pump supplying a pressure of approximately 0.05 mm. of mercury. Specialised condensing equipment was used which is fully described in a recent thesis (1962)[37].

(b) Spectra

All infra-red spectra were recorded on a Perkin-Elmer Infracord 137 (rock-salt optics) either as liquid films or in 0.05 mm cells at 0.125 M concentration in carbon tetrachloride. Ultra-violet spectra were recorded on a Unicam S.P.500 spectrophotometer using 1 cm. closed silica cells and cyclohexane as solvent.

(c) Elemental analysis

Carbon, hydrogen, nitrogen and chlorine analyses were obtained from either Weiler and Strauss, Microanalytical Laboratory, Oxford or Bernhardt, Max Planck Institute, Mülheim.

Easily hydrolysable chlorine (i.e. that in the form B-Cl) was determined by aqueous hydrolysis followed by a volumetric titration using standard alkali to a methyl red end point. Boric acid in the presence of excess mannitol acts as a monobasic acid which may be estimated with standard alkali to a phenolphthalein end-point. The method used to oxidise the boron to boric acid in an organo boron compound depends on the structure of the compound. These are briefly summarised:

(i) Compounds containing the borate nucleus: aqueous or methanolic hydrolysis followed by titration with standard alkali in the presence of mannitol to a phenolphthalein end-point.

(ii) Compounds containing the boronate nucleus:

if the third bond is B - C or B - N, quantitative oxidation is achieved using trifluoroperoxy acetic acid followed by a fixed pH potentiometric titration in the presence of mannitol[62]. Graded oxidative procedure for the analysis of boron compounds is reviewed by Pierson[52].

(d) Purification

Certain compounds were available commercially but were purified prior to use. Benzene : available in "cryoscopic" grade from British Drug Houses (B.D.H.) and was dried over sodium wire before use.

Carbon tetrachloride : Analar grade (B.D.H.) dried over 4 Å molecular sieves (B.D.H.)

Nitrobenzene : Analar grade distilled from anhydrous calcium chloride up a 12" column packed with helices. Fraction collected over 210-211°C./ 760 mm, lit. 210.6-210.8°C./760.

Tri n-butyl borate : Ordinary grade B.D.H.) distilled up a similar column at atmospheric pressure.

Fraction collected over 230-231°C./760 mm. n^{25}_{D} = 1.4071, lit. 232.4°C./760 mm. n^{25}_{D} = 1.4071.

(e) Refractive indeces

All refractive indeces were recorded using an Abbé refractometer with the block thermostatted at 25°C. and with a sodium D line source.

SECTION 2 : Syntheses.

All of the syntheses in this thesis were of the condensation type described by the following equations:-

$$BCl_3 + R(OH)_2 \longrightarrow \overline{O\,R\,O\,B}\,Cl + 2\,HCl$$

$$\overline{O\,R\,O\,B}Cl + R'OH \longrightarrow \overline{O\,R\,O\,B}\,OR' + HCl$$

$$R'\,O\,BCl_2 + R(OH)_2 \longrightarrow \overline{O\,R\,O\,B}\,OR' + 2\,HCl$$

$$2\,BCl_3 + R(OH)_2 \longrightarrow Cl_2\,B - OR - O\,BCl_2 + 2\,HCl$$

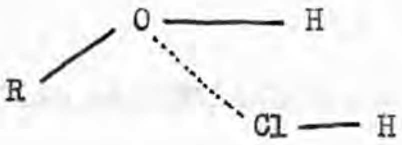
$$Cl_2BO\,R\,O\,BCl_2 + 4R'OH \longrightarrow (R'O)_2\,B - ORO\,B(OR')_2 + 4\,HCl$$

$$2\,BCl_3 + 3\,ROH \longrightarrow \overline{O\,R\,O\,B}\,O\,R\,O\,\overline{B\,ORO} + 6\,HCl$$

The experimental technique in each case is very similar and will be described in detail once in order that subsequent experimental procedure may be recorded in a more concise form.

In each case the boron-containing compound (e.g. BCl_3, $\overline{O\,RO\,B}\,Cl$, etc.) is dissolved in approximately 25 ml. of methylene chloride. The reaction flask is equipped with a variable speed stirrer, a -80°C. reflux condenser and a dropping funnel for the second reactant. The reaction flask is cooled to -80°C. in a mixture of crushed solid carbon dioxide and acetone, the stirrer started and the alcohol or diol added at a rate such that the reaction proceeds smoothly. It is worthy of note that there is often an induction period for these reactions and occasionally the flask must be warmed slightly to initiate the reaction. The reflux condenser prevents loss of boron trichloride or any other volatile component (such reactions usually proceed with appreciable exothermicity) and is connected directly to two -196°C.

traps in series. These serve a dual purpose; they prevent moisture from entering the reaction system and they collect the evolved hydrogen chloride. When the reaction is complete the flask is allowed to warm to room temperature. Often it is observed that the latter stages of the reaction proceed with less vigour than the initial stages. This is probably due to a weak association between the dissolved hydrogen chloride and the alcohol,



this association reducing the nucleophilic tendency of the oxygen atom. The evolved hydrogen chloride collected in the -196°C. traps is estimated volumetrically with standard alkali to a methyl red end-point. This estimation provides a check on the theoretical stoichiometry of the reaction. It is, however, rare that 100% of the theoretical hydrogen chloride is estimated owing to the high solubility of the gas in the solvent, methylene chloride. The reaction flask is removed and the solvent (b.p. 40°/760 mm) stripped by pumping at ice or room temperature. The crude product, if stable, is then vacuum distilled. Any deviations from this standard procedure will be mentioned in the following condensed syntheses:-

Attempted preparation of 2-chloro-1,3,2 dioxaborepan. - Boron trichloride (25 g. 0.21 mol.) was added to butan 1,4 diol (19.2 g. 0.21 mol). After the solvent was removed a brown non-distillable syrup remained (boron content of residue = 6.1%).

Preparation of methyl chloroborinate. - Dry methanol (4.0 g. 0.12 mol) was added to boron trichloride (14.7 g. 0.13 mol.) in the absence of solvent (Found: B, 9.3; Cl, 59.7 Calc. for CH_3BCl_2O : B, 9.6; Cl, 62.9).

Attempted preparation of 2-methoxy-1,3,2 dioxaborepan. - Butan 1,4 diol (10.8 g. 0.12 mol.) was added to methyl chloroborinate (13.5 g. 0.12 mol.) After removal of solvent the product was a non-distillable yellow glass. (Found : C, 46.20; H, 8.53; B, 8.30; easily hydrolysable chlorine (e.h.c.), 0. $C_5H_{11}BO_3$ requires C, 46.23; H, 8.53; B, 8.33).

Preparation of 2-chloroethyl chloroborinate. - 2-chloroethanol (dry, 8.6 g. 0.11 mol.) was added to boron trichloride (12.5 g, 0.11 mol.) in the absence of solvent (90% hydrogen chloride estimated) Found: B, 6.95; Cl, 43.9. Calc. for $C_2H_4BCl_3O$: B, 6.70; e.h.c. Cl, 43.5

Preparation of 2(2'-chloroethoxy) 1,3,2 dioxaborepan. - 2-chloroethyl chloroborinate (15.1 g, 0.09 mol.) was added to butan 1,4 diol (8.4 g, 0.09 mol.) 80% hydrogen chloride estimated . After removal of solvent, the product was a viscous, non-distillable liquid. (Found :

C, 39.09; H, 6.64; B, 6.3; e.h.c. Cl, 0. C_6H_{12} B Cl O_3 requires C, 40.4; H, 6.77; B, 6.1).

Preparation of 2-chloro-1,3,2 dioxaborolan. - Ethan 1,2 diol (13.1 g., 0.21 mol.) was added to boron trichloride (24.0 g., 0.20 mol.) in 50 ml. of methylene chloride (84% hydrogen chloride estimated). After removal of solvent the product was distilled over the range 35-50°C./0.03 mm. (Found : B, 10.12; Cl, 33.2. Calc. for C_2H_4B Cl O_2 : B, 10.18; Cl, 33.35).

Attempted preparation of 2-methoxy-1,3,2 dioxaborolan. - Dry methanol (5.9 g. 0.18 mol.) was added to 2-chloro-1,3,2 dioxaborolan (19.7 g. 0.18 mol.) 91% hydrogen chloride estimated . After removal of solvent, the compound was a straw-yellow transparent glass and was non-dstillable. (Found : C, 33.21; H, 6.70; B, 10.5. $C_3H_7BO_3$ requires : C, 35.38; H, 6.93; B, 10.6).

Attempted preparation of 2-ethoxy-1,3,2 dioxaborolan. - Dry absolute ethanol (7.9 g. 0.17 mol.) was added to 2-chloro-1,3,2 dioxaborolan (18.2 g. 0.17 mol.) 89% hydrogen chloride estimated . After removal of solvent the compound was a glass (non-distillable) Found : C, 38.49; H, 6.95; B, 9.54. n_D^{25} = 1.431. Calc. for $C_4H_9BO_3$: C, 41.45; H, 7.83; B, 9.33 lit.[8] n_D^{25} = 1.4190

Preparation of tris (ethan 1,2 diol) diborate. - Ethan 1,2 diol (21.4 g., 0.34 mol.) was added to boron trichloride (27.0 g., 0.23 mol.) 92% hydrogen chloride estimated. The product precipitated out as a white solid which was filtered off and washed with methylene chloride (Found : C, 35.10; H, 6.22; B, 10.4 m.p. 157°C. Calc. for $C_6H_{12}B_2O_6$: C, 35.72; H, 6.0; B, 10.7 lit.[9] m.p. 162-4°C.).

Preparation of 2(2'-chloroethoxy) 1,3,2 dioxaborolan. - 2-chloroethanol (12.3 g., 0.15 mol.) was added to 2-chloro- 1,3,2 dioxaborolan (16.2 g., 0.15 mol.) 91% hydrogen chloride estimated . After removing the solvent the compound was a colourless viscous liquid b.pt. 52-58°C./0.02 mm, n_D^{25} = 1.4554 (Found : C,31.9; H, 5.7; B, 7.05; Cl, 24.75. $C_4H_8B\,Cl\,O_2$ requires C, 31.95; H, 5.4; B, 7.2; Cl, 23.6).

Preparation of 2(n-butoxy) 1,3,2 dioxaborolan. - Analar grade n-butanol (12.9 g, 0.17 mol.) was added to 2-chloro-1,3,2 dioxaborolan (18.6 g. 0.17 mol.) 74% hydrogen chloride estimated . After removing the solvent the compound was a colourless, viscous liquid b.pt. 66 - 68°C./ 0.05 mm. (Found : C, 50.15; H, 9.28; B, 7.53. Calc. for $C_6H_{13}BO_3$: C, 50.05; H, 9.10; B, 7.52).

Preparation of 2-chloro-4, methyl-1,3,2 dioxaborolan. - Redistilled propan 1,2 diol (b.pt. 86°C./14 mm.) 25.6 g., 0.34 mol. was added to boron trichloride (39.5 g., 0.34 mol.) 87% hydrogen chloride estimated After removal of solvent the compound was colourless viscous liquid, b.pt. 38°C. /0.1 mm. (Found : B, 8.92; Cl, 29.2. Calc. for $C_3H_6BClO_2$: B, 8.99; Cl, 29.5).

Preparation of 2-chloro 4,5-dimethyl-1,3,2 dioxaborolan. - Redistilled butan 2,3 diol (b.pt. 92°C. /14 mm.) 13.5 g., 0.15 mol. was added to boron trichloride (17.5., 0.15 mol.) 86% hydrogen chloride estimated

After removal of solvent, the compound was a colourless, mobile, liquid b.pt. 26-27°C./0.1 mm. (Found : B, 8.03; Cl, 26.2. Calc. for $C_4H_8B\,Cl\,O_2$: B, 8.05; Cl, 26.4).

Preparation of 2-chloro 1,3,2 dioxaborinan. - Redistilled propan 1,3 diol (16.0 g., 0.21 mol.) was added to boron trichloride (24.7 g., 0.21 mol.) 88% hydrogen chloride estimated After removal of solvent, the compound was a straw-yellow mobile liquid which distils to give a colourless liquid b.pt. 20-22°C./0.1 mm., which darkens rapidly on standing at room temperature (Found : B, 8.91; Cl, 29.2. Calc. for $C_3H_6BCl\,O_2$: B, 8.99; Cl, 29.5).

Preparation of 2(2'-chloroethoxy) 1,3,2 dioxaborinan.- 2-chloro-ethanol (6.9 g., 0.08 mol.) was added to 2-chloro-1,3,2 dioxaborinan (10.5 g., 0.09 mol.) 84% hydrogen chloride estimated. After removal of solvent, the compound was a colourless liquid, b.pt. 48-50°C./0.05 mm. $n_D^{25} = 1.4505$ (Found: C, 36.45; H, 6.06; B, 6.58; Cl, 22.00. Calc. for $C_5H_{10}BClO_3$: C, 36.52; H, 5.52; B, 6.45; Cl, 21.57, lit.$n_D^{25} = 1.4510$).

Preparation of trimethylene bis(dichloroborinate). Propan, 3 diol (3.3 g. 0.04 mol.) was added to boron trichloride (10.3 g. 0.09 mol.) in the absence of solvent (100% hydrogen chloride estimated). The compound was a non-distillable mobile liquid darkening rapidly at room temperature. It was stored at -80°C. $n_D^{25} = 1.4418$ (Found: B, 9.1; Cl, 58.3. $C_3H_6B_2Cl_4O_2$ requires B, 9.1; Cl. 59.7).

Attempted preparation of trimethylene bis (di-2-chloroethyl borate). - 2-chlorethanol (8.7 g., .11 mol.) was added to trimethylene bis dichloroborinate (6.4 g., .03 mol.) 84% hydrogen chloride estimated. The liquid product, $n_D^{25} = 1.4500$, was analysed before distillation. (Found : B, 5.3. $C_{11}H_{22}B_2Cl_4O_6$ required B, 5.2). The infra-red spectrum (0.125 M solution in CCl_4 in 0.05 mm. cells, rock salt region) was quantitatively similar to the superimposed spectra of the disproportionation products. The product was distilled, under reduced pressure, boiling over the range 25-75°C. /0.1 mm., and the centre fraction refluxed at 180°C. for 5 hr. After several refractionations the centre fraction distilled over the same range, leaving no residue. The lowest boiling fraction, $n_D^{25} = 1.4481$, b.pt. 48-50°C./0.07 mm. was shown to be principally 2(2'-chloroethoxy) 1,3,2 dioxaborinan by analysis (Found : 6.2 Calc. for $C_5H_{10}BClO_3$: B, 6.6) and comparison of its infra-red spectrum with that of an authentic sample. The highest boiling fraction, b.pt. 70-80°C. /0.1 mm., $n_D^{25} = 1.4520$, was identified as tris-2-chloroethyl borate by analysis (Found : B, 4.8. Calc. for $C_6H_{12}BCl_3O_3$: B, 4.3%) and by its infra-red spectrum. 83% of the theoretical quantity of tris-2-chloroethyl borate calculated on the basis of $(RO)_2\,B\,O\,(CH_2)_3OB(OR)_2 \rightleftharpoons (RO)_3B + RO\,\overline{B\,O\,(CH_2)_3\,O}$ was recorded.

Attempted preparation of trimethylene bis(di-n-butyl borate). - The reaction was conducted in a similar manner to the above experiment with butan 1-ol. (12.5 g., 0.17 mol.) and trimethylene chloroborinate (8.7 g., 0.04 mol.) 78% hydrogen chloride was estimated Repreated refractionation under reduced pressure effected separation into tri-n-butyl borate, n_D^{25} = 1.4079, b.pt. 48-52°C./0.1 mm. (lit.[55] n_D^{25} = 1.4070) [Infra-red spectrum identical with that of an authentic sample, which boiled at 50-52°C./0.1 mm] , and 2-n-butoxy-1,3,2 dioxaborinan, b.pt. 34-37°/0.06 mm. (lit.[37] b.pt. 36-38°/0.12 mm.) [infra-red spectrum identical with that of an authentic sample]

Attempted preparation of trimethylene bis(di-isothiocyanato borinate). - Trimethylene bisdichloroborinate (3.9 g., 0.016 mol.) was run into a solution of potassium thiocyanate (Analar, 6.4 g. 0.066 mol.) in 1,2-dimethoxyethane (100 ml.). Precipitated potassium chloride was filtered off and the solvent evaporated from the filtrate. The residue was distilled into four fractions, the highest boiling of which was 2-isothiocyanato-1,3,2 dioxaborinan b.p. 55-65°/0.05 mm., and which had an infra-red spectrum identical with that of an authentic sample. At the time of this work, boron tri-isothiocyanate had only recently been described.[54]

Preparation of ethylene bis(dichloroborinate). - Ethan 1,2 diol (1.9 g., 0.03 mol.) was added to boron trichloride (7.1 g., 0.06 mol.) in the absence of solvent (96% hydrogen chloride was estimated)

Found : B, 9.67; Cl, 63.1. Calc. for $C_2H_4B_2O_3Cl_4$: B, 9.68; Cl, 63.45

Attempted preparation of ethylene bis (di-2-chloroethyl borate). - This reaction was conducted in a similar manner to the trimethylene derivatives with 2-chloro-ethanol (5.8 g., 0.07 mol.) and ethylene bisdichloroborinate (5.0 g. 0.02 mol.) [93% hydrogen chloride estimated] Repeated refractionation under reduced pressure effected separation into tri-2-chloroethyl borate b.pt. 75-82°/0.2 mm. [Infra-red spectrum identical with that of an authentic sample] (Found : B, 4.6 Calc. for $C_6H_{12}BCl_3O_3$: B, 4.3) and 2-(2' chloroethoxy) 1,3,2 dioxaborolan, b.pt. 52-56°/0.2 mm, $n_D^{25} = 1.4565$, identical in infra-red spectrum with that of an authentic sample (Found : B, 6.4 Calc. for $C_4H_8BClO_2$: B, 7.2).

Preparation of tetramethylene bis (dichloroborinate). - Butan 1,4 diol (3.1 g., 0.034 mol.) was added to boron trichloride (8.1 g., 0.069 mol.) in the absence of solvent. Butan 1,4 diol freezes at 16°C. so the reaction flask was warmed periodically to allow the diol to react. 84% hydrogen chloride estimated). The compound was a white amorphous solid, darkening rapidly at room temperature (Found : B, 8.7; Cl, 53.9 $C_4H_8B_2Cl_4O_2$ requires B, 8.6; Cl, 56.3). After pumping at 0.05 mm. at 0°C. for 2 hr. the composition was B, 8.74; Cl, 46.0.

Preparation of phenyl boron dichloride (1). - The method used was that of Burch et al[53]. Tetraphenyl tin (22.8 g. 0.05 mol.) was added to boron trichloride (10% excess, 27.5 g. 0.23 mol.) at -80°C. under a -80°C. reflux condenser, stirring gently. The mixture was allowed to warm to room temperature when the white suspension turned black and became mobile. The mixture was refluxed for 2 hr. at 80°C. under a -80°C. condenser and for a further 4 hr. under a water condenser. It was then distilled into three fractions, the lowest boiling ($<$ 68/20 mm) being principally stannic chloride, the second (68-76°/14 mm) being principally phenyl boron dichloride and the final fraction (120-140°/ 20 mm. a deep red colour) being probably $\phi SnCl_3$. The centre fraction was redistilled and a cut collected over 66-7°/20 mm. (Found : B, 6.97; Cl, 44.15 Calc. for $C_6H_5BCl_2$: B, 6.81; Cl, 44.65). It was noted that on allowing dry air to come into contact with sample, it turned pink and on standing at room temperature gradually transformed to a deep port red colour. However, analysis indicates it is substantially unchanged. The compound was redistilled (66°/18 mm.) immediately before use in the cryoscope (Found : B, 6.76; Cl, 44.22 Calc. for $C_6H_5BCl_2$: B, 6.81; Cl, 44.65). It was thought that the pink colour was due to contamination by $\phi SnCl_3$ so a sample was prepared by an alternative method. The formal equation for the above synthesis is : $\phi_4Sn + 4\,BCl_3 \rightarrow 4\,\phi BCl_2 + SnCl_4$.

<u>Preparation of phenyl boron dichloride (2)</u>. - The method used was an adaptation of that of Abel et al[56]. Phenyl boronic anhydride (33.8 g. 0.11 mol.) and boron trichloride (10% excess, 28.0 g. 0.24 mol.) were shaken in a sealed ampoule overnight. The white slush turned to a brown mobile suspension and finally to a brown gel. The ampoule was opened and the contents distilled collecting a fraction boiling over

62-66/20 mm. (Found : B, 6.71; Cl, 44.74 Calc. for $C_6H_5BCl_2$: B, 6.81; Cl, 44.65). However, on standing, this sample also turned red.

SECTION 3 : Cryoscope.

The cryoscopic cell was specially designed for use with moisture sensitive materials (see Fig. 1) and is a modification of Zemany's design[38]. The temperature-sensitive element was a thermistor (type F 2311/300, Standard Telephone and Cables Ltd.) sealed into a glass tube with Cold Cure Silastomer (Midland Silicones Ltd.) Agitation was effected by means of a chromium plated stirrer actuated by an external solenoid. The intermittent pulse to the solenoid was supplied by a slowly rotating cam operating a micro-switch connected to a transformer (see Fig.2). The thermistor is one arm of a Wheatstone bridge with fixed ratio arms of 3KΩ and a variable arm spanning 0 to $10^4\Omega$. There are 200 Ω in series with the bridge current to reduce the power output of the thermistor to below the recommended maximum. The out-of-balance bridge current was detected on a Scalamp galvanometer (7902/S, W.G. Pye & Co.Ltd.) At the freezing point of benzene or nitrobenzene (5.53 and 5.76°C. respectively) an F 23 thermistor changes approximately 109 Ω /°C. Using the described equipment a freezing point may be recorded to ± 0.25 Ω i.e. to ± .002°C. For an F 53 thermistor at 25°C. (used in the calorimetry) the sensitivity is ~ 158 Ω/°C. i.e. ± .0015°C. The limiting factor in the determination of cryoscopic molecular weights,

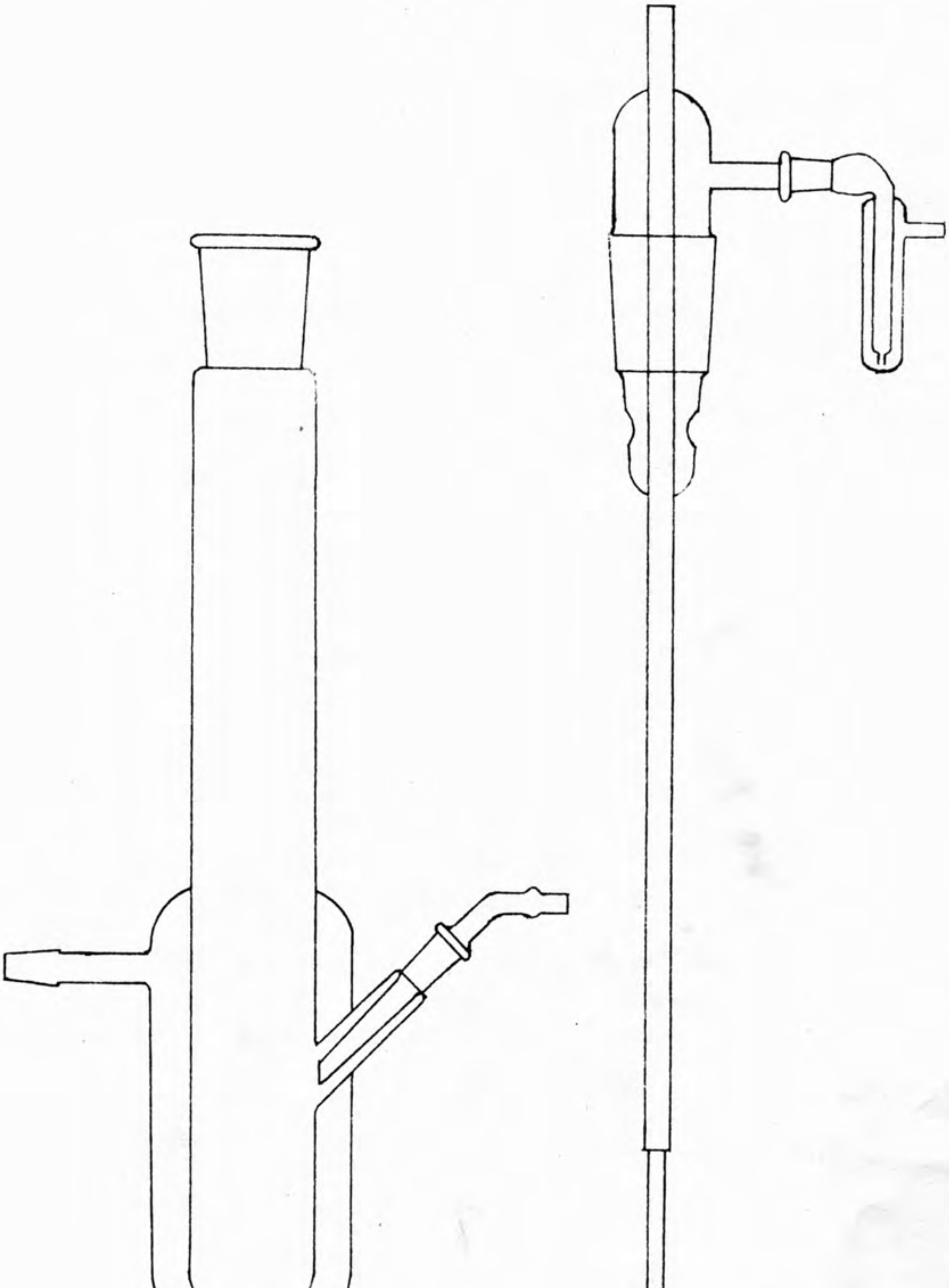


FIG. 1 : CRYOSCOPIC CELL AND THERMISTOR

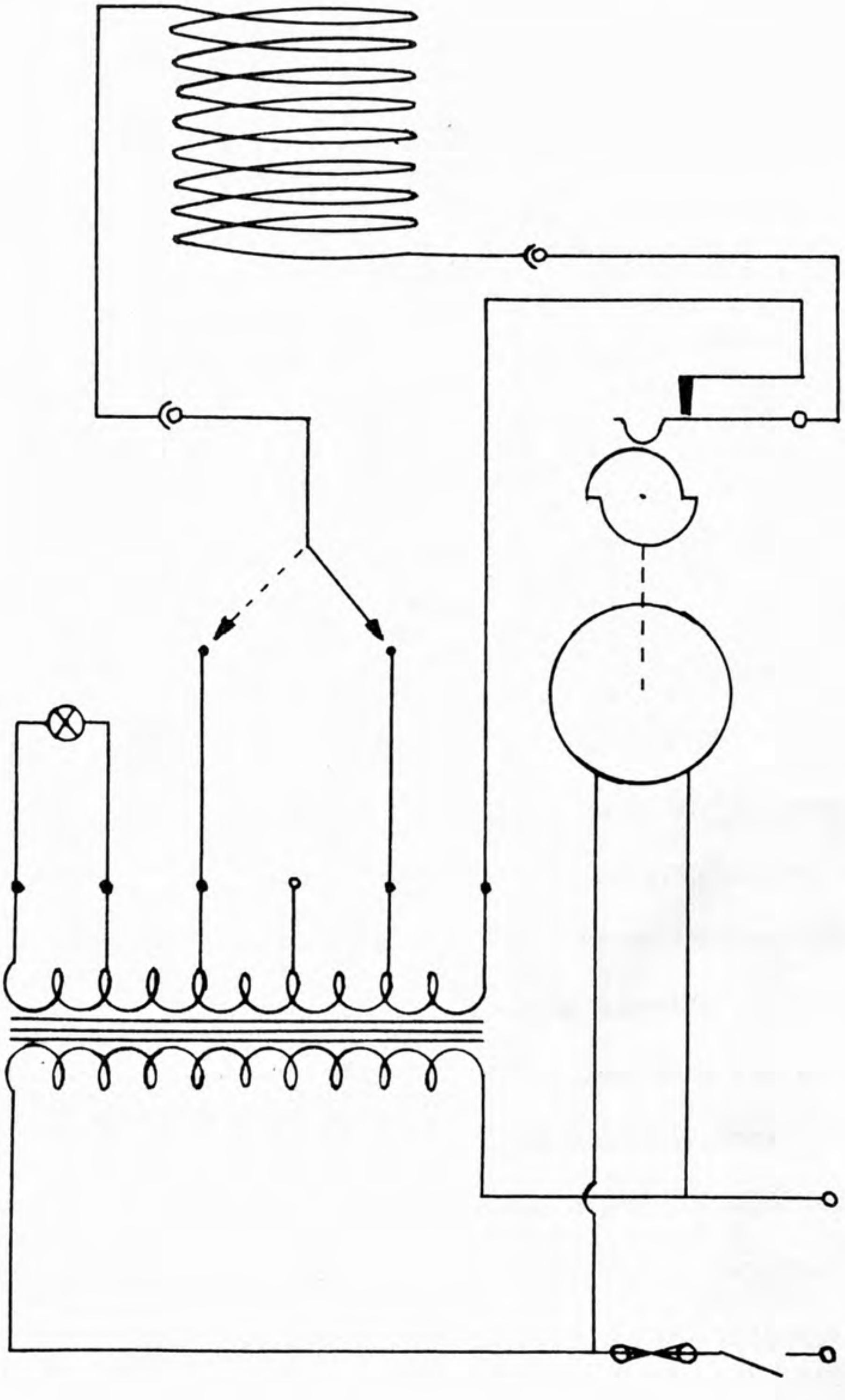


FIG. 2 : MAGNETIC STIRRING CIRCUIT FOR CRYOSCOPE

by this method, is not the thermistor sensitivity but the purity and stability of the compounds studied. The thermistor was calibrated, for cryoscopic work, using a specially purified sample of naphthalene to determine k in the experimental equation

$$M = k \frac{m_2}{\Delta R}$$

M = molecular weight of naphthalene (128.16)

m_2 = concentration of g./10 ml. of benzene

ΔR = depression in ohms.

The depression at eight different concentrations was determined and a graph of m_2 vs. ΔR constructed and the gradient found by a least-squares method. Naphthalene was used as a cryoscopic calibration compound because it is known that benzene/naphthalene mixtures are ideal up to almost eutectic concentration[63]. It should be noted that this calibration technique is not absolute in the sense that the temperature for any resistance may be derived. For an absolute calibration (i.e. the determination of the thermistor constants A and B) the thermistor was calibrated against a Beckmann thermometer itself calibrated via the transition temperature of sodium sulphate decahydate.

In the Discussion and Results (Section 3) the interrelation between the two forms of calibration was developed from the vapour pressure equation and calculated values for k and K_f obtained. In the course of the derivation several approximations were introduced. The evaluation and magnitude of the resultant errors will be discussed in some detail : -

(a) ideality.

In transforming the Clapeyron-Claussius equation to the vapour pressure equation the assumption is made that the solvent vapour is an ideal gas. Subsequently in the derivation the assumption $Pi = p_i^o Ni$ (Raoult's law) is invoked i.e. that the solvent/solute system is an ideal solution. These two assumptions constitute the "ideality" approximation is cryoscopic measurements. With this approximation we have

$$- \ln N_1 = \frac{\Delta H}{R} \left[\frac{1}{T} - \frac{1}{To} \right]$$

(ΔH may be expanded as a function of temperature , [see subsequent] ; terms previously defined). Deviations from ideality are manifested in the non-linearity of a $-\ln N_1$ vs. $^1/_T$ plot. Clearly then, if the ideality of a known compound is established by cryscopic measurement, the ideality of a new system must be assumed or proven by an alternative method. A reasonable approach to this problem is that if known compounds with a similar nucleus to the new systems show no deviations from ideality then the new systems may be assumed ideal. It was found that both tri-n-butyl borate and phenyl boron dichloride were ideal in benzene solution up to concentrations of 0.4 M. From this evidence it is assumed that the heterocycles are ideal in benzene solution and that non-linearity in the concentration vs. depression plot is due to changing structure in solution rather than ideality deviations.

(b) The log approximation.

Combining the thermistor equation with the vapour pressure equation leads to

$$-\ln N_1 = \frac{\Delta H}{\underline{R} B} \ln \left({}^{R}/_{R_0} \right)$$

As $N_1 + N_2 = 1$, $-\ln N_1$ is approximated to $+ N_2$. The percentage proportional error (E) is given by

$$E = \left[1 + \frac{1-N_1}{\ln N_1} \right] \times 100$$

Clearly this error increases with concentration (increasing N_2) and is plotted against molarity for a hypothetical compound of molecular weight 150 dissolved in benzene (hereafter called the test compound) [see Graph 8].

(c) The dilute solution approximation.

This is the largest error and is introduced by ignoring ${}^{m_2}/_{M_2}$ in the expression of N_2

$$N_2 = {}^{m_2}/_{M_2} \Big/ \frac{m_2}{M_2} + \frac{m_1}{M_1} \doteqdot \frac{m_2 M_1}{M_2 m_1}$$

as for the dilute solutions $\frac{m_1}{M_1} \gg \frac{m_2}{M_2}$

The proportional error (E) in this case is given by

$$E = \left[\frac{m_2 M_1}{M_2 m_1 N_2} - 1\right] 100 \%$$

This is also graphed (see Graph 8).

(d) The T^2 approximation.

This is a small error compared with the above errors and is opposite in sign

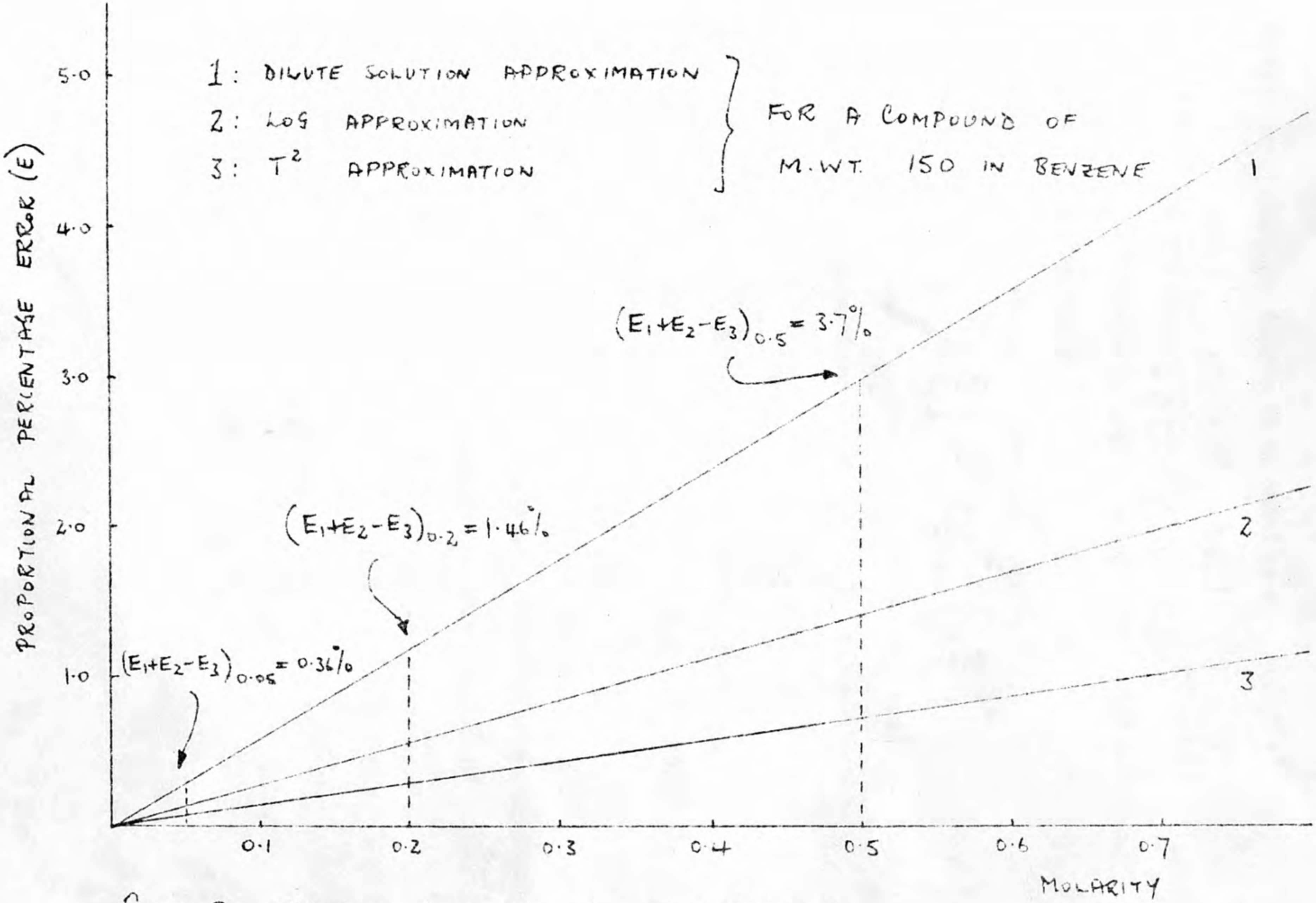
$$-\ln N_1 = \frac{\Delta H}{\underline{R}}\left[\frac{1}{T} - \frac{1}{T_o}\right] = \frac{\Delta H}{\underline{R}}\left[\frac{\Delta T}{T T_o}\right] \doteqdot \frac{\Delta H}{\underline{R}} \cdot \frac{\Delta T}{T_o^2}$$

and $E = \left[\frac{T}{To} - 1\right] 100 \%$

(e) Latent heat approximation.

When integrating the Clapeyron-Claussius equation it is assumed that the latent heat of fusion of the solvent is independent of temperature

$$-\ln N_1 = \frac{\Delta H \, \Delta T}{\underline{R} \, T_o^2}$$



GRAPH 8 : ERROR vs. CONCENTRATION IN CRYOSCOPY

In this expression ΔH may be expanded as a f(T).[45,57]

$$-\ln N_1 = \frac{\Delta H \Delta T}{\underline{R} T_0^2} - \frac{\Delta C_p (\Delta T)^2}{2 \underline{R} T_0^2} - \frac{\Delta C_p (\Delta T)^3}{6 \underline{R} T_0^3} - O(4)$$

where Δ Cp = difference in heat capacity of the solid and liquid solvent at T_0.

Substituting the thermistor equation and ignoring O(3),

$$-\ln N_1 = \frac{\Delta H}{\underline{R} B}\left[\ln \frac{R}{R_0}\right] - \frac{\Delta C_p T_0^2}{2 \underline{R} B^2}\left[\ln \frac{R}{R_0}\right]^2$$

To show that the influence of the second term is very small we introduce the usual approximations and expand the logarithmic terms:

$$\frac{m_2 M_1}{M_2 m_1} = \frac{\Delta H \Delta R}{\underline{R} B R_0} - \frac{\Delta C_p T_0^2 (\Delta R)^2}{2 \underline{R} B^2 R_0^2}$$

Substituting constants; ΔH(benzene)[58]) = 2.35 kcal/mole, $\underline{R}$ = 1.987 cal. mole^{-1} deg.$^{-1}$, B = 1.2 x 10^3 deg. Ro = 2864, Δ Cp = 1.82 cal. mole^{-1} , To = 278.7°A. and selecting R = 100 Ω (which corresponds to an $\sim$ 0.3M concentration of the test compound in benzene), the second term accounts for $\sim$ 0.1% of the whole.

(f) The log expansion.

In the expression

$$-\ln N_1 = \frac{\Delta H}{\underline{R} B} \ln\left[\frac{R}{R_0}\right]$$

we may substitute

$$\frac{R}{Ro} = 1 + \frac{\Delta R}{Ro}$$

and expand

$$-\ln N_1 = \frac{\Delta H}{\underline{R} B}\left[\frac{\Delta R}{R_0} - \frac{1}{2}\left(\frac{\Delta R}{R_0}\right)^2 + \frac{1}{3}\left(\frac{\Delta R}{R_0}\right)^3 \cdots\cdots\right]$$

If we ignore O(3), the R.H.S. becomes

$$\frac{\Delta H \Delta R}{\underline{R} B R_0}\left[1 - \frac{1}{2}\cdot\frac{\Delta R}{R_0}\right]$$

The error introduced by ignoring O(2) as opposed to O(3) is $\left(1 - \frac{1}{2}\cdot\frac{\Delta R}{R_0}\right)\%$. For an approximately 0.3M solution of the test compound i.e. $R = 100\Omega$, the error is ~ 1.7%. This error only occurs however in deriving a theoretical expression for k and by using the experimental value of k the error is avoided.

To summarise, from Graph 8, it may be seen that the combined error in using the standard colligative expression for a hypothetical compound of molecular weight 150 ideally dissolved in benzene at concentrations of 0.05, 0.2, 0.5 M, is 0.36%, 1.46% and 3.7% respectively.

SECTION 4 : Cryoscopic procedure.

The procedure for a cryoscopic determination is outlined below.

1) The cryoscopic cell is cleansed thoroughly and dried in an oven (110°C.) overnight. While it is cooling it is flushed with a stream of dry nitrogen. When it has achieved room temperature, 10 ml. of cryoscopic solvent is loaded and the nitrogen stream cut off. The thermistor is introduced and the circuit connected.

2) The cell is lowered into a freezing mixture (ice/salt, ca. -10°C.) to approximately ½" above the solvent level. The stirrer is actuated and a resistance reading noted (Ro) when the bridge balance is constant.

3) An aliquol of the sample is added from a B/10 flask fitted with a B/10 dropper (usually about 0.04 g.). The majority of the compounds investigated were moisture-sensitive and were added with a slow stream of dry nitrogen playing on the side arm of the cell. A Teflon sleeve was fitted to the joint to avoid transfer of grease and so introduce a weighing error. If the sample is extremely viscous, as in the case of 2-chloro-1,3,2 dioxaborolan, it is added in benzene solution of known concentration (an appropriate correction was made in constructing the graph for the additional solvent added with each sample). When the sample is extremely hydrolysable, as in the case of phenyl boron dichloride, a dilution technique was used i.e. a known amount of ϕBCl_2

was added to the cell and successive amounts of pure solvent added. This involves only one transfer of the sample to be investigated. It has the disadvantage that the concentration range over which the sample may be investigated is considerably limited. If the sample is a solid, as in calibration with naphthalene, it is added in the form of small pellets.

4) After the sample is added the solution is stirred and allowed to warm until the sample has completely dissolved and the solvent has completely melted. The freezing point of the solution is then recorded via the above procedure.

5) The sequence of operations is repeated over the desired concentration range of the solute. A graph of concentration (in g. per 10 ml. solvent) vs. freezing point (in ohms) is constructed and the molecular weight computed at any concentration via the gradient at that concentration and the calibration constant. If the sample is sparingly soluble and has precipitated on cooling this is immediately obvious by a sudden discontinuity in the graph. If necessary the solute may be recovered from the solution at the conclusion of the experiment.

SECTION 5 : Calorimetric accuracy.

The design of the calorimeter and calorimetric procedure are fully discussed in Part II. The expected level of accuracy to be obtained from the equipment, assuming the compounds are 100% pure and stable, is discussed here. The equation for an enthalpy change is of the form

$$\Delta H \quad = \quad (\text{electrical energy}).\ \frac{\Delta T'}{\Delta T}$$

where $\Delta T'$ = temperature change in the reaction period and

ΔT = temperature change in the calibration period. The principcal sources of error in evaluating this function occurs in the measurement of temperature rather than the measurement of energy so as a first approximation,

$$\overline{\Delta H} \quad = \quad \frac{\Delta T'}{\Delta T} \quad \sim \quad \frac{\log {}^{R_2}/_{R_1}}{\log {}^{R_3}/_{R_4}}$$

It is usual calorimetric procedure for $\Delta T'$ to be approximately equal to ΔT so it is only necessary to consider the error in log ${}^{R_2}/_{R_1}$ and then combine errors.

$$\text{Let} \quad U \quad = \quad \log {}^{R_2}/R_1$$

If U = f (x,y,z ...) and the errors in U, x, y ... are $\pm \Delta U$, $\pm \Delta x$, $\pm \Delta y$ ... then

$$(\Delta U)^2 = \left(\frac{\partial U}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial U}{\partial y}\right)^2 (\Delta y)^2 \ldots\ldots\ldots$$

$$= \left(\frac{1}{R_2}\right)^2 (\Delta R_2)^2 - \left(\frac{1}{R_1}\right)^2 (\Delta R_1)^2$$

For an F 53 thermistor, the sensitivity is 158 Ω /deg. so let us consider the error introduced by temperature changes of 0.3, 0.6 and 1°C. i.e. change in resistance being 50, 100, 150 respectively. The approximate resistance of the F 53 thermistor at 25°C. is 4400 Ω and resistance readings may be made to the nearest half-ohm.

Therefore $R_1 = 4400$ $R_2 = 4450$ for 0.3°C. change

4500 for 0.6°C. change

4550 for 1.0°C. change

and $\Delta R_2 = \Delta R_1 = \pm 0.5$

Substituting we obtain the proportional error in U and, by combination of errors, the proportional error in $\overline{\Delta H}$. These errors are tabulated below.

TABLE XVI. CALORIMETRIC ERRORS FOR TEMPERATURE CHANGES OF 0.3, 0.6 AND 1.0°C.

Temp. change °C.	$\frac{\Delta U}{U}$ (%)	$\frac{\Delta \overline{\Delta H}}{\overline{\Delta H}}$ (%)
0.3	0.34	0.49
0.6	0.24	0.34
1.0	0.19	0.27

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PART II

INTRODUCTION

The two most comprehensive reviews on the subject of lattice energies, applies to inorganic systems, are those of Sherman[1] in 1932 and Waddington[2] in 1959.

Lattice energy is defined as the increase in internal energy at absolute zero accompanying the separation of the constituent ions in the gas phase to positions where they are infinitely removed from one another. An expression for evaluating this function is usually associated with the names of Born, Lande and Madelung. It is interesting to follow the derivation of a simple but not universally applicable formula because this expression was subsequently developed by Kapustinkii into a more general form. The Coulombic attraction per gram-molecule for an ion-pair is given by

$$\Phi(r) = -N \frac{e^2}{r}$$

where N = Avogadro's number

r = distance between the centres of the two ions of charges + e and -e.

To evaluate the Coulomb energy of a complete crystal lattice it is necessary to sum the ionic attractions of all ions with respect to all other ions. The potential of an ion within a simple lattice (uni-univalent type) may be evaluated in terms of a power series the summation of which will be put equal to $-Me/r$. The crystal energy which arises from this summation is

$$- N \frac{Me^2}{r}$$

where M = Madelung constant and is dependent only on the structure of the lattice. The mutual repulsion between ions, arising when ion electron clouds penetrate each other, is represented by B/r^n; a function which, provided n is large, increases rapidly with decreasing r, corresponding to a "hard-spheres" model. (B = const.)

The total lattice energy is

$$U = - \frac{NMe^2}{r} + \frac{B}{r^n}$$

At equilibrium the energy is a minimum, the attractive and repulsive forces compensating each other

$$\frac{dU}{dr} = 0 = N \frac{Me^2}{r^2} - \frac{B}{r^{n+1}}$$

Eliminating B we have

$$U = - \frac{NMe^2}{r_o} \left[1 - \frac{1}{n} \right]$$

r_o = equilibrium interionic distance

The repulsive term accounts for about 10% of the total lattice energy.

With the development of quantum mechanics it was realised that electron density of spherically symmetrical ions fell off exponentially with distance and in 1932 Born and Mayer[3] produced an equation where the repulsive energy was represented by B' exp($-r/\rho$) where ρ is a constant with the dimensions of length. Substituting this and eliminating B' by the minimum energy condition they obtained

$$U = - \frac{NMe^2}{r_o} \left[1 - \rho/r_o \right]$$

A more rigorous expression[2] would take account of dispersion forces and zero point energy of the lattice. However these components are normally very small. An extended expression of this type applies only to an array of spherical ions. For non-spherical ions the shape of the "repulsion envelope" must be estimated and the assumption that a charged ion may be replaced by a point charge at its centre is no longer valid. If the charge distribution on the ion is known the total charge may be represented by a point charge plus a permanent electrical multipole. The Coulombic energy is then considered as two terms, the simple Madelung term and the multipole energy. An illustration of this type of calculation on non-spherical ions is provided by Waddington[4,5] who calculated the lattice energies of some azides (N_3^-) and bifluorides

(HF_2^-) by an extended term-by-term formula.

The physical data required for calculations of the above type are extensive and the calculation itself is laborious for all but the simplest lattice types. Kapustinkii^6 modified the simple Born-Mayer equation

$$\text{i.e.} \quad U = \frac{M N Z_1 Z_2 e^2}{r_o} \left[1 - \frac{\rho}{r_o} \right] ,$$

where the ionic charges are Z_1e and Z_2e into a more universal form. He found empirically a parallelism between the change in Madelung constant$^{(M)}$ and interionic distance (r_o) in passing from one lattice type to another. This makes it possible to envisage an "iso-energetic" rebinding of any crystal type into a rock salt type lattice. If the number of ions in the chemical molecule is ν, the number per mole is $N\nu$. The Born-Mayer expression may then be written

$$U = \left(\frac{\nu N}{2} \right) \frac{\alpha Z_1 Z_2 e^2}{r_o} \left[1 - \frac{\rho}{r_o} \right]$$

where $\alpha = M/(\nu/2)$

Utilising the empirical correlation that changes in α are proportional to changes in r_o, the lattice energy can be expressed in terms of rock-salt parameters and replacing r_o by the sum of the anionic and cationic Goldschmidt radii for coördination number 6. For a rock-salt lattice $\alpha = 1.745$ and if $r_o = r_A + r_C$ in Å then $\rho = .345$ Å and $Ne^2 = 329.7$ kcal/$\mathring{A}$. Substituting these constants in the above expression we obtain Kapustinkii's formula for lattice energy in terms of easily accessible parameters.

$$U = \frac{287.2\,\nu\,Z_1Z_2}{(r_c + r_A)}\left[1 - \frac{.345}{(r_c + r_A)}\right] \text{kcal./mole.}$$

This formula cannot be expected to produce lattice energies as accurate as those produced from extended calculations. The principal fault in the formula lies in the replacement of r_o by $r_A + r_c$. In many salts, especially those involving a large anion and a small cation, or vice versa, (e.g. Li I or Cs F) unlike ions cannot be considered in contact. Also, when applying this formula to complex salts, it is difficult to assign an anionic radius. This problem, however, was overcome by Yatsimirskii[7] who considered the enthalpy changes in the following reactions:-

$$M_1.\,X\ (S) \longrightarrow M_1^+(g) + X^-(g)$$

$$M_2.\,X\ (S) \longrightarrow M_2^+(g) + X^-(g)$$

$$\text{Now}\quad U_{M_1X} - U_{M_2X} = \Delta H_f^o\,M_1^+(g) - \Delta H_f^o\,M_2^+(g)$$

$$- (\Delta H_f^o\,M_1\,X\,(s) - \Delta H_f^o\,M_2\,X\,(s))$$

or, using Kapustinkii's formula

$$U_{M_1X} - U_{M_2X} = A\left[\frac{1}{r_{M_1^+}+r_{X^-}}\left(1-\frac{\rho}{r_{M_1^+}+r_{X^-}}\right) - \frac{1}{r_{M_2^+}+r_{X^-}}\left(1-\frac{\rho}{r_{M_2^+}+r_{X^-}}\right)\right]$$

If enthalpies of formation of $M_1X(s)$, $M_2X(s)$, $M_1^+(g)$ and $M_2^+(g)$ are known and the Goldschmidt radii of M_1 and M_2 are known, r_{X^-} may be found. Yatsimirskii has calculated values of "thermochemical radii" for numerous oxy-anions by the above method and finds that they are relatively independent of the cation. Usually it is found that lattice energies calculated by the Kapustinkii formula and "thermochemical radii" are lower than the correct lattice energy.

Lattice energies are readily obtainable from hydration enthalpy data; consider the following enthalpy cycle:-

$$\begin{tikzcd}
MX\ (c) \arrow[rr, "U+2\ RT"] \arrow[dr, "\Delta H^o_s"'] & & M^+(g) + X^-(g) \arrow[dl, "\phi = \Sigma H_i"] \\
& M^+(aq) + X^-(aq) &
\end{tikzcd}$$

where

U = lattice energy of $MX(c)$ at 298°A.

$U + 2\ RT$ = corresponding lattice enthalpy.

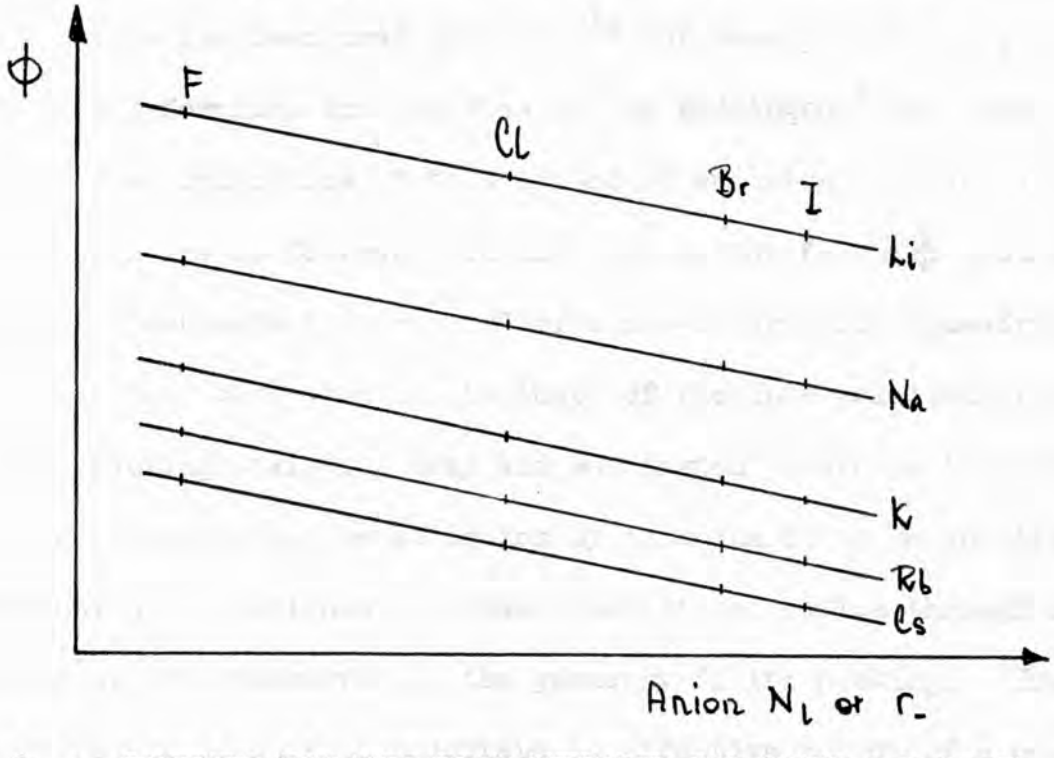
ΔH^o_s = standard heat of solution of the crystalline salt

ϕ = combined ion hydration enthalpy to the solution phase of unit activity.

$\therefore\ \Delta H^o_s = (U + 2\ RT) + \phi$

(the convention used hereis to consider lattice energies as positive and hydration enthalpies as negative).

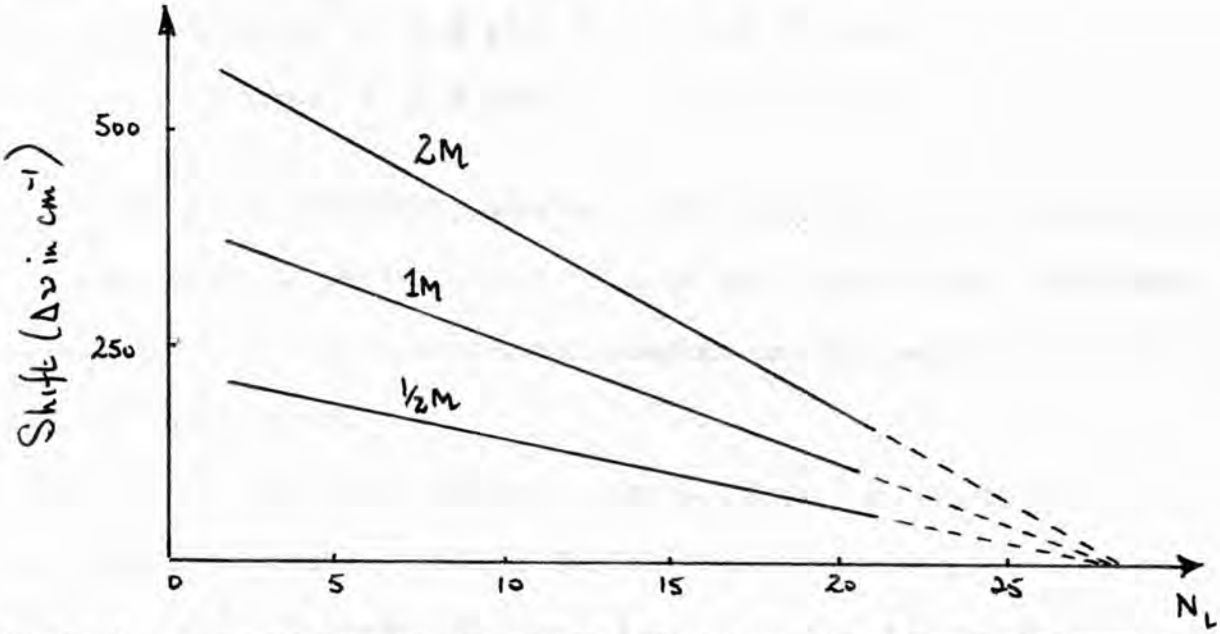
The standard heat of solution of salts is a readily obtainable experimental quantity but the opposite is true of ionic hydration enthalpies. However, hydration enthalpies for the alkali halide ion pairs are well established by Latimer et al[8]. Methods of determining these functions will be discussed later. It is found, empirically, the combined ion hydration enthalpies for the alkali halides are approximately linear with either anion lyotropic numbers or Pauling anion radii.



Graph 1 : COMBINED ION HYDRATION ENTHALPY FOR GROUP I HALIDES VS. LYOTROPIC NUMBER OR ANION RADIUS.

Lyotropic number (N_1) is a function obtained for many anions by Büchner et al[9-13] and represents a quantitative estimation of the position of an anion in the Hofmeister (or lyotropic) series. Physically, it represents the power of an ion to bind water to itself at the expense of hydrated colloids in suspension and so cause coagulation. The plots of N_1 vs. ϕ are more linear than those of r_- vs. ϕ. Clearly, then, if the lyotropic number or the radius for a particular anion is known, then the combined ion hydration enthalpy for the Group I salts may be interpolated from the above graph. If, in addition, the standard heat of solution is known the lattice energy is deduced from the cycle. This technique has been used by Morris[14] for Group I nitrates, chlorates, thiocyanates, formates and acetates and by Waddington[4] for Group I azides. The limitations of this method of empirical lattice energy determination are as follows: in the case of the r_- vs. ϕ plot it is difficult to estimate the "radius" of a non-spherically symmetrical anion on a scale corresponding to that of the interpolation graph (i.e. usually a Pauling scale). Gray and Waddington[4] overcame this difficulty when considering the azide ion by assuming it to be an ellipsoid of revolution and assigned it a mean statistical radius through a knowledge of its structure and the geometry of its packing. Ideally one requires to be able to calculate an effective radius of a complex anion which is independent of the cation. The curve for r_- vs. ϕ is reasonably shallow however with an approximate gradient of 6 kcal. per 0.1 Å. In the case of the N_1 vs. ϕ plot the accuracy of interpolated data depends on the accuracy to which N_1 is known. The accuracy which may be assigned to effective radius data and lyotropic numbers is discussed in a subsquent section.

In a recent publication Meyerstein and Treinin[15] investigate the effect of different concentrations of a range of anions on the absorption spectrum of I^- (in particular the band at 260-70 mμ). They find that the spectroscopic shifts ($\Delta\nu$), due to the presence of the foreign anions, at any one particular concentration bears an approximately linear relation to the lyotropic no. of the anion.



GRAPH 2 : INFLUENCE OF DIFFERENT ANIONS ON ABSORPTION SPECTRUM OF IODIDE ANION.

They quote values for $\Delta\nu$ of several ions for which N_1 data is not available (e.g. CN^-, PO_4^{3-}, $HPO_4^{=}$). It seems possible then that interpolation on these graphs will provide new lyotropic data and hence lattice energies. All $\Delta\nu$ data is quoted accurate to ± 15 cm.$^{-1}$ and closer inspection of the data shows interpolated figures to be both irreproducible from one concentration to another and to have too large an inherent error to be of any practical use.

e.g. interpolated data :-

N_1 ($HPO_4^{=}$; $\frac{1}{2}$ M plot) = 4.1 ± 1.6
($HPO_4^{=}$; 1 M plot) = 1.0 ± 0.9
N_1 (PO_4^{3-} ; $\frac{1}{2}$ M plot) = 2.0 ± 1.5
N_1 (citrate^{3-} ; $\frac{1}{2}$ M plot) = -2.8 ± 1.8
(citrate^{3-}; 1 M plot) = -9.9 ± 1.0

It is pertinent, however, that Meyerstein and Treinin carried out this study to derive information on the nature of the electronic transition in the charge-transfer complex and the correlation with N_1 was incidental only.

As mentioned previously the combined ion hydration enthalpy i.e. the total enthalpy change for the two processes

$$\left.\begin{array}{lll} M^{Z+}\,(g) \longrightarrow M^{Z}\,(aq) & \Delta H_+ \\ X^{Z-}\,(g) \longrightarrow X^{Z-}\,(aq) & \Delta H_- \end{array}\right\} \quad \phi = \Delta H_+ + \Delta H_-$$

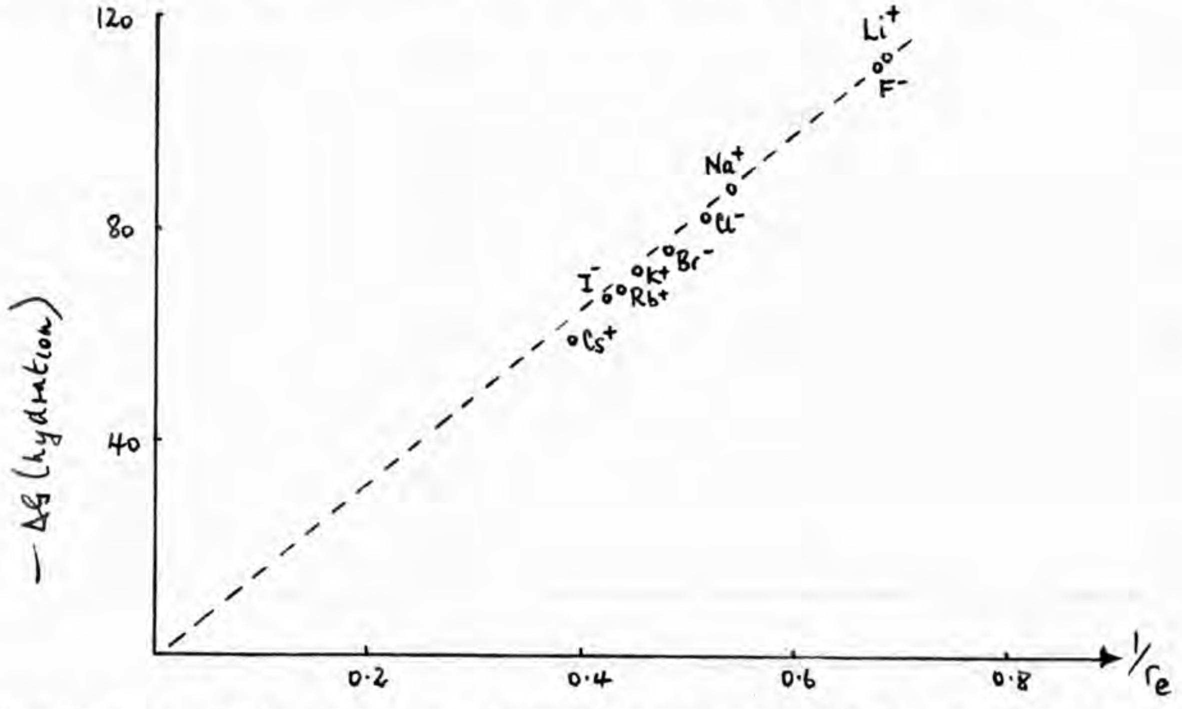
is related to the lattice energy (U) via

$$\phi = \Delta H_s^o - U$$

For simple crystals such as the Group I halides, U may be determined by extended calculation[16]. Combining this with heat of solution data accurate values of ϕ are available for the alkali halides. The problem still remains of separating ϕ into its cationic (ΔH_+) and anionic (ΔH_-) components. The classical solution to this problem, due to Latimer, Pitzer and Slansky[8], makes use of the Born solvation equation. This equation gives the free energy difference between the charging of N (Avogadro's number) spheres of radius r and charge e in a vacuum and in a medium of dielectric D.

$$\Delta G^o = - \frac{Ne^2}{2r} \left[1 - \frac{1}{D} \right]$$

The direct application of this equation to the calculation of individual hydration enthalpies (hydration free energies actually - but $\Delta S^o = - (d\Delta G^o / dT)$ from which ΔH^o is determined) may be criticized on two counts : - (i) the assignment of an ionic radius to a hydrated ion is difficult because this distance refers to the distance between the ionic centre and the centre of the water dipole; this is further complicated by the fact that the solvating water molecules are orientated in different directions for positive and negative ions and (ii) because of the intense electrostatic field near the vicinity of the ion surface causing extreme solvent polarization, the assumption that the solvent is a continuum on a microscopic level with macroscopic dielectric properties is invalid. Latimer et al.[8] constructed a graph of the differences of ion hydration energies of the cations relative to the value for Cs^+ and of the anions relative to I^- versus the inverse of the crystal radii. (the criticism of the exact significance of ionic radius in solution is least important for large ions of small charge). They found that by adding 0.1 Å to the crystal radii of the anions and 0.85 Å to the crystal radii of the cations two lines of equal slope were produced. They then divided the sum of the hydration energies for Cs^+ and I^- such that both positive and negative ions lie on the same line as shown below.



GRAPH 3 : FREE ENERGY OF HYDRATION OF GROUP I METALS AND HALIDES VS. INVERSE OF EFFECTIVE RADIUS.

The dotted line is the theoretical line given by the Born equation using the bulk dielectric constant for water. The hydration energy, then, is given by

$$\Delta G^{o}\ (\text{hydration}) = -\frac{Ne^{2}}{2(r+\epsilon)}\left[1-\frac{1}{D}\right] \quad ; \quad r+\epsilon = r_{e}$$

where $\epsilon = 0.85$ Å for cations and 0.1Å for anions. The accepted data of Latimer et al is given in the table below.

TABLE I : LATIMER'S HYDRATION FUNCTIONS FOR GROUP I METALS AND HALIDES.

Ion	$-\Delta G^{o}$(kcal/mole	$-\Delta H^{o}$(kcal/mole)	$-\Delta S^{o}$(kcal/mole)
Li^{+}	115	121	22
Na^{+}	90	95	17
K^{+}	74	76	8
Rb^{+}	68	69	6
Cs^{+}	61	62	4
F^{-}	114	123	29
Cl^{-}	84	89	15
Br^{-}	78	81	12
I^{-}	70	72	7

In a recent paper Noyes[17] deduces individual ion hydration enthalpies for 37 cations and 5 anions from a different approach.

He is interested in the magnitude of the dielectric constant at the vicinity of the ion surface. To this end he compares hydration energy calculated directly from the Born equation, taking r to be the crystal radius, with an electrostatic free energy (ΔG°_{el}) calculated by the following argument. Using Noyes' notation, the equation

$$M^{Z+}\,(g) \longrightarrow M^{Z+}\,(aq) \qquad\qquad \Delta G^{\circ}\text{ hydration}$$

may be expanded to

$$M^{Z+}(g) \xrightarrow[-\,e^{2}/2r]{} M\,(g) \xrightarrow[\Delta G^{\circ}\text{ neut.}]{} M(aq) \xrightarrow[e^{2}/2rD]{} M^{Z+}(aq)$$

i.e. the hydration proceeds by discharging the gaseous ion ($-\ e^{2}/2r$), hydrating the resulting neutral species (ΔG° neut) and then re-charging it ($e^{2}/2rD$).

$$\therefore\ \Delta G^{\circ}\text{ hyd} \;=\; \Delta G^{\circ}\text{ neut} \;-\; e^{2}/2r\,(1 - 1/D)$$

$$= \Delta G^{\circ}_{\text{neut.}} + \Delta G^{\circ}_{\text{el.}}$$

The energy change on hydrating the neutral species ($\Delta G^{\circ}_{\text{neut.}}$) is estimated simply from the enthalpy and entropy changes accompanying a change in volume of an ideal gas i.e. when 1 mole of the neutral gaseous species (ideal) dissolves in water at 25°C. to form an ideal 1 molal solution under a pressure of 1 atmosphere

$$(\ \Delta H^{\circ} = -\,P\Delta V\ ;\quad \Delta S^{\circ} = R\ \mathrm{In}\ V_1/V_2\ )$$

The other term (ΔG^o hyd) is obtained from

$$\Delta G^o \text{ hyd} = \left[\Delta G^o\text{aq} - \Delta G^o\text{ion}\right] \pm Z\ G^o_H \qquad \begin{matrix} + \text{cation} \\ - \text{anion} \end{matrix}$$

The expression in the bracket is the conventional energy change (ΔG^ocon) from the aqueous species (ΔG^oaq) to the ion gas (ΔG^oion) and these functions are available from standard thermodynamic references. The term ΔG^o_H refers to the reaction

$$\tfrac{1}{2} H_2 \text{ (g)} \longrightarrow H^+ \text{ (aq)} + e^- \text{ (g)} \qquad \Delta G^o_H$$

and is introduced because using the normal convention of assigning zero values to G^o, H^o and S^o of H^+ (aq) and elements in their standard states, the thermodynamic relationship $\Delta G^o = \Delta H^o - T\Delta S^o$ is not satisfied where there is a net change in charge on the hydrated ions (i.e. ion half-reactions) because tabulated entropies are usually based on application of the third law

$$\text{i.e.} \quad \overline{S}^o \text{ ion (absolute)} = \overline{S}^o \text{ ion (relative)} - Z\,\overline{S}^o_H$$

The relative value is that usually found in standard tables and $\overline{S}^o_H$ is the absolute partial molal entropy of H^+ (aq). Noyes then estimates ΔG^o_H by assuming that the discrepancy caused by the bulk dielectric assumption breaking down may be accounted for, to a first approximation, by an additional term in a power series of $1/_r$.

i.e. combining constants in the Born eqn., we have $\Delta G^{o}_{el} = -\frac{K}{r}$;

this is now modified to account for saturation effects to the form:-

$$\Delta G^{o}_{el} = -\frac{K}{r} + \frac{C}{r^2}$$

Now combining this equation with

$$\Delta G^{o}_{hyd} = \Delta G^{o}_{neut} + \Delta G^{o}_{el}$$

$$\Delta G^{o}_{hyd} = \Delta G^{o}_{aq} - \Delta G^{o}_{ion} + Z\ \Delta G^{o}_{H} \quad \text{(cation)}$$

and $\Delta G^{o}_{con} = \Delta G^{o}_{aq} - \Delta G^{o}_{ion}$

Noyes obtains

$$\Delta G^{o}_{H} + \frac{K}{r} - \frac{C}{r^2} = -\Delta G^{o}_{con} + \Delta G^{o}_{neut}.$$

Equations of similar form are obtained for anions and in terms of ΔS^{o} (to estimate ΔS^{o}_{H}). These equations were graphed for the halides and alkali metals and using a three-parameter least squares technique ^{C} anion and ^{C} cation were determined. Extra polation to zero on the $^1/_r$ axis yields a figure for ΔG^{o}_{H}.

It seems obvious, at this point, that having determined ^{C} anion and ^{C} cation, ΔG^{o}_{el} may be determined directly from

$$\Delta G^{o}_{el} = -\frac{K}{r} + \frac{C}{r^2}$$

However, Noyes implies that this procedure is impracticable in view of the "moderate failure" of the power series expansion approximation. This does not affect the determination of ΔG^{o}_{H} which may be "estimated with considerable confidence", the value quoted agreeing to within a few kilocalories of the values of other investigators. To summarise, knowing ΔG^o_H, ΔG^ohyd may be determined by combining this with conventional data (ΔG^ocon). ΔG^ohyd is then combined with ΔG^oneut. and values of ΔG^oel tabulated. A selection of these values (ΔH^oel) are shown below compared with Latimer's data and "the most probable values" obtained by a group of Russian[18] workers abstracting the literature up to 1960.

TABLE II : COMPARISON OF AVAILABLE ION HYDRATION ENTHALPIES

Ion	$-\Delta H^o$ (Noyes[17])	$-\Delta H^o$ (Latimer[8])	$-\Delta H^o$ (Russian[18])
Li^+	130	121	127
Na^+	103	95	101
K^+	83	76	81
Rb^+	77	69	75
Cs^+	70	62	67
Be^{++}	608	-	601
Mg^{++}	473	-	467
Ca^{++}	394	-	386
Sr^{++}	359	-	353
Ba^{++}	325	-	320
F^-	98	123	116
Cl^-	80	89	84
Br^-	72	81	76
I^-	62	72	67

(all values in kcal/g.ion.)

The data of Noyes was selected as being the most recent (1962) self-consistent set and used for all lattice energy determinations for Group II salts.

It remains now to survey the literature on the determination of lyotropic numbers. This topic, under the title of "Quantitative lyotropy", was reviewed by Voet[19] in 1937 some five years after the majority of lyotropic data was recorded[9,10].

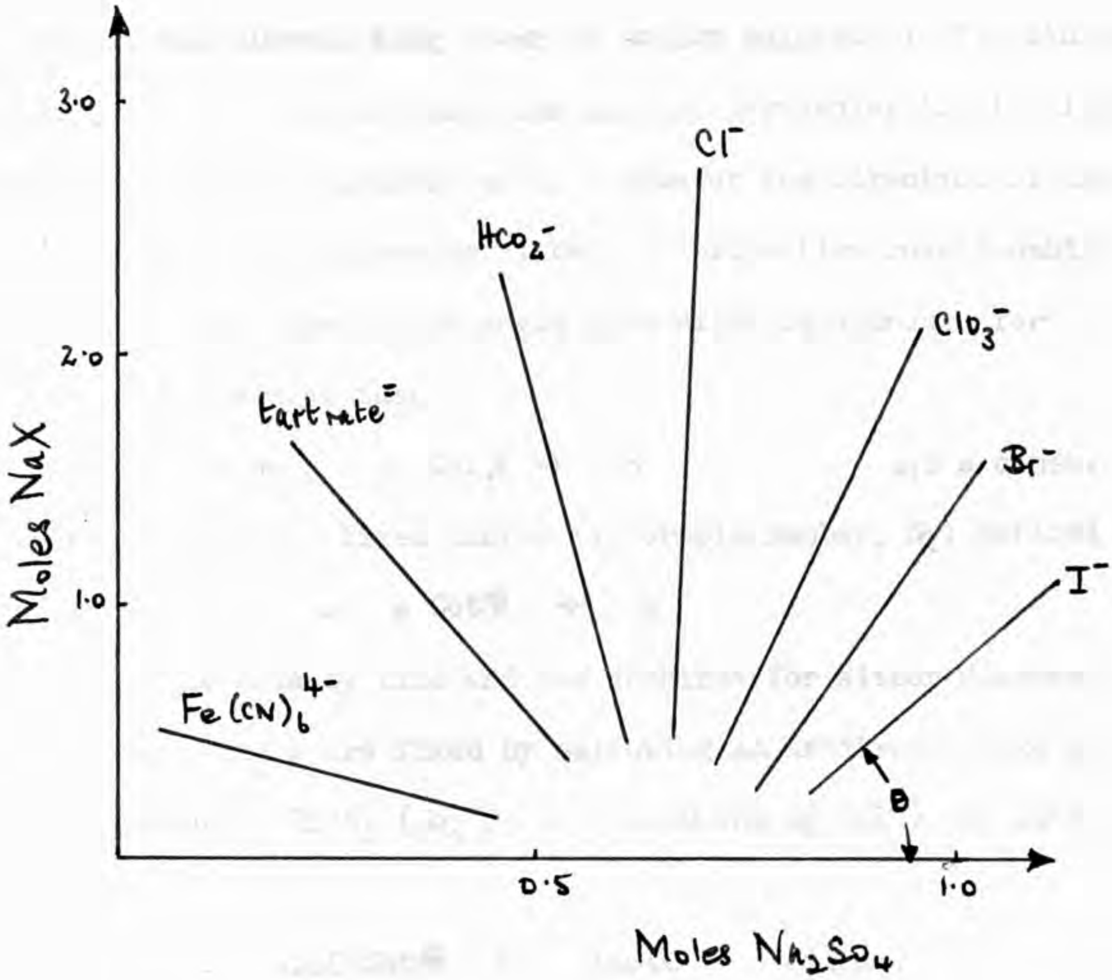
The addition of electrolytes to lyophilic sols results in the disperse phase being precipitated. The extent of this "salting out" effect depends on the ion and a series (Hofmeister (1891) series) may be constructed of salts with a common anion or cation

$Mg^{++} > Ca^{++} > Sr^{++} > Ba^{++} > Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$

$\text{Citrate}^{3-} > \text{tartrate}^{=} > SO_4^{=} > CH_3COO^{-} > Cl^{-} > NO_3^{-} > ClO_3^{-} > I^{-} > CNS^{-}$

$\longleftarrow$ increasing effect.

In 1927 Büchner and Klein[9] working with agar-agar sols and in 1931 Büchner and Postma[10] working with gelatin sols established a quantitative basis for the lyotropic series. These workers found that mixtures of sodium sulphate with other sodium salts caused flocculation of the sol, the amount of sodium salt required bearing a linear relation to the amount of sodium sulphate (except at very low concentrations). This was expressed graphically:-



GRAPH 4 : CONCENTRATIONS OF DIFFERENT SODIUM SALTS VS. CONCENTRATIONS OF SODIUM SULPHATE, MIXTURES OF WHICH ARE NECESSARY TO BRING ABOUT FLOCCULATION OF SOLS.

From the graph it may be seen that, considering a constant amount of sodium sulphate (say 0.4 mole) more tartrate than ferrocyanide is required to cause flocculation i.e. tartrate has a smaller lyotropic effect than ferrocyanide. On the other hand for 0.4 mole of sodium sulphate a negative amount of halide ion is required i.e. halide ions exhibit an anti-flocculating effect in presence of the sulphate ion;

they inhibit the flocculating power of sodium sulphate (a "salting-in" effect). The gradient of lines for any one particular ion is slightly different for agar and gelatin sols. However the direction of the lines, as pointed out by Bruins[20], bear a "projective relationship" to each other i.e. if α is the angle made with the abscissa for gelatin and β for agar then

$$\mathrm{Cot}\,\alpha = A\ \mathrm{Cot}\,\beta + B \qquad A, B = \text{const.}$$

Each ion is ascribed a fixed number (lyotropic number, N_1) defined by

$$N_1 = a\ \mathrm{Cot}\,\theta + b$$

(θ is the angle made by line and the abscissa for either diagram). The constants a and b are fixed by selecting an arbitrary scale for lyotropic number. If $N_1\ (SO_4^{=}) = 2.00$ and $N_1\ (Cl^-) = 10.00$, then

$$N_1 = 4.00\ \mathrm{Cot}\,\theta + 10.00 \qquad \text{(Agar)}$$

and

$$N_1 = -4.78\ \mathrm{Cot}\,\theta + 11.15 \qquad \text{(Gelatin)}$$

Some typical values are shown in the table below.

TABLE III : SOME LYOTROPIC NUMBERS

Sol : Ion	BrO_3^-	NO_2^-	ClO_3^-	Br^-	I^-
Agar	9.72	10.1	10.74	11.50	12.50
Gelatin	9.38	10.2	10.58	11.14	12.48
Accepted figure	9.55	10.1	10.65	11.30	12.50

As well as bearing a linear relationship with combined ion hydration enthalpy or spectroscopic shift, lyotropic number as defined above is linear with a variety of solution and ionic properties e.g. viscosity at a fixed concentration, gelation temperature, surface tension of ionic melts, ionization potential (cations)[19] etc. Such a ubiquitous function would appear easy to define but apart from saying lyotropic number is the extent "to which an ion binds water to itself at the expense of hydrated colloids in suspension", an admittedly imprecise definition, its exact physical significance is uncertain. One of the few attempts to correlate lyotropic number with solution properties is due to Rutskov[21] who rejects the apparent partial molal properties of ions as defined by G.N. Lewis[22] and defines instead two functions representing the "hardness" of ions and the "looseness' of the solvent. The basis of this concept is that, at constant temperature, ions in solution charge neither their volume nor their heat capacity and the change in extensive or intensive property of the solution with changing concentration be ascribed to the solvent rather than the solute, contrary to classical thermodynamics. This may be illustrated in terms of molal volume, a property readily visualizable. The volume of an electrolyte solution at constant temperature, is given by

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2$$

(1 and 2 refer to solvent and solute respectively and $\bar{V}$ is the partial molal function).

In classical terms this equation becomes

$$V = n_1 \bar{V}_1^o + n_2 \phi V_2$$

($\bar{V}_1^o$ being the volume that would be occupied by the solvent in its standard state (at infinite dilution) and ϕV_2 is the apparent partial molal volume of the solute).

Rutskov proposes that the constant component of the solution be the solute and charges in concentration be expressed in terms of the apparent partial molal volume of the solvent

$$\text{i.e.} \quad V = n_1 \phi V_1 + n_2 \bar{V}_2^o$$

This is possibly a realistic concept in very concentrated solutions but suffers from the defect that $\bar{V}_2^o$ may not be evaluated readily because the standard state of a solute is defined in terms of its properties at infinite dilution rather than in terms of the pure phase.

Rutskov's new functions bear a definite qualitative parallel with N_1 but no simple quantitative relationship is discernible.

Finally it is difficult to assign limits of error to lyotropic number data because the experimental conditions of the original determinations were not reproducible; as Buchner[10] says, "Although the pH of the mixture has been shown to have a great influence on the salting out of the gelatin no special measures were taken to make all the experiments at the same pH". Lyotropic numbers which may be cross-checked from both agar and gelatin data will be considerably more reliable than those derived from experiments on one gel only.

DISCUSSION AND RESULTS

The lattice energies derived here originate from the following types of data:-

(i) hydration enthalpies

(ii) lyotropic numbers

and (iii) parameters required for the Kapustinkii equation.

Accordingly, the discussion of the accuracy and validity of these magnitudes is outlined under these headings. Combined ion hydration enthalpy figures are well established for the alkali halides but the enthalpy data for the alkaline earth halides is recent and its validity is checked for these halides by the determination of lattice energies via a Born-Haber cycle not involving the solution process.

SECTION 1) Hydration enthalpy data.

The data used for the Group I metals is that of the alkali halides for which the heats of solution are well established [23]. The lattice energies are those of Huggins[16] corrected to 298°K. - these values are generally considered to be the most accurate available for alkali halides. Values of combined ion hydration enthalpy (ϕ) are obtained via the equation,

$$\Delta H_S^o = \phi + U$$

and are tabulated below

TABLE IV : COMBINED ENTHALPIES OF HYDRATION (ϕ) OF ALKALI HALIDES

(all values in kcal/g.ion pair at 298° K.)

	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	-243.8	-217.2	-198.4	-191.8	-184.6
Cl^-	-209.9	-183.3	-164.5	-157.9	-150.7
Br^-	-202.6	-176.0	-157.2	-150.6	-143.4
I^-	-193.3	-166.7	-147.9	-141.3	-134.1

It is of interest to compare the values of Noyes[17] obtained by direct summation

$$\phi = \Delta H_+ + \Delta H_-$$

TABLE V : COMBINED ENTHALPIES OF HYDRATION (ϕ) OF ALKALI HALIDES

from Noyes' DATA - values in kcal/g.ion pair 298°K.

	Li^+	Na^+	K^+	Rb^+	Cs^+
F^-	-227.4	-201.3	-181.2	-174.5	-167.4
Cl^-	-210.0	-183.8	-163.7	-157.8	-149.9
Br^-	-202.0	-175.7	-155.6	-149.7	-141.8
I^-	-191.5	-165.3	-145.2	-139.3	-131.4

The principal differences occur in the alkali fluorides.

The hydration enthalpies used for calculations on Group II were all taken from Noyes and combined values obtained via direct summation are recorded below

$$\phi = \Delta H_{+} + 2\Delta H_{-}$$

TABLE VI : COMBINED ION HYDRATION ENTHALPIES FOR ALKALINE EARTH HALIDES

(values in kcal./g.ion pair at 298°K)

	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
F^-	-803.6	-668.9	-590.1	-554.8	-521.1
Cl^-	-768.6	-633.9	-555.1	-519.8	-486.1
Br^-	-752.4	-617.7	-538.9	-503.6	-469.9
I^-	-731.6	-596.9	-518.1	-482.8	-449.1

These data were combined with experimental heats of solution obtained from standard references[23] and lattice energies were derived. An alternative method for obtaining lattice energies, in this case, is to make use of a Born-Haber cycle which does not include the solution process. It does however assume a knowledge of the electron affinity of the anion and is therefore generally applied to halides, the only anions for which accurate electron affinities are available.

Cycle for MX_2 :-

$$\begin{tikzcd}
MX_2\ (\text{cryst.}) \arrow[r, "-\Delta H_f^o"] & M\ (S\text{-}S) \arrow[d, "S"] & + & X_2\ (S\text{-}S) \arrow[d, "D"] \\
 & M(g) \arrow[d, "I"] & & 2X\ (g) \arrow[d, "-2E"] \\
 & M\ (g) \arrow[uul, "\Delta H_L"] & + & 2X^-\ (g)
\end{tikzcd}$$

All magnitudes refer to 25°C. and 1 atmosphere.

ΔH_f^o = enthalpy of formation of the crystalline salt.

S = enthalpy of sublimation of the metal M

D = dissocation energy of the halide, X_2.

E = electron affinity of the gaseous X radical.

I = ionization potential of the metal atom, M.

ΔH_L = lattice enthalpy of the crystalline salt.

Using the convention that lattice energy is positive then, for a salt MX_n, the lattice energy is related to the lattice enthalpy via

$$\begin{aligned} U &= -\left(\Delta H_L - [n+1]\ RT\right) \\ &= -\left(\Delta H_L - 0.6\,[n+1]\right)\ \text{kcal/mole.} \end{aligned}$$

from the above cycle :-

$$\Delta H_L = \Delta H_f^o - S - D - I + 2E$$

The parameters in this equation are tabulated below for the Group II halides and the derived lattice energies are compared with the theoretical lattice energies of Morris[24], where data is available.

TABLE VII : PARAMETERS FOR THE CALCULATION OF LATTICE ENERGIES OF GROUP II HALIDES

Crystal	$\Delta H_f^{o\dagger}$	$-S^{*}$	$-D^{*}$	$-I^{*}$	$2E^{*}$	ΔH_L	U	U_{theo}
Be F_2	-	-78	-38.2	-634	166	-	-	-
Be Cl_2	-122.3	-78	-58.0	-634	171.6	-720.7	719	-
Be Br_2	- 88.4	-78	-53.4	-634	161	-692.8	691	-
Be I_2	- 50.6	-78	-51.0	-634	148.4	-665.2	663	-
Mg F_2	-263.5	-36	-38.2	-522	166	-693.7	692	684
Mg Cl_2	-153.4	-36	-58.0	-522	171.6	-597.8	596	-
Mg Br_2	-123.7	-36	-53.4	-522	161	-574.1	572	513
Mg I_2	-86.0	-36	-51.0	-522	148.4	-546.6	545	486
Ca F_2	-290.3	-42	-38.2	-415	166	-619.5	618	622
Ca Cl_2	-190.0	-42	-58.0	-415	171.6	-533.4	531	-
Ca Br_2	-161.3	-42	-53.4	-415	161	-510.7	509	-
Ca I_2	-127.8	-42	-51.0	-415	148.4	-487.4	485	455
Sr F_2	-290.3	-39	-38.2	-385	166	-586.5	585	592
Sr Cl_2	-198.0	-39	-58.0	-385	171.6	-508.4	506	496
Sr Br_2	-171.1	-39	-53.4	-385	161	-487.5	485	-
Sr I_2	-135.5	-39	-51.0	-385	148.4	-462.1	460	-
Ba F_2	-286.9	-42	-38.2	-350	166	-551.1	549	561
Ba Cl_2	-205.6	-42	-58.0	-350	171.6	-484.0	482	-
Ba Br_2	-180.4	-42	-53.4	-350	161	-464.8	463	-
Ba I_2	-144.0	-42	-510	-350	148.4	-438.6	437	-

† Data from N.B.S. Circular 500, 1952.

* Data from Ketelaar, "Chemical Constitution", 1958 (Elsevier).

The difference between the "experimental" lattice energy (from Born-Haber cycle) and the "theoretical" value (from Born equation) indicates the departure from strict heteropolarity in the crystal. This is due to the fact that the derivation of the Born equation

$$U = \frac{Z^2 e^2 N M}{r_o} \left(1 - \frac{1}{n}\right)$$

assumes the crystal structure to be totally ionic. Morris [25, 26] points out that within a given series of halide salts the deviation between experimental and theoretical values becomes greater as the ionization potential of the metal increases. The ionization potential may be considered as the attraction exerted by an ion on the last electron removed. In a crystal lattice this force of attraction will be directed towards the more loosely-bound electrons of the anions and therefore with increasing ionization potential of the cation an increase in the covalent contribution to the lattice bonding is to be expected. This is an admittedly simplified picture, the polarizability and electron affinity of the anion being ignored.

The combined ion hydration enthalpies of Table VI were combined with heats of solution and the lattice energies so derived are tabulated below and compared with the Born-Haber cycle values in Table VII.

TABLE VIII : LATTICE ENERGIES OF ALKALINE EARTH HALIDES FROM HYDRATION ENTHALPY DATA.

	ϕ	ΔH^{o}_{S} *	ΔH_{L}	U	U(B-H cycle)
MgF_2	-668.9	- 4.4	-664.5	663	693
$MgCl_2$	-633.9	-37.1	-596.8	595	596
$MgBr_2$	-617.7	-44.5	-573.2	571	573
MgI_2	-596.9	-51.2	-545.7	544	545
CaF_2	-590.1	3.2	-593.4	592	618
$CaCl_2$	-555.1	-19.8	-535.3	533	532
$CaBr_2$	-538.9	-26.3	-512.6	511	510
CaI_2	-518.1	-28.7	-489.4	487	486
SrF_2	-554.8	2.5	-557.3	555	585
$SrCl_2$	-519.8	-12.4	-507.4	505	507
$SrBr_2$	-503.6	-17.1	-486.5	485	486
SrI_2	-482.8	-21.6	-461.2	459	461
BaF_2	-521.1	0.9	-522.0	520	550
$BaCl_2$	-486.6	- 3.1	-483.5	482	484
$BaBr_2$	-469.9	- 6.1	-463.8	462	465
BaI_2	-449.1	-11.4	-437.7	436	437

* Data from N.B.S. Circular 500, 1952.

The agreement between the final two columns of the above table is very good, the error being less than ± 0.5%, except in the case of the fluorides where the error is systematically + 4%. It would appear that the value calculated by Noyes for the ion hydration enthalpy of F^- is considerably too low. A value for ΔH_{F^-}, calculated to give internal consistency within the above table, is compared with the other available literature values in the table below.

TABLE IX : ION HYDRATION ENTHALPY OF THE FLUORIDE ANION.

Workers	ΔH_- (F^-)
Latimer[8] et al, 1939	-123
Russian[18] workers (best values), 1960	-116
Noyes[17], 1962	-98
Randles[27], 1956	-108.7 ± 1
This work	-114 ± 1

Randles[27] calculates the free energy of hydration of F^- by a precise electro-chemical method to be -99.1 ± 1 kcal/g ion. This figure was converted into an enthalpy of hydration using the relationship,

$$\Delta G_- = \Delta H_- - T(\bar{S}_i^o - S_-(g)).$$

$\bar{S}_i^o$ = partial molal entropy of F^-

$S_-(g)$ = molal entropy of F^- ion gas.

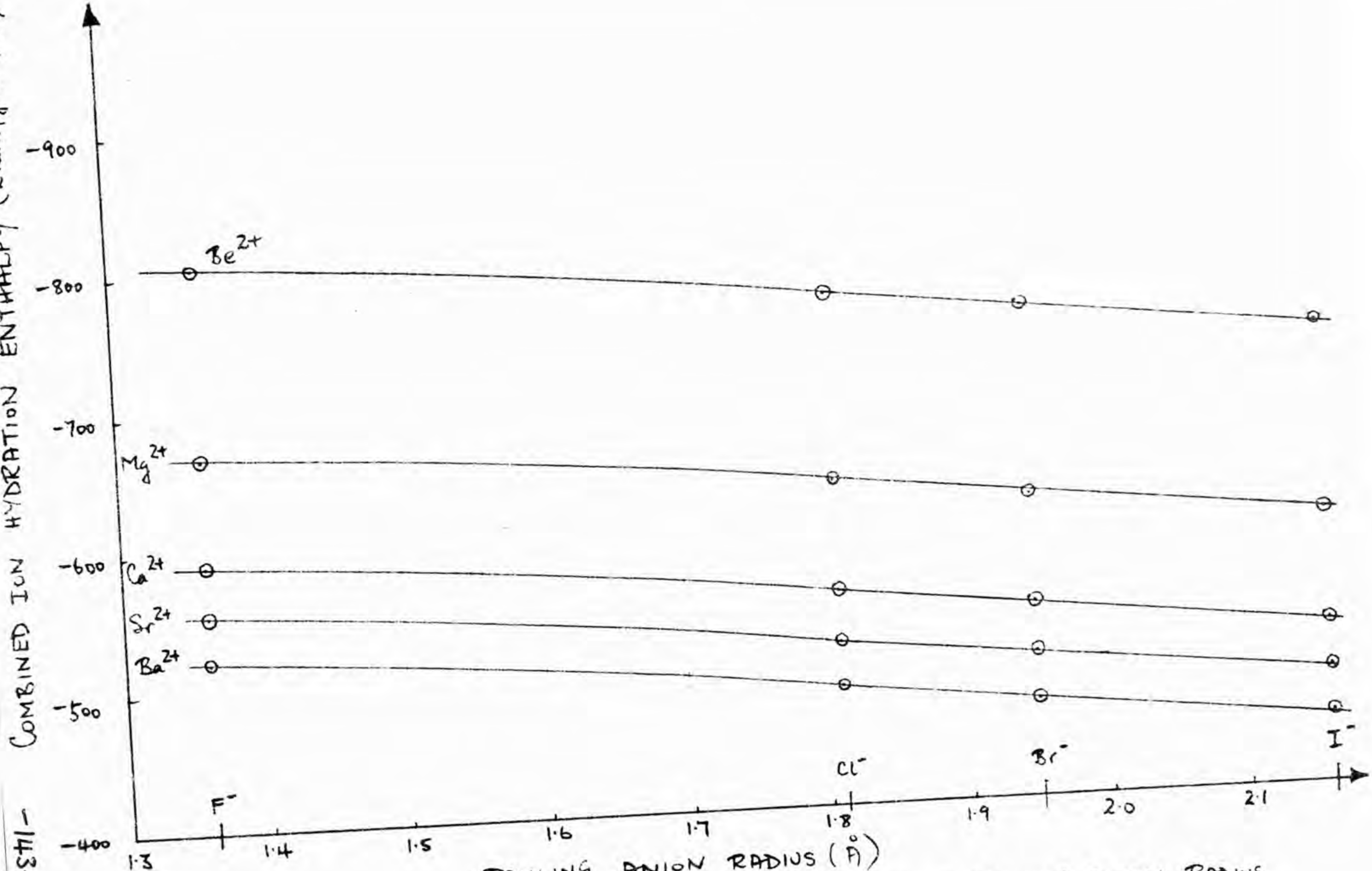
Tabulated $\bar{S}_i^o$ values are usually relative to a zero partial molal entropy of H^+ (aq). For this calculation, Bockris' figure[28] of -5.0 cal./mole deg. for $\bar{S}^o_i$ (H^+ aq.) was accepted

i.e. $$\Delta H_- = \Delta G_- + 298.2 \left[\bar{S}^o_i \text{ (rel. } F^- \text{)} - 5Z_i - S_- \text{ (g)} \right]$$

However there remains a considerable discrepancy between the figures for hydration enthalpy of F^- and Randles' data (~ 5 kcal/g. ion). It was decided, in subsequent calculations, to accept Noyes' data as a complete self-consistent set.

Now that the validity of Noyes' hydration enthalpy data is established two large scale plots of (i) combined ion hydration enthalpy of the Group II halides vs. lyotropic number of the anion and (ii) combined ion hydration enthalpy vs. Pauling anion radius, were constructed for interpolation purposes (see Graph 5A).

The curvature may be interpreted as further evidence for Noyes' anomalous value for the ion hydration enthalpy of the fluoride ion.



GRAPH 5A: COMBINED ION HYDRATION ENTHALPY FOR GROUP II HALIDES VS. PAULING ANION RADIUS

SECTION 2) Lyotropic numbers.

Lyotropic numbers were recalculated from the original data of Büchner and Klein[9], Büchner and Postma[10], and Büchner[11-13] and are presented in the table below.

TABLE X. LYOTROPIC NUMBERS.

Anion	Source			N_1 (accepted)
	Gelatin	Agar	Viscosity interpolation.	
$Fe(CN)_6^{4-}$	-4.08	-4.93	-	
tartrate$^{=}$	2.93	4.60	-	
IO_3^-	6.43	-	6.25	6.3
BrO_3^-	9.37	9.68	-	9.5
Cl^-	10.00	10.00	-	10.00*
ClO_3^-	10.58	10.74	-	10.7
Br^-	11.09	11.46	-	11.3
I^-	12.48	12.45	-	12.5
CNS^-	13.29	-	13.25	13.3
$C_6H_5SO_3^-$	14.90	-	-	
$SO_4^{=}$	-	-	-	2.00*
Citrate^{3-}	-	1.42	-	
$S_2O_3^{=}$	-	7.15	-	
$WO_4^{=}$	-	7.40	-	7.4
$MoO_4^{=}$	-	8.26	-	8.3
$HCOO^-$	-	9.15	-	9.1
CH_3COO^-	-	9.51	-	9.5
$Cr_2O_7^{=}$	-	17.07	-	

Anion	Source Gelatin	 Agar	 Viscosity interpolation.	N_1 (accepted).
N_3^-	11.5	-	10.3	11.5 ‡
F^-	-	-	4.8	4.8
NO_3^-	-	-	11.6	11.6
ClO_4^-	-	-	11.8	11.8
NO_2^-	10.2 †	10.1 †	-	10.1 †

* $SO_4^=$ and Cl^- are reference anions

† conflicting reports exist for NO_2^- : probably unreliable

‡ this figure accepted by Waddington.

As mentioned in the introduction, limits of error are difficult to assign to these data but probably for ions where there exist two independent determinations the error is ± 0.2 (with the exception of NO_2^-) while for other values the error may be as high as ± 1.0.

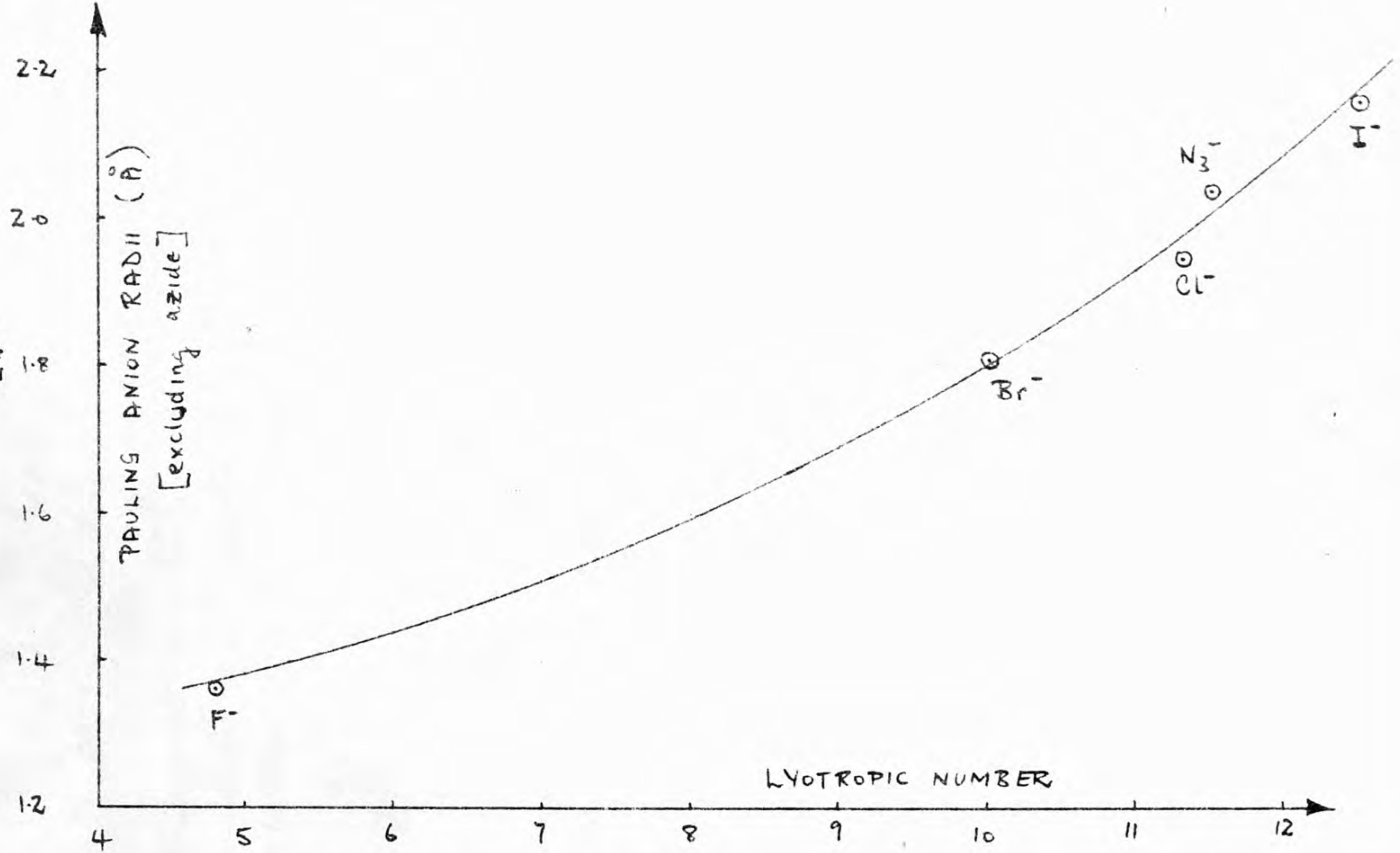
SECTION 3) Parameters required for the Kapustinkii equation.

Kapustinkii's equation in its most usual form is

$$U = \frac{287.2\,\nu Z_1 Z_2}{r_C + r_A}\left[1 - \frac{0.345}{r_C + r_A}\right] \text{ kcal./mole.}$$

for a salt $M_m X_n$ where $m + n = \nu$ and $mZ_1 + nZ_2 = 0$ and r_C and r_A are the cationic and anionic radii respectively.

The parameters ν , Z_1, Z_2 are obtained from the stoichiometry of the compound and r_C is the Goldschmidt ionic radius for coördination number 6. It is the determination of r_A, in the case of complex anions, which raises problems. Yatsimirskii overcame this by determining a series of "thermochemical radii" by a method outlined in the introduction. This technique is by no means of universal application however as it is necessary to know $\Delta H^{o}_{f}\ M_1X$ (c), $\Delta H^{o}_{f}\ M_2X$ (c), $\Delta H^{o}_{f}\ M_1^{+}$ (g) and $\Delta H^{o}_{f}\ M_2^{+}$(g) to ascertain r_{X^-}. The standard enthalpies of formation of the metal ion gases are well established but only enthalpies of formation of conventional crystalline salts are available. Also, in Yatsimirskii's derivation one uses a small thermodynamic quantity (i.e. $\Delta H^{o}_{f}\ M_1X$ - $\Delta H^{o}_{f}\ M_2X$) to calculate a relatively large one and this will tend to produce large errors. For anions for which the charge distribution and structure is known, a statistically averaged radius for the repulsion envelope may be determined (e.g. for N_3^- and HF_2^-; Waddington[4,5]). A more empirical approach was attempted here; both lyotropic number and halide radii are approximately linear with combined ion hydration enthalpy, therefore N_1 should bear an approximately linear relationship to anion radius. A graph of N_1 vs. anion radii for halides (and azide using Waddington's mean figure) was constructed and "effective crystal radii" for other anions interpolated (see Graph 6). A correlation between these interpolated figures and some other easily accessible ionic parameter was attempted. Pauling radii, "thermochemical radii", partial molal volume and "effective crystal radii" for some oxyanions are tabulated below.



GRAPH 6 : PAULING ANION RADIUS FOR HALIDES VS. LYOTROPIC NUMBER.

TABLE XI. IONIC PARAMETERS AND LYOTROPIC NUMBER

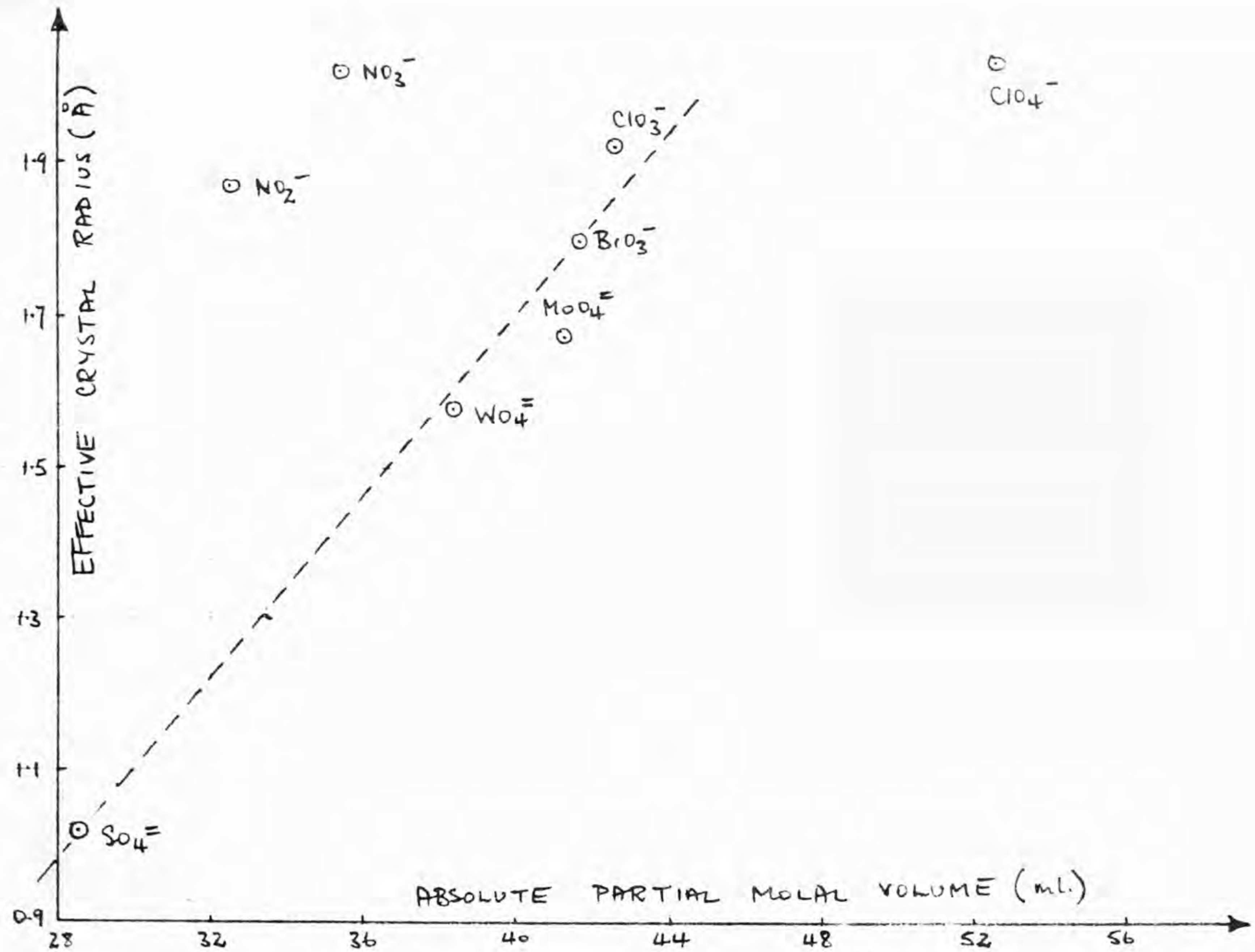
Ion	N_1	r(Å) Pauling	r(Å) "thermo-chemical"	r(Å) "effective crystal"	$\bar{V}^{o}_{i}$ (abs.)
F^-	4.8	1.36			
Cl^-	10.0	1.81			
Br^-	11.3	1.95			
I^-	12.5	2.16			
N_3^-	11.5	2.04			
IO_3^-	6.3		1.82	1.46 ± .05	
BrO_3^-	9.5	1.68	1.91	1.80 ± .04	41.6
NO_2^-	10.2	1.24	1.55	1.87 ± .04	32.5
ClO_3^-	10.7	1.48	2.00	1.92 ± .04	42.4
NO_3^-	11.6	1.24	1.89	2.01 ± .04	35.3
$SO_4^{=}$	2.0	1.50	2.30	1.02 ± .06	28.4
$WO_4^{=}$	7.4	1.95		1.58 ± .04	38.3
$MoO_4^{=}$	8.3	1.83	2.54	1.67 ± .04	41.5
ClO_4^-	11.8	1.52	2.36	2.03 ± .03	52.4

Because lyotropic number is linear with "effective crystal radius" (e.c.r.) an attempt to correlate this latter function with established data constitutes an attempt to elucidate the lyotropic effect in terms of well-known parameters. It is not expected that this will be proportional to size effect only; therefore various reasonable functions of charge, radius, number of charge bearing ligands were tried in an attempt to connect "e.c.r." with physical data. All were conspicuously unsuccessful. However an approximately linear correlation between "e.c.r." and absolute partial molal volume (assuming[29] $\bar{V}^{\circ}$ (H^{+} aq.) = - 6.0 ml.) was observed (see Graph 7). Extensive deviations were apparent for perchlorate, nitrate, and nitrite however. It is significant that these three ions are those for which lyotropic number is obtained via interpolation of viscosity data. Moreover Büchner points out that conflicting data appears in the literature for the nitrite ion. Couture and Laidler[29] have established the following empirical correlation between absolute ionic partial molal volume and Pauling radius

$$\bar{V}^{\circ}_{-} = 58.8 + 0.89\,(0.25\,n\,r)^{3} - 26\,|Z_{-}|$$

where r = Pauling radius + van der Waals radius for oxygen (1.40 Å)

n = number of charge bearing ligands on anion



GRAPH 7: EFFECTIVE CRYSTAL RADIUS VS. ABSOLUTE PARTIAL MOLAL VOLUME

As may be seen from the graph the correlation is not a satisfactory one. Further work is in progress, however, on the three anomalous ions because if this correlation were accurate, by combining it with Couture and Laidler's data, lyotropic numbers for many ions could readily be deduced.

Finally, the accuracy obtainable using the Kapustinkii equation is illustrated in the following table comparing the most accurate values (Huggins[16]), Born-Haber cycle values and Kapustinkii values of the lattice energies of the alkali halides (percentage error in brackets in final column).

TABLE XII : LATTICE ENERGIES OF THE ALKALI HALIDES.

(all values in kcal./mole)

Salt	U (Born Haber)	U (Huggins)	U (Kapustinkii)	
Li F	241.2	243.6	227.7	(-6.5%)
Li Cl	198.2	200.2	192.1	(-4.0)
Li Br	188.5	189.5	189.5	(0.0)
Li I	175.4	176.1	170.4	(-3.2)
Na F	216.0	215.4	211.5	(-1.8)
Na Cl	183.8	183.5	179.9	(-2.0)
Na Br	175.9	175.5	175.5	(0.0)
Na I	164.5	164.3	161.0	(-2.0)
K F	191.5	192.5	188.5	(-2.1)
K Cl	166.8	167.9	162.7	(-3.1)

Salt	U(B.H)	U (Huggins)	U (Kapustinkii)	
K Br	160.7	161.3	161.3	(0.0)
K I	151.0	152.4	146.8	(-3.7)
Rb F	183.6	183.0	181.7	(-0.7)
Rb Cl	162.0	162.0	158.2	(-2.3)
Rb Br	155.2	156.1	149.7	(-4.1)
Rb I	146.5	148.0	141.0	(-4.7)
Cs F	171.0	175.7	170.4	(-3.0)
Cs Cl	153.2	153.1	149.4	(-2.4)
Cs Br	148.3	149.6	143.9	(-3.8)
Cs I	140.3	142.5	134.7	(-5.5)

SECTION 4) Group I salts.

The lattice energies of Group I salts, determined by the hydration enthalpy method, has been quite extensively studied, principally by Morris[14]. However with the advent of new data, further derivations can be made.

(a) Bromates.

Boyd and Vaslow[30] have recently determined the standard heats of solution for the alkali metal bromates. These data and other available data are tabulated below.

TABLE XIII : HEATS OF SOLUTION FOR GROUP I BROMATES.

Salt	ΔH°_S †	ΔH°_S ‡	ΔH°_S *
$LiBrO_3$	0.34	-	-
$NaBrO_3$	6.35	6.43 ± .06	-
$KBrO_3$	9.70	9.76 ± .05	9.8
$RbBrO_3$	11.69	-	-
$CsBrO_3$	12.01	-	-

† Boyd & Vaslow[30], ‡ Spencer and Hepler[31], * NBS Circ. 500, 1952.

From Boyd's data and interpolated combined ion hydration enthalpies, lattice energies are derived.

Using

$$\phi = \Delta H_+ + \Delta H_-$$

where ΔH_+ is taken from Latimer's data[8], ΔH_- is also determined.

Using

$$M\,BrO_3(c) \longrightarrow M^+(g) + BrO_3^-(g)$$

i.e. $$-\Delta H_L = \Delta H^o_f\,M^+(g) + \Delta H^o_f\,BrO_3^-(g) - \Delta H^o_f\,M\,BrO_3(c)$$

where $\Delta H^o_f\,M\,BrO_3$ is taken from Boyd and $\Delta H^o_f\,M^+(g)$ from standard references, $\Delta H^o_f\,BrO_3^-(g)$ is derived. An independent check on the validity of the assumption of ionic nature and on the accuracy of the calculation is provided by the consistency of $\Delta H_f^o BrO_3^-(g)$ from salt to salt. In addition, the lattice energy was calculated directly using Kapustinkii's equation and a Yatsimirskii "thermochemical radius" for BrO_3^- of 1.91 Å. These data are presented below.

TABLE XIV : LATTICE ENERGIES AND DERIVED FUNCTIONS FOR ALKALI METAL BROMATES.

Salt	ΔH_S^o	ϕ	ΔH_L	U	ΔH_-	$\Delta H_f^o M^+(g)$	$\Delta H_f^o MBrO_3(c)$	U (calcd)	$\Delta H_f^o BrO_3^-(g)$
$LiBrO_3$	.34	-2120	-212.3	211	-91	160.86	-85.19	197	-33.7
$NaBrO_3$	6.35	-186.5	-192.8	192	-91.5	146.01	-81.93	177	-35.1
$KBrO_3$	9.70	-168.5	-178.2	177	-92.5	123.07	-88.04	158	-32.9
$RbBrO_3$	11.7	-161.5	-173.2	172	-92.5	118.3	-88.90	152	-34.0
$CsBrO_3$	12.0	-154.0	-166.0	165	-92	110.1	-89.51	144	-33.6

Mean value for ΔH_- = -91.9 kcal/g.ion (lit. -91.6)*

" " " $\Delta H_f^o BrO_3^-(g)$ = -33.9 kcal/g.ion.

* This lit. value (Morris) is derived from an unspecified salt[14].

(b) Sulphates.

The heats of solution of alkali metal sulphates were obtained from the N.B.S.[23] Circular 500 using

$$\Delta H_S^o = \Delta H_f^o M_2SO_4(aq) - \Delta H_f^o M_2SO_4(c)$$

Combined ion hydration enthalpies were obtained by interpolation followed by addition of the relevant ion hydration enthalpy of the metal. This is because the graphs were constructed for salts of the type MX and alkali metal sulphates are of the type M_2X

$$\text{i.e. } \phi = (\Delta H_+ + \Delta H_-)_{\text{interpolated}} + (\Delta H_+)_{\text{Latimer}}$$

Enthalpy of formation of the sulphate ion gas was obtained using

$$\Delta H_f^o \, SO_4^=(g) = -\Delta H_L - 2\,\Delta H_f^o \, M\,(g) + \Delta H_f^o \, M_2 \, SO_4(c)$$

Calculated values are based on the Yatsimirskii "thermochemical radius" for $SO_4^=$ of 2.30 Å.

TABLE XV : LATTICE ENERGIES OF ALKALI METAL SULPHATES.

Salt	ΔH_s^o	ϕ	ΔH_L	U	ΔH_-	$\Delta H_f^o M_2SO_4(c)$	U (calcd.)	$\Delta H_f^o SO_4^=(g)$
Li_2SO_4	-7.2	-382	-374.8	373	-140	-342.83	523	-289.7
Na_2SO_4	-0.56	-330	-329.4	327	-140	-330.90	457	-293.5
K_2SO_4	5.93	-294	-299.9	298	-142	-342.66	430	-288.8
Rb_2SO_4	5.8	-278	-283.8	282	-140	-340.5	402	-293.3
Cs_2SO_4	4.1	-265	-269.1	267	-141	-339.4	394	-290.5

The agreement between "experimental" values and calculated values is very poor - inaccurate data for "thermochemical radius" cannot account for this gross error. It is possible to make an independent calculation of lattice energy from

$$\Delta H_L = \Delta H_f^o\ MX(c) - \Delta H_f^o\ M^+(g) - \Delta H_f^o\ X^-(g)$$

if independent data for $\Delta H_f^o\ X^-(g)$ exists.

Using the following cycle, this function was estimated

$$\begin{tikzcd}
 & SO_4^{=}(g) \arrow[dr, "-\Delta H_-"] & \\
S(s\text{-}s) + 4O_2(g) \arrow[ur, "\Delta H_f^o(SO_4^{=})aq"] \arrow[rr, "\Delta H_f^o\ SO_4^{=}(aq)"'] & & SO_4^{=}\ (aq)
\end{tikzcd}$$

i.e. $\Delta H_f^o\ SO_4^{=}(g) = -\Delta H_- + \Delta H_f^o\ SO_4^{=}(aq)$

$\Delta H_f^o\ SO_4^{=}(aq)$ is readily available but the only value for ΔH_- is a "best" value of a group of Russian workers[18]. From the equation, $\Delta H_f^o\ SO_4^{=}(g) = -48.1$ kcal./g.ion. This yields the following values for lattice energy (U')

	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
U'	616.4	574.8	540.6	529.0	511.5
U(Kapustinkii)	523	457	430	402	394

The agreement is still poor, although the calculated values lie on the right side of the experimental values, and data on lattice energies of alkali metal sulphates must be regarded as inconclusive.

(c) Iodates.

Stern and Passchier[32] report the standard enthalpy of formation of the aqueous iodate ion as -54.8 ± 0.5 kcal/g.ion. Hepler[31] reports standard heats of solution for sodium, ammonium and potassium iodates and Murgulescu[33] has determined heats of solution for sodium and lithium iodates.

TABLE XVI : LATTICE ENERGIES OF SOME IODATES.

Salt	ΔH_s°	ϕ	ΔH_L	U	ΔH_-	$\Delta H_f^\circ M^+(g)$	$\Delta H_f^\circ MIO_3(c)$	U^* (calcd.)	$\Delta H_f^\circ IO_3^-(g)$
$LiIO_3$	1.59	-233	-234.6	233	-112	160.86	-122.9	203.5	-49.2
$NaIO_3$	4.83	-207	-211.8	211	-112	146.01	-116.9	181.5	-51.1
NH_4IO_3	7.62	-191	-197.6	196	-113	150	- 94.2	177.2	-46.6
$Ba(IO_3)_2$	11.2	-513	-524.2	522	-94	395.70	-249.5	484	-60.5
KIO_3	6.5	-191	-197.5	196	-115	123.07	-121.3	162	-46.9

* "thermochemical radius" for IO_3^- = 1.82 Å.

† calcd. from $\Delta H_f^\circ (IO_3^-)$ aq.

‡ calcd. from ΔH_- of NH_4^+ (Russian "best" value).

SECTION 5) GROUP II SALTS.

Relative to the alkali metal salts, alkaline earth salts have received scant attention in the literature of thermochemistry.

(a) SULPHATES.

Standard heats of solution of alkaline earth sulphates are available in N.B.S. Circular 500, 1952. Using the methods outlined under Group I salts, the following data were derived.

TABLE XVII : LATTICE ENERGIES AND DERIVED DATA OF GROUP II SULPHATES.

Salt	ΔH^{o}_{s}	ϕ	ΔH_L	U	ΔH_-	ΔH^{o}_{f} MSO_4 (c)	U (calcd.)	ΔH^{o}_{f} $SO_4^{=}$(g.)
$BeSO_4$	-24	-815	791	790	-207	-286.0	764	-209
$MgSO_4$	-21.8	-683	661	660	-210	-305.5	688	-206
$CaSO_4$	- 4.25	-603	599	598	-208	-342.4	625	-207
$SrSO_4$	- 2.0	-568	566	565	-209	-345.3	602	-207
$BaSO_4$	4.6	-532	537	535	-207	-350.2	570	-208

The agreement here is only a little better than for the Group I sulphates although in both cases the results are internally consistent as indicated by the values for ΔH^{o}_{f} $SO_4^{=}$(g)

(b) HYDROXIDES.

Standard heats of solution are available in N.B.S. Circ. 500. The value for $Be(OH)_2$ was estimated from the standard heats of formation of the aqueous ions and the crystal. No lyotropic data is available for OH^- but Goubeau[34] proposes a crystal radius of 1.47 Å. Accordingly interpolation of combined ion hydration enthalpy was via the r_- vs. ϕ plot. Yatsimerskii calculates a value of 1.40 Å. for the "thermochemical radius". Data is tabulated below.

TABLE XVIII : LATTICE ENERGIES AND DERIVED DATA FOR ALKALINE EARTH HYDROXIDES.

Salt	ΔH°_s	ϕ	ΔH_L	U	ΔH_-	$\Delta H^\circ_f M(OH)_2(c)$	$\Delta H^\circ_f M^{++}(g)$	U (calcd.)	$\Delta H^\circ_f OH^-(g)$
$Be(OH)_2$ (α-form)	13.8	-988	-1001.8	1000	-190	-216.8	714.4	794	35.3
$Mg(OH)_2$	0.7	-851	-851.7	850	-189	-221.0	561.8	665	34.5
$Ca(OH)_2$	-3.9	-772	-768.1	766	-189	-235.8	463.6	602	34.3
$Sr(OH)_2$	-11.0	-735	-724.0	722	-188	-229.3	427.7	562	33.5
$Ba(OH)_2$	-12.4	-703	-690.6	689	-189	-226.2	395.7	535	34.3

There is a wide divergence in the literature for values of ΔH°_f $OH^\circ(g)$ values varying from 43 to 76 kcal/g. ion. The value found here (34.4) seems too low. Waddington[2] proposes a value of 50 kcal/g.ion which is in accord with experimental determinations[47] of electron affinity for OH^-.

(c) NITRATES

There is no data available for beryllium nitrate but other heats of solution were taken from N.B.S. Circular 500. The "thermo-chemical radius" for nitrate is 1.89 Å.

TABLE XIX : LATTICE ENERGIES AND DERIVED DATA FOR ALKALINE EARTH NITRATES.

Salt	ΔH°_s	ϕ	ΔH_L	U	ΔH_-	$\Delta H^\circ_f M(NO_3)_2(c)$	U(calcd.)	$\Delta H^\circ_f NO_3^-(g.)$
$Mg(NO_3)_2$	-20.43	-612	-591.6	590	-69.4	-188.72	578	-79.5
$Ca(NO_3)_2$	- 4.51	-534	-529.5	528	-69.8	-224.00	527	-79.1
$Sr(NO_3)_2$	4.23	-498	-502.2	500	-69.4	-233.25	505	-79.4
$Ba(NO_3)_2$	9.65	-464	-473.6	472	-69.3	-237.06	475	-79.6

Literature data on nitrates is reasonably consistent and is tabulated below.

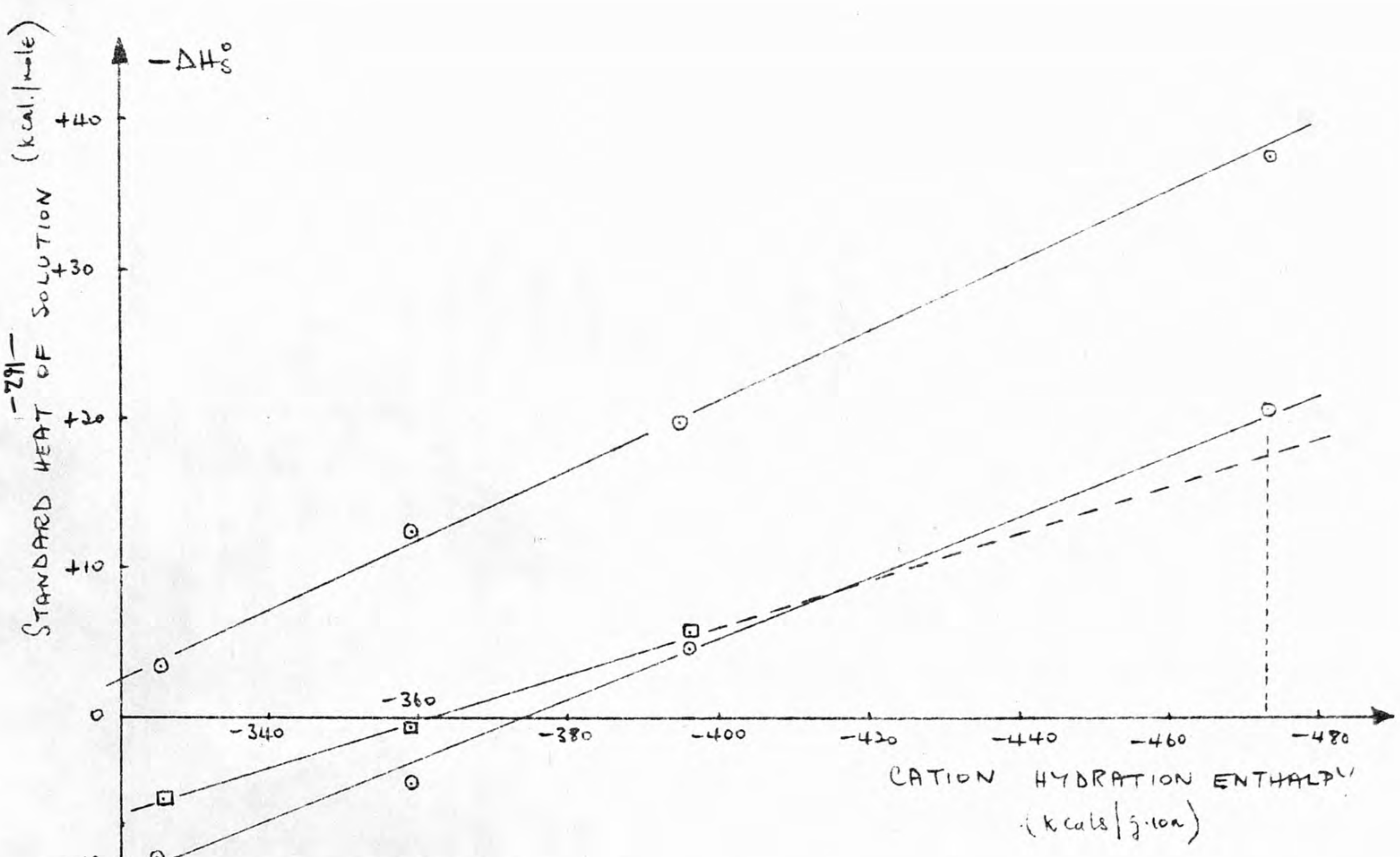
TABLE XX : COMPARISON OF DATA FOR NITRATE

Source	ΔH_-	Source	$\Delta H^\circ_f NO_3^-(g)$
Morris, 1958	-78.2	Waddington, 1955	-81.4
Russian group, 1960	-74	Yatsimirskii, 1947	-80
This work	-69.5	This work	-79.4
		Morris, 1958	-79.1

(d) CHLORATES.

Heats of solution of alkaline earth chlorates were determined experimentally in a constant-temperature-environment solution calorimeter. All salts of commercial grade were purified by crystallisation, dehydrated and analysed. Unfortunately magnesium chlorate decomposes before it dehydrates. However, standard heat of solution bears an approximately linear relationship with cation hydration enthalpy as shown for Group II nitrates and chlorides. Thus the heat of solution of magnesium chlorate was interpolated and assigned an error of ± 10% (see Graph 8A). Combining these data with the National Bureau of Standards value for ΔH_f^o ClO_3^-(aq.), new values for the standard heats of formation of the crystals may be derived.

The heat of solution data is presented below i.e. ΔH_S^o at T^oC. and mole ratio N (detailed calorimetric data is tabulated in Appendix II).



GRAPH 8A: STANDARD HEAT OF SOLUTION VS. CATION HYDRATION ENTHALPY

TABLE XXI : HEATS OF SOLUTION OF ALKALINE EARTH CHLORATES.

Salt	T°C	N	ΔH_S	ΔH^{o}_S (accepted)
$Ba(ClO_3)_2$	24.1	555	5.62	5.64 ± 0.05
	24.8	497	5.71	
	24.6	305	5.67	
	24.7	473	5.58	
$Sr(ClO_3)_2$	24.7	453	0.64	0.61 ± 0.05
	24.6	381	0.58	
$Ca(ClO_3)_2$	24.2	525	-5.59	-5.60 ± 0.02
	25.1	977	-5.61	
$Mg(ClO_3)_2$*	(25)	-	-	-17.5 ± 2.00

* estimated.

Derived data is shown in the following table.

TABLE XXII : LATTICE ENERGIES AND DERIVED DATA FOR ALKALINE EARTH CHLORATES.

Salt	ΔH^{o}_S	ϕ	ΔH_L	U	ΔH_-	U(calcd.)*	$\Delta H^{o}_f M^{2+}(aq.)$	$\Delta H^{o}_f M(ClO_3)_2(aq)$	$\Delta H^{o}_f M(ClO_3)_2(c)$†	$\Delta H^{o}_f ClO_3(g)$
$Mg(ClO_3)_2$	-17.5 ±2	-626	-608 ±2	607	-76.3	565	-110.41	-157.41	-175±2	-64±3
$Ca(ClO_3)_2$	- 5.6	-548	-542	540	-76.7	510	-129.77	-176.77	-182.4	-52.0
$Sr(ClO_3)_2$	0.6	-512	-513	511	-76.5	490	-130.38	-177.38	-176.8	-45.8
$Ba(ClO_3)_2$	5.6	-479	-485	483	-76.7	461	-128.67	-175.67	-170.0	-40.4

* "thermochemical radius" of ClO_3^- is 2.00 Å.

† using $\Delta H^{o}_f(ClO_3^-)$aq = -23.50 kcal./g.ion.[23]

ECTION 6) : Electron affinity of XO_3^-

Electron affinity is defined by the equation

$$XO_3(g) + e^- \longrightarrow XO_3^-(g) \qquad 298^\circ K.$$

from which, by convention

$$E = \Delta H_f^\circ \; XO_3(g) - \Delta H_f^\circ \; XO_3^-(g)$$

The determination of electron affinities both direct and indirect (of which this section is an example) has been reviewed by Pritchard[35]. Values of $\Delta H_f^\circ \, XO_3^-(g)$ may be derived from lattice enthalpy data as indicated in the previous two sections. It is necessary, then, to estimate $\Delta H_f^\circ \, XO_3(g)$ where X = Cl, Br, or I. Unless the oxide XO_3 is more than transiently stable, a direct determination is not possible. The only direct determination is for ClO_3 which exists in the following solution equilibrium[36]

$$Cl_2O_6 \rightleftharpoons 2ClO_3$$

N.B.S. Circular 500 quotes a value of 37.0 kcal/mole for $\Delta H_f^\circ \, ClO_3(g)$. Values for the other "oxides" may be estimated from the following cycle

$$\begin{tikzcd}
X(g) & + & 3\,O(g) & & XO_3(g) \arrow[ll, "3\,D(X-O)"'] \\
X(SS) \arrow[u, "A"'] & + & {}^3/_2\,O_2(g) \arrow[u, "3\bar{D}"'] \arrow[urr, "\Delta H_f^\circ \, XO_3\,(g)"'] & &
\end{tikzcd}$$

where $\bar{D}$ = Heat of formation of gaseous oxygen

A = Heat of formation of the gaseous halogen

D(X - O) = Dissociation energy for the X - O bond.

Values of $\bar{D}$ and A are available from Lewis and Randall[22] (revised, 1961 edition). Unfortunately the literature on dissociation energies of halogen oxygen bonds may be described, at best, as in a state of flux. Ideally to calculate $\Delta H_f^o XO_3(g)$ one requires data for D(X - O) in XO_3, XO_2 or possibly corrected values for the transient species XO which exist at high temperatures. Values for D (HO - X), which are well established, are clearly not suitable. The available data is tabulated below.

TABLE XXIII : DISSOCIATION ENERGIES FOR HALOGEN-OXYGEN BONDS.

Source		D (X - O)
Cottrell[37], 1958	Cl - O	63
Cottrell, 1958	Cl - O in ClO_2	57
"	Br - O	50 ?
"	Br - O in BrO_2	70 ?
"	I - O	44 ± 4
Morris[14] (lit.unspecified), 1958	Cl - O	55
Durie and Ramsay[38], 1958	Cl - O	63.31 ± .03
"	Br - O	55.2 ± 0.6
"	I - O	42 ± 5.0
Philips and Sugden[39], 1961	I - O	57 ± 6

It was decided to use Durie and Ramsay's data as the only self-consistent set with quoted limits of error and recalculate a figure for $\Delta H_f^o\ ClO_3(g)$ ignoring the data quoted in N.B.S. Circular 500 due to Goodeve and Marsh (1939)[40].

Using $\Delta H_f^o\ XO_3\ (g) = 3\bar{D} + A - 3D\ (X - O)$

and $E = \Delta H_f^o\ XO_3(g) - \Delta H_f^o\ XO_3^-(g)$

the following electron affinities are derived.

TABLE XXIV : ELECTRON AFFINITIES FOR XO_3^-

Ion	$\Delta H_f^o\ XO_3(g)$	$\Delta H_f^o\ XO_3^-(g)$	E
ClO_3^-	17.66 ± 0.1	-47*	65 ± .5
BrO_3^-	39.81 ± 0.2	-34†	74 ± .5
IO_3^-	78 ± 15	-48†	126 ± 16

* Morris[14] † This work.

EXPERIMENTAL

SECTION 1. Alkaline earth chlorates.

All chlorates were supplied by B.D.H., only barium chlorate being technical grade. Barium chlorate was crystallised from water. All chlorates, with the exception of magnesium chlorate were then dehydrated under vacuum (14 mm. Hg. at 100°C.) Magnesium chlorate decomposes before it dehydrates. An analytical procedure due to Rupp[41] was standardised using "Analar" grade potassium chlorate. The procedure is as follows:-

(i) Weigh out the equivalent of 20 ml. N/10 chlorate.

(ii) Add 1 g. of potassium bromide and dissolve in approximately 20 ml. of water.

(iii) Add 30 ml. of concentrated hydrochloric acid and let stand for five minutes.

(iv) Dilute with two volumes of water and add 1 g. of potassium iodide.

(v) Titrate the liberated iodine with standard sodium thiosulphate

$$\left[ClO_3^- \equiv 6\ S_2O_3^{=} \right]$$

Analysis results were : Calcium chlorate, 99.1%; Strontium chlorate, 99.2%; Barium chlorate, 99.7%.

SECTION 2. Solution calorimeter.

The calorimeter described in this section was also used to determine heats of solution of certain diols and heats of reaction of boron heterocycles (see Part I).

The principle of the calorimetric method is very simple; it is to measure the temperature change produced by a known weight of sample undergoing reaction or solution, then to introduce a known amount of heat (determined electrically) and again measure the temperature rise and by proportion deduce the heat charge per unit mass of sample.

The calorimeter was of the constant-temperature-environment type[46] consisting of a flanged glass Dewar vessel, approximately 2" internal diameter, completely immersed in a water thermostat maintained at 25 ± .01°C. (see Figs. 3 and 4). The glass stirrer and ampoule breaker were mounted in the flanged top via ground glass joints and precision-bore tubing. Additional holes carried the thermistor, mounted in a B/10 leak, the heater (for calibration purposes), and the platinum resistance thermometer. An additional hole was available for gas inlet and outlet if measurement under an inert atmosphere was necessary. The samples were contained in thin glass ampoules mounted on the end of precision rod. Two types of calorimeter were used dependent on the method used to break the ampoule (Figs. 3 and 4). The original design had a rounded base, in which case the ampoule was broken by rotating it (it was mounted slightly skew) into the stirrer blades. This method suffers from the defect that the setting-up and the equilibration of the calorimeter takes several hours and occasionally the stirrer broke instead of the ampoule. A later design had a flat base and the ampoules were broken directly on the base by a sharp tap. However the efficiency of the stirring is somewhat reduced using a calorimeter with a flat base. The heater was constructed of a length of Nichrome wire, spirally wound, which was submerged in transformer oil encased in very thin glass. The leads from the heater were of heavy gauge copper. The temperature changes were followed using a thermistor (F 53, Standard Telephone and Cable Ltd.). A thermistor is essentially a resistance with a very high negative temperature coefficient. The resistance-temperature relationship is of the form[42]

$$R = A \exp \left[{}^{B}/_{T} \right]$$

R = resistance (in Ω) T = temperature (in $^{\circ}$A.)

A = thermistor const. (effectively, the resistance of the thermistor at infinite temperature).

B = constant ($^{\circ}$A.)

Becker[42] et al propose a more accurate relationship of the form

$$R = A\,T^{-C} \exp \left[{}^{D}/_{T} \right]$$

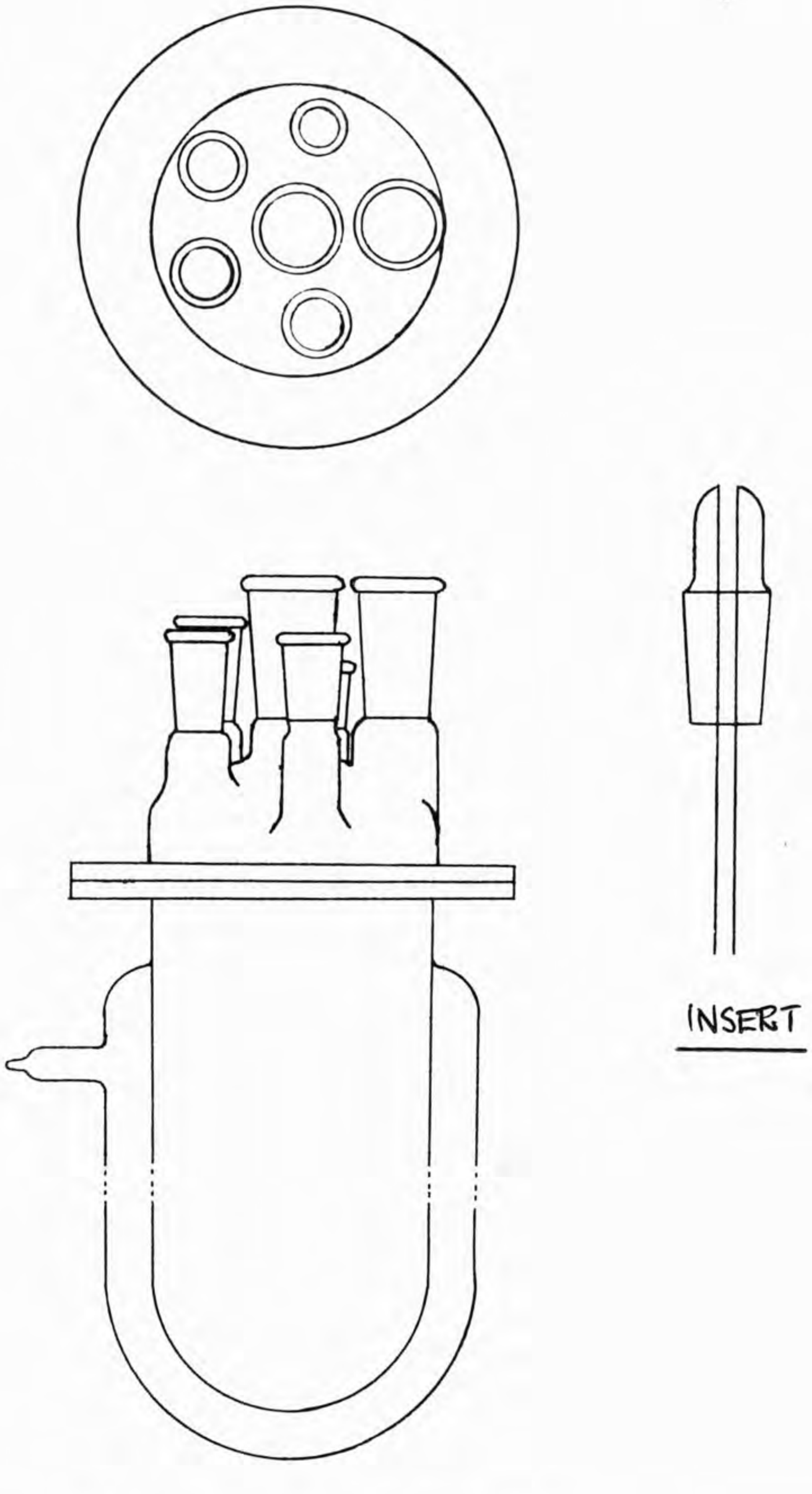


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FIG. 3 : SOLUTION CALORIMETER

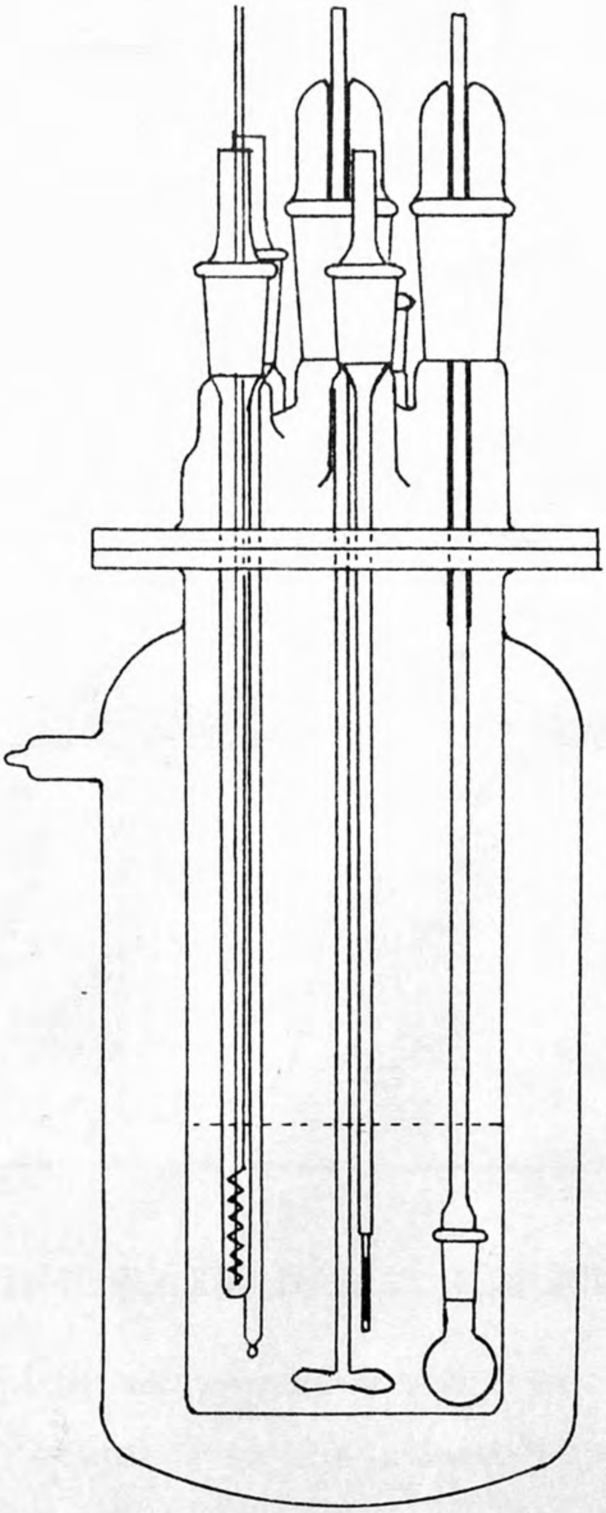
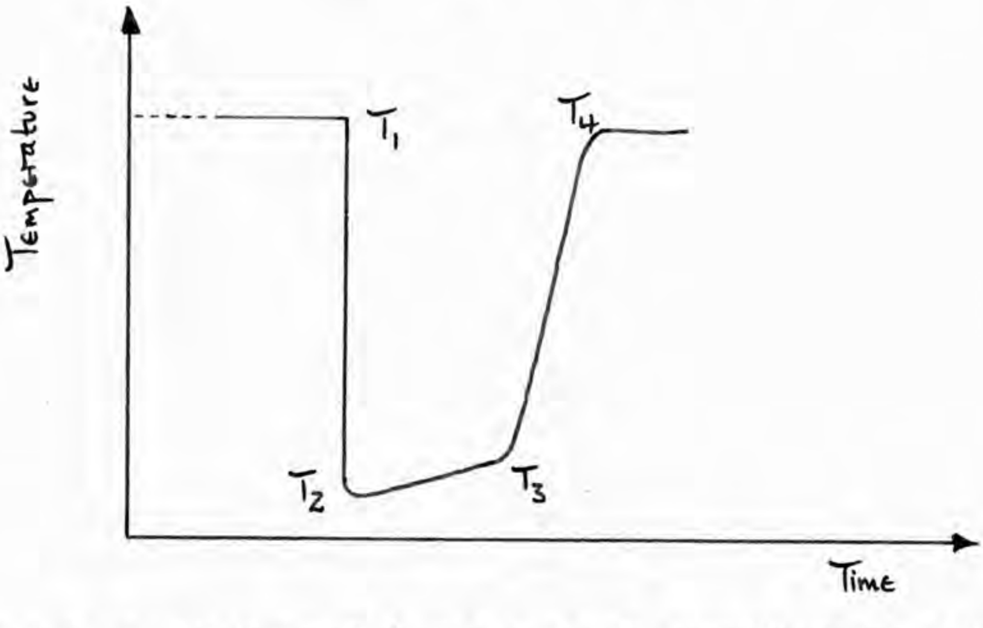


FIG. 4 : SOLUTION CALORIMETER (LOADED)

where A, C, D = constants, but the error involved in using the simpler expression is negligible. During an experiment, two changes in temperature are recorded, the reaction temperature change ($\Delta T'$) and the calibration temperature change (ΔT). If $\Delta T' = T_1 - T_2$ and $\Delta T = T_4 - T_3$

then

$$\frac{\Delta T'}{\Delta T} = \frac{\log {}^{R_2}/_{R_1} \quad \log {}^{R_4}/_{A} \quad \log {}^{R_3}/_{A}}{\log {}^{R_3}/_{R_4} \quad \log {}^{R_1}/_{A} \quad \log {}^{R_2}/_{A}}$$



GRAPH 9 : TEMPERATURE / TIME TRACE OF AN ENDOTHERMIC REACTION

For such an endothermic reaction it can be arranged that $T_1 \sim T_4$ and if the calorimeter insulation is effective then $T_2 \sim T_3$.

In this case,

$$\frac{\Delta T'}{\Delta T} = \frac{\log {}^{R_2}/_{R_1}}{\log {}^{R_3}/_{R_4}}$$

However for the following reasons it is preferable not to use this simple expression:-

(i) not all reactions studied were endothermic (i.e. $T_1 \neq T_4$).

(ii) the time between recording T_2 and T_3 is considerable because of thermal equilibration (i.e. $T_2 \neq T_3$).

(iii) the expression for ΔT requires a thermal loss correction added (or subtracted) because the calibration period usually lasts approximately three minutes unlike the reaction which is immediate (always less than 15 sec.). The expression for the ratio of temperature change is

$$\frac{\Delta T'}{\Delta T} = \frac{B \log {}^{R_2}/_{R_1}}{\log {}^{R_1}/_{A} \; \log {}^{R_2}/_{A}} \Bigg/ \left(\frac{B \log \frac{R_3}{R_4}}{\log \frac{R_3}{A} \; \log \frac{R_4}{A}} - \epsilon \right)$$

ϵ = thermal loss correction (°C.).

It is clearly necessary, then, to have a knowledge of A and B, the thermistor constants. These were obtained by calibrating the thermistor over the range 22° to 28°C. against a Beckmann thermometer previously directly calibrated via the transition point of sodium sulphate decahydrate (32.384 ± .001°C.).

The calorimeter circuit is shown in Fig.5; the Wheatstone bridge for the thermistor is similar to that described for the cryoscopic cell, (see Part I). The potentiometer was a Tinsley Type 3387B used in conjunction with a Scalamp galvanomometer (7902/S, W.G. Pye & Co. Ltd.) and was accurate to ± 0.00005 V. The standard cell used with the potentioner was a Weston Cadmium Cell (Tinsley & Co.Ltd. Type 1149). The electric timer was supplied by Precision Scientific Co. and was accurate to ± 0.05 sec. The whole calorimetric run was monitored with a miniature platinum resistance thermometer (100 Ω, Degussa) coupled to a six-inch potentiometric recorder (Elliot) accurate to ± 0.01°C. Samples were weighed on a balance sensitive to ± .00005 g. In the case of the readily hydrolysable boron heterocycles the weight of sample used was checked by post-hydrolysis analysis. The resistors for the potential divider circuit were supplied by Arcol Precision Resistors (2W, tolerance to 0.025%). These were checked against a sub-standard resistance supplied by Cambridge Instrument Co.Ltd.

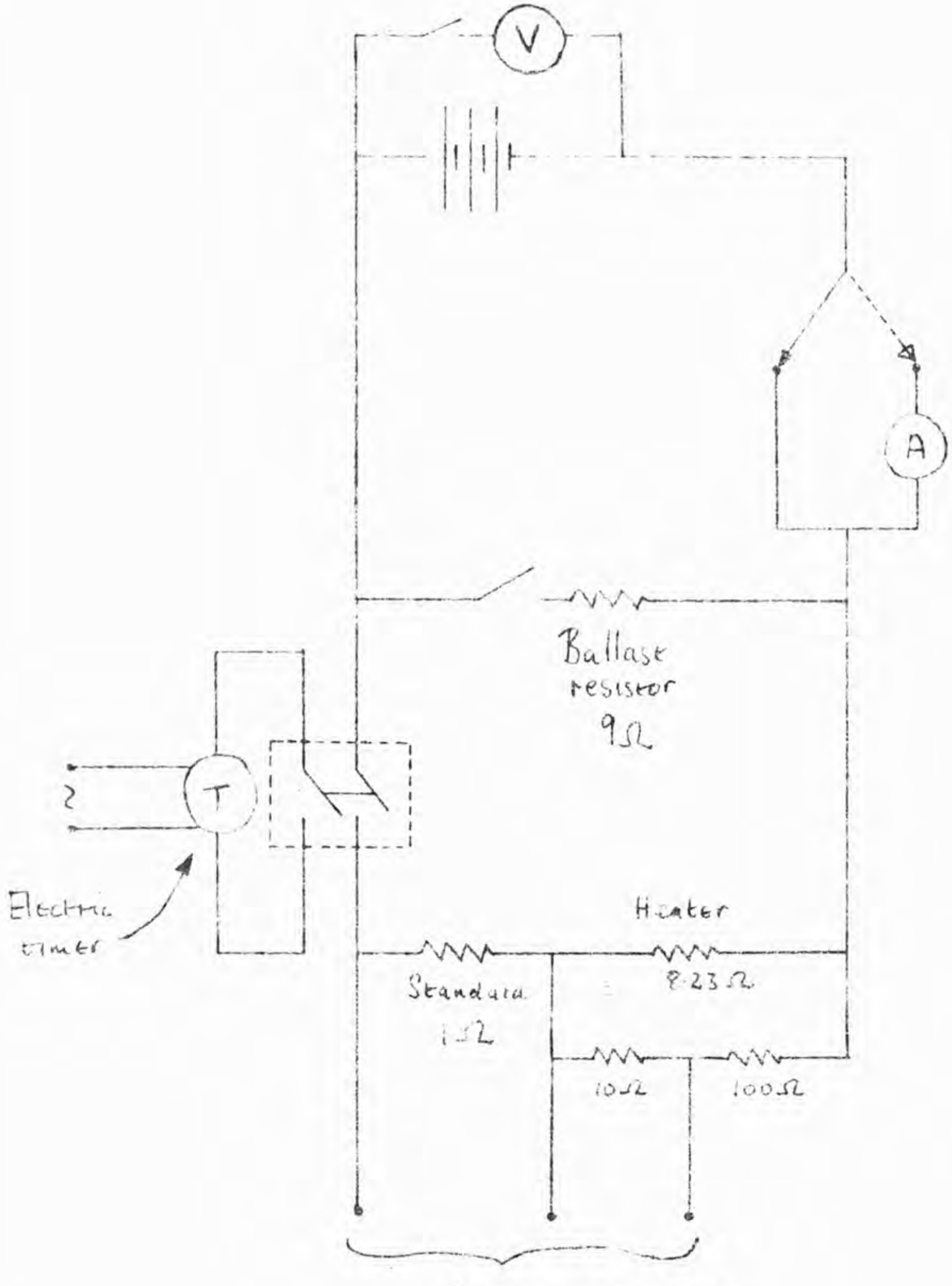
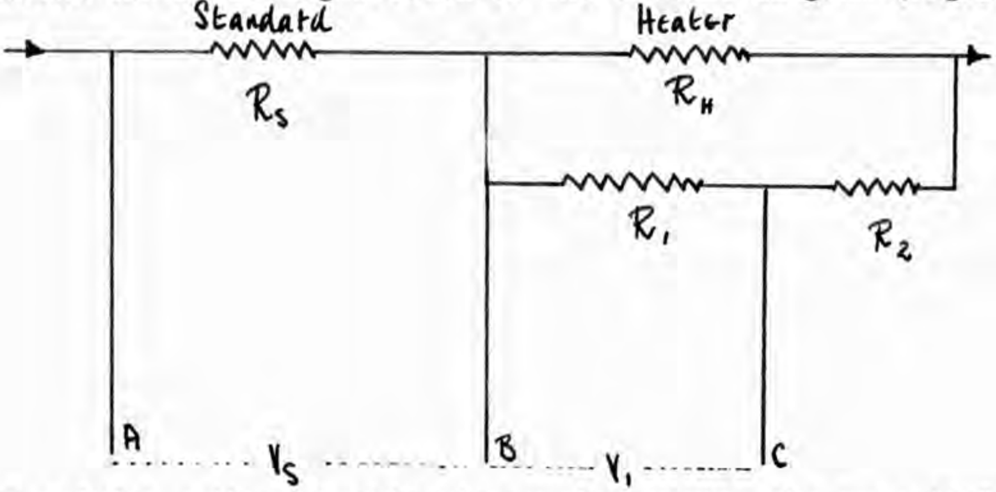


FIG. 5 CIRCUIT DIAGRAM FOR CALORIMETER

(guaranteed 9.9985 Ω). The circuit standard resistance was also supplied by the above firm at 0.999903 Ω . The temperature coefficient of these resistors is better than 20 p.p.m. per degree centigrade. The expression for the heat change is of the form

$$Q = \frac{\text{(electrical energy)}}{\text{J x weight}} \cdot \frac{\Delta T \text{ reaction}}{\Delta T \text{ calibration}} \quad \text{cal/gm.}$$

Consider the following section of the circuit diagram (Fig.5).



A, B and C are the potentiometer probe points, the potentials recorded experimentally being that across the standard (Vs) and that across the smaller component of the potential divider (V_1). It may readily be shown that the power output across the heater is given by

$$P = V_1 \left[\frac{R_1 + R_2}{R_1} \right] \left[\frac{V_s}{R_s} - \frac{V_1}{R_1} \right]$$

Now R_s = 1 Ω , R_1 = 10 Ω and R_2 = 100 Ω

(these data were accurate to 0.05%)

$$P = 11\,V_1 \left[V_s - \frac{V_1}{10} \right] \quad \text{Watts.}$$

$$\text{(electrical energy)} = 11\,V_1 \left[V_s - \frac{V_1}{10} \right] t \quad \text{joules}$$

where t = time of heating in seconds.

The complete expression for enthalpy change is

$$\Delta H = \frac{f\,11\,V_1 \left[V_s - \dfrac{V_1}{10} \right] M\,t \left[\dfrac{B \log \dfrac{R_2}{R_1}}{\log \dfrac{R_1}{A} \log \dfrac{R_2}{A}} \right]}{J\ w \left[\dfrac{B \log \dfrac{R_3}{R_4}}{\log \dfrac{R_3}{R} \log \dfrac{R_4}{A}} - \epsilon \right]} \quad \text{kcal/mole}$$

where f = factor correcting for heater lead resistance (varies between 0.981 and 1.000).

V_1 = potential across the 10 Ω component of the potential divider (in V).

V_s = potential across the standard (in V).

M = Molecular Wt.

t = Heating time (in secs.).

A, B = thermistor constants (A in Ω, B in °A).

$R_1, R_2, R_3, R_4 \equiv$ temperatures T_1, T_2, T_3, T_4 (°A).

w = wt. of sample (in g.)

J = 4.1840 abs. joules (definition).

The evaluation of the thermal leakage correction (ϵ) by the "first Geophysical Laboratory Method"[43] is described in Appendix I. All ΔH values, to be meaningful, must be quoted in conjunction with the mean temperature of the reaction period and the mole ratio (N = no. of moles of calorimeter liquid : no. of moles of reactant).

It is desirable to check the accuracy of a calorimeter via the use of standard reaction for which enthalpy data is internationally accepted. Several reactions are available but the reaction chosen here is the dissolution of potassium chloride in water under standard conditions. This was recently (1963) recommended as an international standard for solution calorimetry by Somsen et al[44]. The most reliable value in the literature is considered to be that of Gunn (1958)[45]. The advantages of potassium chloride are

(i) it is easy to purify.

(ii) it shows no enantiomorphism.

(iii) the heat of solution is independent of the pretreatment of the salt.

(iv) the heat change is fairly large for a dissolution.

(v) the rate of dissolution is not too low.

The only disadvantage, mentioned by Sunner and Wadsö[46], is that the temperature coefficient of heat of solution is rather large (-36 cal. $mole^{-1}deg^{-1}$). However the calorimeter used here is at least two orders of magnitude less accurate than the best calorimeters used at large Thermochemical Institutes. Therefore, potassium chloride as a standard is acceptable.

The results of the accuracy check are presented below.

TABLE XXV : ACCURACY OF THE SOLUTION CALORIMETER VIA DISSOLUTION OF POTASSIUM CHLORIDE.

Expt.	T	N	ΔH_s^o (kcal./mole)
1	25°C.	200	4.24 ± 0.02
2	24°C.	200	4.19 ± 0.02
3	24.9°C.	200	4.22 ± 0.02
		Mean	4.22 ± 0.02
Literature (Gunn)[45]	25	200	4.2065 ± 0.0003

The calorimeter, then, is accurate to better the ± 0.25% (this accuracy limit assumes, of course, the perfectly stable reactant; the limits of error when working with unstable boron heterocycles are considerably larger).

SECTION 3) Calorimetric procedure.

The procedure used to operate the calorimeter is outlined and the calculation of results illustrated by a typical example.

(i) The heater cells are discharged through the ballast resistor for at least 6 hours prior to starting the run because the derivation of the experimental equation assumes a constant potential drop across the heater throughout calibration. Also the standard cell and the backing cell are connected to the potentiometer some hours previous to the run commencing.

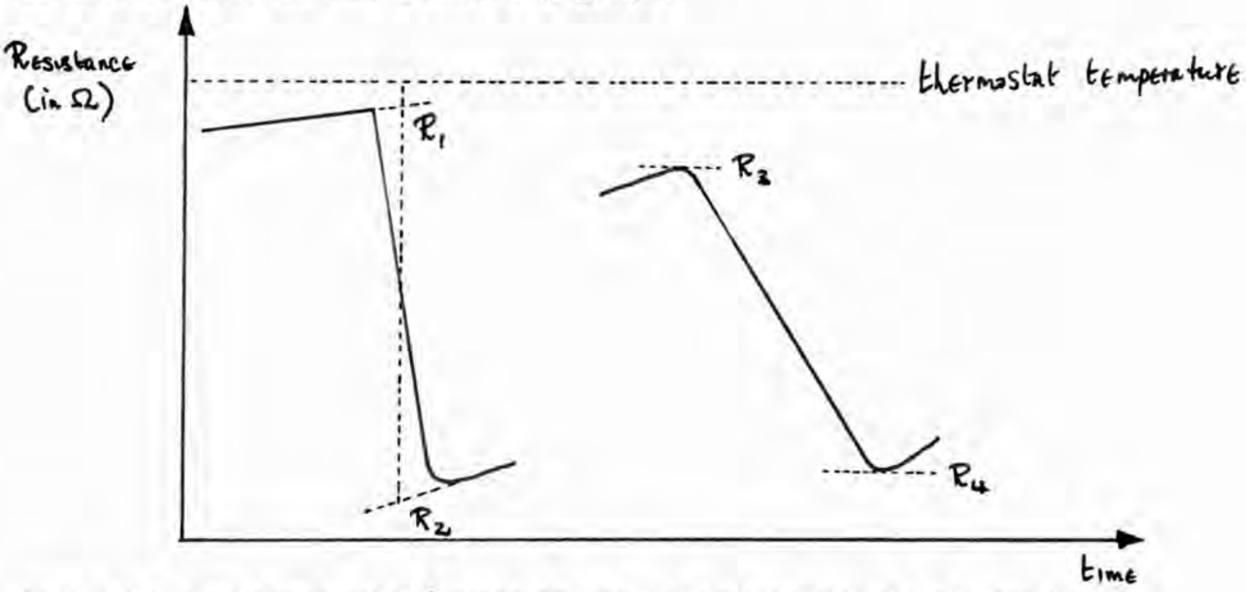
(ii) The calorimeter is now loaded with a known weight of sample and calorimeter fluid (usually 100 g. distilled water). It is then completely immersed in the thermostat and the stirrer started. It is essential to leave the system to equilibrate for at least an hour before commencing readings. This point is made very clear by Sunner and Wadsö who experimented with constant-temperature-environment calorimeters of different design[46].

(iii) After equilibration resistance/time readings are taken at half minute intervals. After approximately five minutes the ampoule is broken by which ever method is appropriate. Resistance readings are recorded for a further five minutes and then the system is left to temperature equilibrate for approximately twenty minutes.

(iv) Resistance readings are recommenced five minutes before breaking the discharge circuit and making the heater circuit simultaneously. The electric timer is coupled to the heater switch. The potential drop across the heater (V_1) and the standard resistance (V_s) is now recorded and the heater circuit broken when the calibration temperature change is approximately equal to the reaction temperature change (estimated from the recorder plot). Resistance readings are now discontinued but the recorder is left on for a further five minutes.

(v) The calorimeter contents are now analysed if necessary.

To derive the result a graph is constructed of resistance vs. time. The temperature change during the reaction period is obtained by back-extrapolation of the fore and aft periods to a perpendicular erected at the mid-point of the reaction period. The resistance readings for the calibration period are "turn-over" readings. This is illustrated in the following graph.



GRAPH 10 : RESISTANCE / TIME TRACE OF AN EXOTHERMIC REACTION.

The procedure of back extrapolation is a very approximate method for accounting for thermal leakage. It is quite satisfactory for a reaction which is almost immediate but unsatisfactory for the calibration period which is usually of the order of three minutes.

A calorimetric determination of the integral heat of solution of propan 1,2 diol in water is recorded below to illustrate the method of calculation.

TABLE XXVI : DETERMINATION OF THE INTEGRAL HEAT OF SOLUTION OF PROPAN 1,2 DIOL IN WATER.

Wt. of diol in ampoule (distilled immediately prior to use) = 2.9136 g.

Volume of water in calorimeter = 100 ml. (N = 145).

Thermostat temperature = 25 ± 0.01°C.

Log of Run.

Time (in mins.)	Resistance (in Ω)	Remarks.
0	4390	
$\frac{1}{2}$	4390	
1	4390	
$1\frac{1}{2}$	4390	Temperature
2	4390	rising very slowly
$2\frac{1}{2}$	4389	$1\ \Omega \sim 6 \times 10^{-3}$ °C.
3	4389	
$3\frac{1}{2}$	4389	
4	4389	
$4\frac{1}{2}$	4389	

5	-	Ampoule broken at
5½	4256	4 m. 58 s.
6	4257	
6½	4259	
7	4259	Reaction exothermic
7½	4260	so temperature now
8	4261	above 25°C. and
8½	4261	falling slowly
9	4262	0.01°C./min.

Temperature equilibrate.

15	4270	
15½	4271	
16	4271	
16½	4271 -----------	Heater on
17	4252	
17½	4225	(V_1 = 0.4776 V
18	4193	(V_s = 0.6814 V
18½	4165	(t = 150.1 secs.
19	4136 -----------	Heater off
19½	4127	
20	4127	
20½	4128	

21	4130
$21\frac{1}{2}$	4132
22	4133

By back extrapolation : $R_1 = 4389$ and $R_2 = 4256\ \Omega$

from graph (direct) : $R_3 = 4271$ and $R_4 = 4127\ \Omega$

Calculated heater resistance == $8.291\ \Omega$

Actual heater resistance = $8.230\ \Omega$

"lost" resistance = $0.6\ \Omega$

$f = (8.291/8.230)^2 = 0.985$

$$\text{Power} = 11\, V_1 \left[V_s - \frac{V_1}{10} \right] = 3.3289 \text{ Watts.}$$

Molecular wt. of diol = 76.09

$\Delta T'$ (solution period) = -0.8525°C.

ΔT (calibration period) = 0.9572°C.

From the recorder trace the thermal leakage is estimated as -0.0388°C. (see Appendix).

ΔT (corrected) = $T(\text{obs.}) - \epsilon$

= 0.9960°C.

(the derivation of ϵ is algebraic w. r. t. sign).

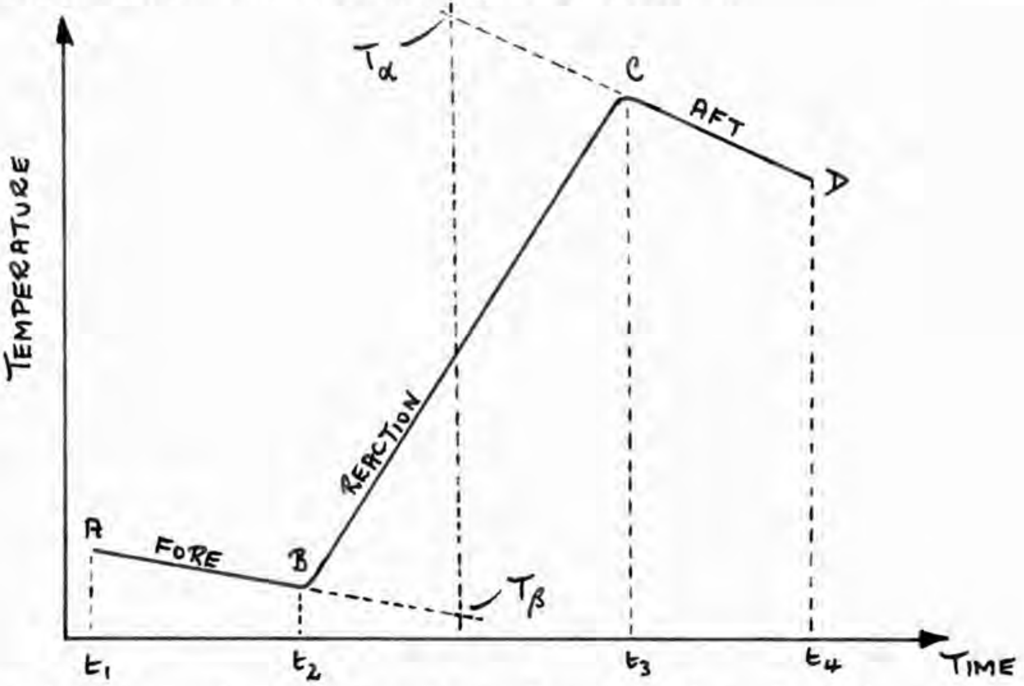
Mean temperature of solution period = 25.6°C.

$\Delta H_{\text{soln.}}$ (at 25.6°C. and $N = 145$) = -2.62 kcal./mole.

APPENDIX I

Correction for thermal leakage.

This method, the "first Geophysical Laboratory method", is due to W.P. White[48] and outlined by Sturtevant[43].



This graph represents a temperature change taking place in a calorimeter the thermostat temperature being below the abscissa. Two cases will be considered:-

Case A : If the heat exchange is very rapid i.e. if BC is nearly parallel with the ordinate axis, then the corrected temperature is $(T_\alpha - T_\beta)$. These circumstances are realised in the solution of readily soluble ionic salts or in the hydrolysis of easily-hyrolysable compounds. They will not be realised in

(i) the calibration period

(ii) solution of sparingly soluble salts

(iii) hydrolysis of sterically hindered compounds

(iv) some types of complex formation

i.e. in any process which is slow to reach equilibrium or completion at a fixed temperature.

Case B : Correction for thermal leakage in any slow process (for the point of view of the calorimeter used here, "slow" means taking longer than 60 secs.)

The basic assumption is that the heat exchange is Newtonian i.e. that the rate of change of temperature during the fore and aft periods is given by

$$\frac{dT}{dt} = K\,(Tj - T) + w$$

where Tj = jacket (thermostat) temperature

K = constant

w = constant which takes account of stirring effects and evaporation (assumed linear with time)

Let $\phi = Tj - T$ and

Φ_f = mean value of ϕ for the fore period

Φ_r = " " " " " "reaction "

Φ_a = " " " " " " aft "

then
$$\Phi_f = Tj - \tfrac{1}{2}(T_1 + T_2)$$

$$\Phi_r = Tj - \frac{\int_{t_2}^{t_3} Tdt}{(t_3 - t_2)}$$

$$\Phi_a = Tj - \tfrac{1}{2}(T_3 + T_4)$$

If R_f and R_a are the mean rates of temperature change during the fore and after periods respectively then

$$R_f = \frac{T_2 - T_1}{t_2 - t_1} = k\Phi_f + \omega$$

$$R_a = \frac{T_4 - T_3}{t_4 - t_3} = k\Phi_a + \omega$$

The corrected temperature rise is

$$\Delta T = (T_3 - T_2) - (k\Phi_r + \omega)\ (t_3 - t_2)$$

The evaluation of Φ_r includes the determination of

$$\int_{t_2}^{t_3} Tdt$$

This integral may be evaluated by "counting squares" or using a planimeter. This is a tedious procedure and Dickinson[43] has evolved a simpler technique. A time t_m may be found such that

$$(Tj - T_2)\ (t_m - t_2) + (Tj - T_3)\ (t_3 - t_m) = \int_{t_2}^{t_3} (Tj - T)\ dt$$

$$= Tj\ (t_3 - t_2) - \int_{t_2}^{t_3} T dt$$

$$\therefore \Phi_r = \frac{(Tj - T_2)\ (t_m - t_2)}{(t_3 - t_2)} + \frac{(Tj - T_3\ (t_3 - t_m)}{(t_3 - t_2)}$$

Dickinson found that the temperature corresponding to time t_m is given approximately by

$$\theta = 0.60\ (T_3 - T_2) + T_2$$

$$\text{i.e.}\ \Phi_r = Tj - \theta$$

From the recorder trace the following functions may be read off directly :

T_1, T_2, T_3, T_4 (N.B. $t_4 - t_3 = t_2 - t_1$), Φ_f and Φ_a. From these (and hence Φ_r), R_f and R_a are calculated. Newton's equation is set up for the fore and aft periods and solved simultaneously. From this k and w are obtained (k is always positive, the sign of w depends on the speed of stirring and the volatility of the solvent). Knowing k, w, Φ_r and $(t_3 - t_2)$ the error is computed.

APPENDIX II

Compd.	Propan 1,3 diol	Propan 1,3 diol	Propan 1,2 diol	Propan 1,2 diol
f			.980	.98
V_s	.6660	.6796	.6814	.6814
V_l	.4680	.4775	.4776	.4767
t	179.5	119.8	150.2	119.8
M	76.09	76.09	76.09	76.09
weight	4.0250	2.048	2.9136	1.7997
$\Delta T'$	0.9062	.5021	.8525	.5378
ΔT	1.1382	.8731	.9572	.7813
Φf	*	*	-.61	-.49
Φr			-1.16	-.916
Φa			-1.5	-1.19
Rf			-.010	-.0081
R_a			-.019	-.0156
K			.0103	.0108
W			-.0035	-.0028
ϵ			-.0388	-.0245
T_j	25	25	25	25
ΔT(corrected)			.9960	.8058
N	105	206	145	235
$\bar{T}$	25	25	25.6	25.6
ΔH	-2.05	-2.03	-2.62	-2.63

* these two runs were performed before the Newtonian thermal leakage correction was investigated.

Compd.	Butan 2,3 diol	Butan 2,3 diol	Butan 2,3 diol	Butan 2,3 diol (in H_3BO_3)
f	.981	.981	.985	.988
V_s	.6804	.68075	.6785	.67965
V_1	.4780	.47825	.4755	.4760
t	149.5	119.8	119.9	149.6
M	90.12	90.12	90.12	90.12
weight	2.8809	1.9039	2.3236	2.5117
$\Delta T'$	.9446	.6388	.8153	.7830
ΔT	.9196	.7822	.7631	.9535
Φ_f	-1.17	-.35	-.50	-.70
Φ_r	-1.66	-.794	-.928	-1.23
Φ_a	-1.97	-1.05	-1.20	-1.56
R_f	-.016	-.006	-.008	-.008
R_a	-.024	-.014	-.013	-.014
K	.0100	.0115	.0069	.0072
w	-.0053	-.0024	-.0046	-.0033
ϵ	-.0438	-.0231	-.0220	-.0303
T_j	25	30 *	30 *	25
ΔT (corrected)	.9634	.8053	.7852	.9654
N	174	263	215	-
$\bar{T}$	26.2	30.5	30.5	26
ΔH	-3.57	-3.54	-3.62	-3.40

* this diol appears to solidify over the range 22/26°C. so two runs were performed at 30°C. to avoid correcting for the latent heat of fusion.

Compd.	2-chloro-1,3,2 dioxaborinan	2-chloro-1,3,2 dioxaborinan	2-chloro-4-methyl-1,3,2-dioxaborinan	2-chloro-4-methyl-1,3,2-dioxaborinan
f	.981	.98	.988	.988
V_s	.6764	.6675	.6798	.6796
V_l	.4775	.4698	.47615	.4761
t	356.6	477.7	209.9	119.8
M	120.3	120.3	120.3	120.3
weight	1.9905	2.054	.798*	.446*
$\Delta T'$	3.0162	3.1240	1.3015	.7379
ΔT	2.0430	2.8890	1.3430	.8089
Φ_f	-2.04	-.42	-1.18	-.12
Φ_r	-3.16	-2.1	-1.92	-.588
Φ_a	-3.80	-3.14	-2.42	-.89
R_f	-.034	-.013	-.013	0
R_a	-.056	-.044	-.026	-.0086
K	.0125	.0114	.0104	.011
W	-.0088	-.0082	-.0006	.0013
ϵ	-.295	-.180	-.0722	-.011
T_j	25	25	25	25
ΔT(corrected)	2.3380	3.0630	1.4152	.8200
N	336	329	838	1497
$\bar{T}$	27.5	25.2	26.2	25.2
ΔH	-22.18	-22.12	-22.76	-22.72

* estimated from post-hydrolysis analysis.

Compd.	2-chloro-1,3,2-dioxaborolan	2-chloro-1,3,2-dioxaborolan	2-chloro-1,3,2-dioxaborolan.
f	.988	.988	.9855
V_s	.67945	.6789	.6815
V_l	.4758	.4755	.4775
t	180.2	119.7	149.9
M	106.3	106.3	106.3
weight	.679 *	.419 *	.265 *
$\Delta T'$	1.2093	.7315	.4564
ΔT	1.1591	.7918	.9953
ϕ_f	-1.06	-.41	-.33
ϕ_r	-1.70	-.856	-.90
ϕ_a	-2.12	-1.15	-1.25
R_f	-.015	-.005	-.005
R_a	-.021	-.0129	-.014
K	.005	.0105	.0105
W	-.0102	-.0008	-.0014
ϵ	-.0560	-.0085	-.0270
T_j	25	25	25
ΔT(corrected)	1.2151	.8108	1.0223
N	870	1410	2230
$\bar{T}$	26	25.5	25.6
ΔH	-21.72	-21.21	-20.92

* estimated from post-hydrolysis analysis

Compd.	2-chloro-1,3,2-dioxaborolan	2-chloro-1,3,2-dioxaborolan	2-chloro-4,5 dimethyl 1,3,2-dioxaborolan
f	.988	*	.9855
V_s	.6781	*	.68055
V_1	.47475	*	.47695
t	208.8	*	299.4
M	106.3	106.3	134.4
weight	.538	.550	1.371
$\Delta T'$	.7850	.8352	2.1907
ΔT	1.1960	*	1.9014
ϕf	-.60	*	-1.62
ϕr	-1.28	*	-2.62
ϕa	-1.74	*	-3.22
R_f	-.0064	*	-.0242
R_a	-.015	*	-.0435
K	.0075	*	.0121
w	-.0019	*	-.0046
ϵ	-.0406	*	-.18145
T_j	25	25	25
ΔT(corrected)	1.2366	*	2.0829
N	1098	1074	545
$\bar{T}$	26	26	26.5
ΔH	-20.39	-21.2	-24.14

* calibration data used as for previous run due to circuit failure during experiment.

† estimated by post-hydrolysis analysis.

Compd.	2-chloro-4,5 di-methyl 1,3,2-dioxaborolan	2-chloro-1,3,2 dioxa borolan/benzene mixture	2-chloro-1,3,2 dioxa borolan/benzene mixture.
f	.9855	.993	.987
V_s	.67945	.68275	.6820
V_l	.47595	.4782	.4777
t	359.8	480	478.3
M	134.4	106.3	106.3
weight	1.457	1.6580(olan)	1.9166(olan)
$\Delta T'$	2.3143	2.9256	3.2599
ΔT	2.1949	2.9881	2.8061
Φ_f	-1.42	-1.50	-2.29
Φ_r	-2.67	-3.30	-3.92
Φ_a	-3.42	-4.38	-4.87
R_f	-.0184	-.002	-.017
R_a	-.0460	-.043	-.067
K	.0138	.0145	.0192
w	.0012	.0202	.0268
ϵ	-.2135	-.2228	-.3880
T_j	25	25	25
ΔT(corrected)	2.4084	3.2109	3.1941
N	512	356	308
$\bar{T}$	26.5	26.6	27
ΔH	-24.84	-22.23	-21.28

Compd.	2-chloro-1,3,2-dioxaborolan/benzene mixture.	2-chloro-1,3,2-dioxaborolan/benzene mixture	Barium chlorate
f	.9855	.9855	.980
V_s	.6780	.6778	.6600
V_1	.4754	.4752	.4642
t	239.4	299.8	149.9
M	106.3	106.3	304.3
weight	.9591 (olan)	1.3314 (olan)	3.0435
$\Delta T'$	1.6651	2.3564	.5076
ΔT	1.5412	1.8828	1.0052
Φ_f	-1.70	-1.85	1.01
Φ_r	-2.62	-2.94	.38
Φ_a	-3.16	-3.57	-.03
R_f	0	-.009	.0112
R_a	-.0193	-.0355	0
K	.01325	.015	.0108
w	.02252	.0181	.0003
ϵ	-.0486	-.1301	.0111
T_j	25	25	25
ΔT(corrected)	1.5898	2.0130	.99417
N	616	443	555
$\bar{T}$	26.6	26.7	24.1
ΔH	-21.58	-21.74	5.62

Compd.	Barium chlorate	Barium chlorate	Barium chlorate
f	.993	.985	.988
V_s	.6648	.6720	.6730
V_1	.4647	.4712	.4711
t	248.7	179.4	150.1
M	304.3	304.3	304.3
weight	3.4216	5.5390	3.5731
$\Delta T'$	.54704	.92350	.57848
ΔT	1.6369	1.2259	1.0303
Φ_f	.25	.52	.40
Φ_r	-.822	-.252	-.21
Φ_a	-1.47	-.73	-.60
R_f	.0322	.0129	.0081
R_a	0	-.0048	-.0064
K	.0187	.0142	.0145
w	.0275	.0055	.0022
ϵ	.0486	.0058	-.0020
T_j	25	25	25
ΔT(corrected)	1.5883	1.2240	1.0150
N	497	305	473
$\bar{T}$	24.8	24.6	24.7
ΔH	5.71	5.67	5.58

Compd.	Strontium chlorate	Strontium chlorate	Calcium chlorate	Calcium chlorate
f	.980	.983	.988	.985
V_s	.6617	.6592	.67175	.67215
V_r	.4647	.4627	.47025	.4711
t	89.8	120.1	90.0	89.9
M	254.6	254.6	207.1	207.1
weight	3.1332	3.7126	2.1929	1.1771
$\Delta T'$	.07016	.07630	.51796	.28616
ΔT	.58837	.83847	.59712	.63426
Φf	.16	.18	-.49	-.55
Φr	-.204	-.364	-.844	-.772
Φa	-.44	-.72	-1.06	-1.06
R_f	.0043	.029	0	.0129
R_a	0	.016	-.00484	.0129
K	.0072	.0144	.0085	0
W	.0031	.0264	.0042	.0129
ϵ	.00253	.04238	-.00451	.0193
T_j	25	25	25	25
ΔT(corrected)	.58583	.79619	.60163	.61491
N	453	381	525	977
$\bar{T}$	24.7	24.6	24.2	25.1
ΔH	0.64	0.58	-5.59	-5.61

THERMISTOR CONSTANTS (A,B) = 9.084×10^{-2} , 1.396×10^{3} °A. (base 10)

APPENDIX III

The detailed cryoscopic results are recorded in their most concise form i.e. as tables of concentration (in g. per 10 ml. solvent) vs. freezing point (in Ω).

Thermistor constants : F23; $A = 7.082 \times 10^{-2}$, $B = 1.282 \times 10^{3}$ ^{o}A (base 10)

2-chloro- 1,3,2 dioxaborolan in benzene

Conc.	F.P.	Conc.	F.P.
0	2865	.0232	2835
.0129	2870	.0347	2840.5
.0505	2888	.0478	2846
.0574	2890	.0591	2850.5
		.1028	2866
.0692	2894	.1653	2884
.0852	2899	.2333	2899
.1059	2905	.2977	2915
.1776	2925	.3921	2935
		.4662	2948.5
.2608	2944	.5559	2965
.3576	2964	.6428	2977.5
.4412	2977	.7851	2997
		.9036	3015
0	2864	1.052	3035.5
.0168	2871	1.179	3052
.0338	2880	1.342	3072
.0486	2887	1.519	3093.5
.0635	2892	1.719	3112.5
.0783	2896	1.904	3128.5
0	2826	2.085	3148
		2.297	3170
.0116	2830		

2-chloro-4-methyl-1,3,2 dioxaborolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865	.2351	2980
.0352	2883	.3221	3019
.0680	2900	.4335	3066
.1120	2921.5	.6100	3136
.1431	2936	.7602	3190
.1725	2950	.9208	3241

2-chloro-4,5 dimethyl- 1,3,2 dioxaborolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2860	.1857	2945
.0144	2866.5	.2372	2968
.0304	2873.5	.3027	2997.5
.0468	2881	.3709	3028
.0630	2889	.4658	3070
.0795	2896.5	.5917	3125.5
.0961	2904	.7617	3199
.1131	2912	.9111	3263.5
.1494	2928		

2-chloro- 1,3,2 dioxaborolan in nitrobenzene

Concn.	F.P.	Concn.	F.P.
0	2845	.2520	2936
.0219	2854	.3293	2954
.0393	2863	.4326	2977
.0583	2873	.5750	3005
.0694	2877	.7502	3036
.1011	2889	.9056	3060
.1298	2899	1.0282	3078
.1767	2914		

2-n-butoxy-1,3,2 dioxa borolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2864	.3599	2986
.0218	2874	.4304	3003.5
.0443	2884	.4984	3019.5
.0655	2893	.5905	3040
.0869	2901.5	.7106	3065
.1091	2910	.8544	3093
.1309	2918	1.0205	3124
.1973	2940	1.2010	3155.5
.2919	2968	1.3710	3185

2(2'-chloro ethoxy)-1,3,2 dioxaborolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2864	.3286	2967
.0292	2878	.3663	2975.5
.0573	2889	.4026	2983.5
.0887	2900.5	.4768	2999.5
.1192	2910	.5842	3021
.1518	2920.5	.6910	3041
.1836	2930	.7986	3061
.2190	2940	.9148	3082.5
.2546	2949	1.0246	3101
.2924	2958.5	1.1345	3119
		1.2803	3142

2(2'-chloro ethoxy)-1,3,2 dioxaborinan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865	.0808	2902
.0209	2875	.1304	2921.5
.0397	2883	.2089	2951.5
.0593	2892	.3153	2991
.0777	2899.5	.4406	3040
.0957	2907	.5697	3085.5
.1753	2937.5	.7264	3142.5
.2725	2973.5	.9482	3221
.0253	2878	1.1816	3301
.0501	2889	1.5002	3379.5

Tri-n-butyl borate in benzene

Cncn.	F.P.	Concn.	F.P.
0	2865	.1545	2914
.0223	2873	.2172	2932
.0430	2880	.3055	2958
.0660	2887.5	.3891	2982
.0887	2894	.5446	3028
.1101	2900.5	.7228	3078

2-chloro-1,3,2-dioxaborinan in nitrobenzene

Concn.	F.P.	Concn.	F.P.
0.	2844	.3252	3001.5
.0285	2857	.4711	3072
.0573	2872	.6619	3165
.0901	2887.5	.8971	3284
.1215	2904	1.1709	3421
.1563	2920	1.3927	3530
.2343	2958		

Naphthalene (cryoscopic) in benzene

Concn.	F.P.	Concn.	F.P.
0	2865	.1753	2984
.0385	2885	.2228	2977.5
.0812	2906	.2730	3003
.1255	2928.5		

2-chloro-1,3,2 dithioborolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865	.0806	2902.5
.0441	2884	.2037	2959.5
.0665	2894.5	.3347	3019.5
.0889	2905.5	.4810	3087

2-chloro-1,3,2 dioxaborinan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865.5	.6409	3181
.0354	2885	.9010	3305
.1199	2929	1.1559	3421
.3269	3032		

2-chloro-1,3,2 dithioborinan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865.5	.1529	2926
.1271	2916.5	.2348	2960
.2468	2964	.3193	2993.5
.3687	3012	.4075	3031
.5176	3071	.4979	3060
.6626	3125	.5896	3101
.0768	2896	.6864	3140

2-phenyl-1,3,2 dithioborinan in benzene

Concn.	F.P.	Concn.	F.P.
0	2865	.2716	2957
.0840	2894	.3448	2981.5
.1579	2919	.4378	3012
.2172	2938.5		

Phenyl boron dichloride in benzene

Concn.	F.P.	Concn.	F.P.
.1110	2911	.0143	2872
.0784	2898	.0109	2871
.0664	2893.5	.431	3041
.0540	2888.5	.349	3007
.0437	2884	.299	2987
0	2865	.249	2966.5
.0329	2878.5	.205	2949
.0256	2875.5	.172	2936.5
.0183	2873	.137	2922.5

2-phenyl-1,3,2 dithioborolan in benzene

Concn.	F.P.	Concn.	F.P.
0	2864	.2611	2961
.0494	2882.5	.3654	2999
.1276	2911.5	.4878	3043.5
.1941	2936.5		

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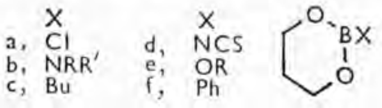
270. *Boron Ring Compounds. Part II.*[1] *Some New 2-Substituted* 1,3,2-*Dioxaborinans.*

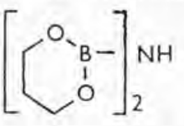
By Arthur Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn.

Use has been made of the reactive halogen in 2-chloro-1,3,2-dioxaborinan [1] (Ia) to prepare new dioxaborinans. Other syntheses of 2-alkyl and 2-phenyl compounds are described. Anomalous reactions of methanol and butane-1-thiol with compound (Ia) are interpreted.

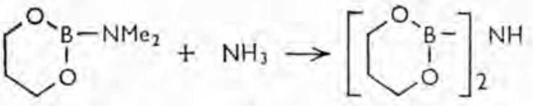
Some new compounds (Ib–e) with the 1,3,2-dioxaborinan skeleton have been prepared by nucleophilic substitution of the labile halogen in the diozaborinan (Ia). Substitution with alkylamines to give compounds (Ib) was successful when at least two molar equivalents of amine were used, precipitating the hydrogen chloride formed as amine hydrochloride. Use of one equivalent of amine gave no identifiable products on distillation. This is in accord with certain previous findings on reaction of amines with the boron–chlorine link.[2] Triethylamine or a second mole of the substituting amine is required to break the complex initially formed with one mole of amine. Ammonia itself did not give the corresponding amine compound (Ib; $R' = R'' = H$), nor was it obtained by transamination [3] or use of sodamide. An undistillable material, probably the bis(dioxaboraninyl) compound (II) was obtained from the transamination reaction of ammonia with 2-dimethylaminodioxaborinan. This compound showed infrared absorption in the N–H stretching frequency region.



(I)



(II)



(II)

Simple nucleophilic substitution with butanethiol could not be achieved, for the conditions used resulted in pyrolysis. A mixture of thiol and compound (Ia) at 100°/1 atm. gave the pyrolysis product, 3-chloropropyl metaborate, previously noted.[1] Heating at reduced pressure resulted in another known pyrolysis product,[4] 2-3'-chloropropoxy-1,3,2-dioxaborinan, but no hydrogen chloride was evolved and no boron–sulphur bond was formed. Formation of 2-butylthio-1,3,2-dioxaborolan in low yield has been reported [5] in a similar reaction at high temperatures with the chloroborolan, which is apparently less readily pyrolysed.

Several routes to a carbon–boron link were attempted: reaction of butyl-lithium with the amine (Ia; $R = R' = H$) gave a good yield of 2-butyldioxaborinan (Ic); reaction with tripropylboron gave a very low yield of the 2-propyl derivative. The 2-alkylborolans [6] and -borinans have previously been made from the alkylboronic acid and the appropriate 1,2- or 1,3-diol, water being removed as the toluene azeotrope.[7] 2-Phenyldioxaborinan (If) has been similarly prepared from phenylboronic anhydride and propane-

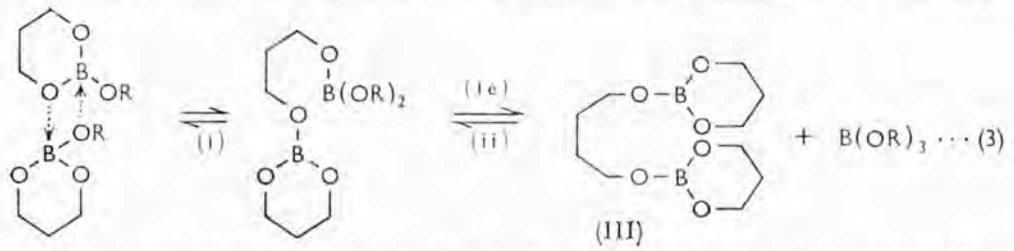
· · · · · ·(I)

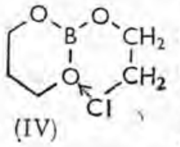
1,3-diol (reaction 2). Complex formation with these alkyl and aryl ring compounds is in progress.

$$3HO{\cdot}[CH_2]_3{\cdot}OH + (PhBO)_3 \longrightarrow 3Ph{\cdot}B{\cdot}O{\cdot}[CH_2]_3{\cdot}O + 3H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Formally analogous to reaction (1) is the metathetical reaction of chloroborinan (Ia) with potassium thiocyanate in 1,2-dimethoxyethane[8] to give the thiocyanato-compound (Id). This had the infrared absorption expected for a covalent isothiocyanate rather than a thiocyanate.[9] Lappert and Pyszora[9a] recently prepared a series of boron isothiocyanates with a characteristic, very broad band at 2083—2101 wave numbers, and a half-band width 150—170 wave numbers. This band appears in the spectrum of the new compound (Id).

Addition of cyclohexanol to the chloroborinan (Ia) gave, on distillation, the corresponding ester (Ie; $R = C_6H_{11}$) as expected from previous work[1] with 2-chloroethanol, 3-chloropropanol, and butan-1-ol. Methanol, however, gave, on distillation, almost quantitative yields of methyl borate and trimethylene diborate (III); no methyl ester (Ie; R = Me) was isolated. However, if a mixture of methanol and chloroboronate was evacuated under a condenser cooled to −80°, so as to remove hydrogen chloride but not methyl borate, the liquid residue had a molecular weight of 103·5. The methyl ester (Ie; R = Me) should have a molecular weight of 116, the diborate 243·6. The reaction may take place as shown (reaction 3), the equilibrium depending on (*a*) the volatility of the trialkyl borate and (*b*) the nature of the alkyl group R. Reaction of the chloro-compound (Ia) with ethanol likewise produced no ethyl ester (Ie; R = Et) on distillation; instead, diborate could be distilled off in good yield. This may be contrasted with the reaction of 2-chloroethanol which gives 2-2′-chloroethoxy-1,3,2-dioxaborinan[1] (IV), where the complete stability with respect to disproportionation may be attributable to back-donation from the halogen. Molecular-weight studies[10] on 2-butoxy-1,3,2-dioxaborolan show an apparent association value of 1·27. Hence partial association, as shown in (3i) may be assumed; disproportionation does not occur on distillation, as with the methyl ester (Ie), because of the much lower volatility of butyl than of methyl borate. Stability to disproportionation is in the sequence Me < Et < Pr < Bu < $Cl{\cdot}[CH_2]_2$ < $Cl{\cdot}[CH_2]_3$.




(IV)

Attempts were made to extend esterification studies to the seven-membered dioxaborepan system. The methyl and the 2-chloroethyl ester were obtained by reaction of butane-1,4-diol with the appropriate dichloroborinate (4), but neither ester was stable on distillation. In general, the dioxaborepan system is more readily disproportionated than the borolan or borinan analogue. Thus the 2-chloro-1,3,2-dioxaborepan (V) could not be made by reaction of boron trichloride and butane-1,4-diol, or from 2-methoxy-1,3,2-dioxaborepan and chlorodimethoxyboronate, which might be expected to undergo reaction (5) with the facility of similar reactions in the borinan series.[1]

$$RO{\cdot}BCl_2 + HO{\cdot}[CH_2]_4{\cdot}OH \longrightarrow RO{\cdot}B{\cdot}O{\cdot}[CH_2]_4{\cdot}O + 2HCl \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$(RO)_2BCl + RO{\cdot}B{\cdot}O{\cdot}[CH_2]_4{\cdot}O \longrightarrow (RO)_3B + \underset{(V)}{Cl{\cdot}B{\cdot}O{\cdot}[CH_2]_4{\cdot}O} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

EXPERIMENTAL

2-Dimethylamino-1,3,2-*dioxaborinan*.—Dimethylamine (13·8 g.) and 2-chloro-1,3,2-dioxaborinan (13 g.) were mixed at −180° and allowed to warm under a condenser kept at −80°. A white solid was precipitated. The mother-liquor, mostly 2-*dimethylamino*-1,3,2-*dioxaborinan*, had b. p. 24°/0·1 mm., n_D^{25} 1·4330 (14 g., 93%) (Found: C, 46·3; H, 9·1; N, 11·0%; *M*, 128, 132. $C_5H_{12}BNO_2$ requires C, 46·5; H, 9·3; N, 10·9%; *M*, 128·9). The solid was dimethylamine hydrochloride, m. p. 169° (9 g., 96%).

2-Diethylamino-1,3,2-*dioxaborinan*.—Diethylamine (25 ml.) and chloroborinan (Ia) (15 g.) were treated as for the dimethylamino-compound. The *diethylamino-compound* had b. p. 33—34°/0·01 mm., n_D^{25} 1·4365 (14·9 g., 76%) (Found: C, 53·7; H, 10·0; N, 9·0; B, 7·1%; *M*, 150. $C_7H_{16}BNO_2$ requires C, 53·9; H, 10·3; N, 9·0; B, 6·9%; *M*, 157). Diethylamine hydrochloride was recovered (13·2 g., 97%).

2-Ethylamino-1,3,2-*dioxoborinan*.—Ethylamine (25 ml.) and chloroborinan (17 g.) gave the *ethylamino-compound*, b. p. 24°/0·05 mm., n_D^{25} 1·4340 (13·8 g., 70%) (Found: C, 46·5; H, 9·1; N, 11·0; B, 8·4. $C_5H_{12}BNO_2$ requires C, 46·5; H, 9·3; N, 10·9; B, 8·3%). Ethylamine hydrochloride (11·6 g., 100%) was recovered.

Reaction of Ammonia with Chloroborinan (Ia).—Chloroborinan (8·6 g.) and liquid ammonia (20 ml.) were sealed in a glass tube and left at room temperature for 2 days. Ammonium chloride was identified but no other nitrogen-containing compound was isolated by the usual methods.

Reaction of Ammonia with 2-Dimethylamino-1,3,2-*dioxaborinan*.—2-Dimethylaminoborinan (10 g.) was sealed off with a ten-fold excess (20 ml.) of sodium-dried ammonia and shaken. Ammonia was evaporated off at a low temperature, then dimethylaminoborinan (2·7 g.) was recovered (confirmed by its infrared spectrum). The residual liquid was distilled but appeared to decompose, leaving a residue (Found: C, 18·4; H, 6·3; N, 20·7; B, 13·5%). A second experiment gave a residual clear yellow liquid which was not distilled (Found: C, 39·8; H, 7·4; N, 8·2; B, 11·7. Calc. for $C_6H_{13}B_2NO_4$: C, 39·0; H, 7·1; N, 7·6; B, 11·6%). This had a characteristic infrared N–H stretching band and was probably bis(dioxaborinanyl)-amine (II).

Reaction of Butanethiol with Chloroborinan.—(*a*) Chloroborinan (20 g.) and butane-1-thiol were refluxed at 0·1 mm. under a condenser cooled to −80°. No hydrogen chloride was evolved. On distillation of the mixture chloroborinan (18·9 g.) was recovered and 2-3′-chloropropoxy-1,3,2-dioxaborinan [4] (3·97 g.), b. p. 65°/0·1 mm., was identified by its infrared spectrum. (*b*) The chloroborinan (14 g.) and butane-1-thiol (16 ml.) were heated at 100° for 25 hr. No hydrogen chloride was evolved. The infrared spectrum of the residue when butanethiol was pumped off corresponded exactly to that of 3-chloropropyl metaborate,[1] which cannot be distilled without decomposition.

2-Butyl-1,3,2-*dioxaborinan*.—An ether solution (50 ml.) of chloroborinan (16 g.) was added dropwise to a solution of butyl-lithium (18·0 g.) in ether under nitrogen. Heat was evolved and the mixture was cooled in ice. A white precipitate was formed. The ether was removed on a water-pump and the remaining liquid distilled at 80—100°/15 mm. (12·0 g., 66%). *2-Butyl*-1,3,2-*dioxaborinan* was redistilled at 166°/760 mm. and had n_D^{25} 1·4205 (Found: C, 58·5; H, 10·1; B, 8·3. $C_7H_{15}BO_2$ requires C, 59·2; H, 10·6; B, 7·6%). The residue was impure lithium chloride but contained some boron.

2-Phenyl-1,3,2-*dioxaborinan*.—Phenylboronic anhydride (23·5 g.) and trimethylene glycol (19 g.), reacting in toluene (75 ml.) according to Letsinger and Skoog's [7] procedure, gave 2-*phenyl*-1,3,2-*dioxaborinan* (32·6 g., 90%), b. p. 70—75°/0·2 mm., which was a super-cooled liquid at room temperature and could be maintained for weeks in this form (Found: C, 66·1; H, 6·8; B, 6·9%; *M*, 170. $C_9H_{11}BO_2$ requires C, 66·7; H, 6·8; B, 6·7%; *M*, 162).

2-Isothiocyanato-1,3,2-*dioxaborinan*.—A solution of potassium thiocyanate (12 g.) in 1,2-dimethoxyethane [8] was added dropwise to the 2-chloroborinan (Ia) (15 g.) in solvent (20 ml.). An immediate precipitate and heat of reaction were observed. After being shaken for 30 min. the mixture was filtered. The residue (9·5 g.) was mostly potassium chloride. The filtrate was pumped to remove solvent, and the residual 2-*isothiocyanato*-1,3,2-*dioxaborinan* was distilled (b. p. 62—64°/0·2 mm.). Redistillation (b. p. 58—60°/0·01 mm.) gave a yellow liquid (Found: C, 33·8; H, 4·3; N, 9·7; B, 7·3; S, 22·4; NCS, 38·1. $C_4H_6BNO_2S$ requires C, 33·6; H, 4·2; N, 9·8; B, 7·6; S, 22·4; NCS, 40·6%).

2-Cyclohexyloxy-1,3,2-*dioxaborinan*.—Esterification of chloroborinan with cyclohexanol in the manner previously described[1] gave an 84% yield of *2-cyclohexyloxy*-1,3,2-*dioxaborinan*, b. p. 64—65°/0·05 mm., n_D^{25} 1·4608 (Found: C, 57·8; H, 9·2; B, 6·0. $C_9H_{17}BO_3$ requires C, 58·7; H, 9·3; B, 5·9%).

Reaction of Methanol and Chloroborinan.—A mixture of compound (Ia) (10·4 g.) and methanol (2·8 g.) was pumped at 0°/26 mm. under a condenser at −80°. Hydrogen chloride (2·7 g. Calc., 3·2 g.) was collected. The condenser was then taken away and trimethyl borate removed (2·6 g. Calc., 3·0 g.) (Found: B, 10·2. Calc. for $C_3H_9BO_3$: B, 10·4%), b. p. 69—70° (lit., 68°), n_D^{25} 1·379 (lit., 1·362). The residue was mostly trimethylene diborate,[1] identified by its infrared spectrum (3000—400 wave numbers), b. p. 120—125°/0·05 mm., and n_D^{25} 1·4500 (lit.,[1] b. p. 125°/0·05 mm., n_D^{25} 1·4520) (Found: C, 43·8; H, 7·7; B, 9·3%; *M*, 240·6. Calc. for $C_9H_{18}O_6B_2$: C, 44·4; H, 7·4; B, 8·9%; *M*, 243·6).

2-2′-*Chloroethoxy*-1,3,2-*dioxaborepan*.—To 2-chlorethyl dichloroborinate[11] (15·1 g.) (Found: B, 6·55; easily hydrolysed Cl, 41·6. Calc. for $C_2H_4BCl_3O$: B, 6·7; Cl, 43·5%) was added at 0° butane-1,4-diol (8·2 ml.). Hydrogen chloride (94%) was removed and the residual viscous *borepan* analysed without distillation (Found: C, 39·1; H, 6·6; B, 6·3; easily hydrolysed Cl, 0. $C_6H_{10}BClO_3$ requires C, 41·3; H, 5·8; B, 6·2%; easily hydrolysed Cl, 0).

2-*Methoxy*-1,3,2-*dioxaborepan*.—Dichloromethoxyborinate[12] (13·5 g.) (Found: B, 9·3; Cl, 59·7. Calc. for $C_5H_{11}BO_3$: B, 9·6; Cl, 62·9%) and butane-1,4-diol (10·6 ml.), by a similar reaction, gave a pale yellow plastic *methoxy-compound* (Found: C, 46·2; H, 8·5; B, 8·3; Cl, 0. $C_5H_{11}BO_3$ requires C, 46·2; H, 8·5; B, 8·3%; Cl, 0).

Reaction of Methoxyborepan with Chlorodimethoxyboronate.—Borepan (4·1 g.) was added to the chloromethoxyboronate (4·9 g.) at −80°. After the mixture had warmed to room temperature volatile materials were removed. No methyl borate was detected. The residue had a boron content of 10·8%.

Molecular weights were determined cryoscopically. The infrared absorption spectra of some of the compounds described will be reported later.

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DISPROPORTIONATION OF BISBORATES AND BISBORINATES

BY

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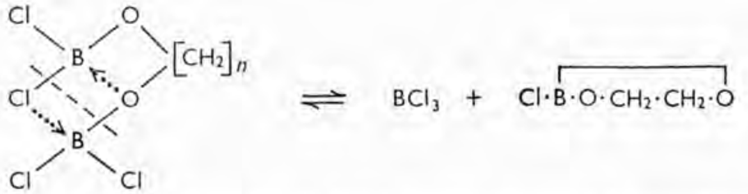
119. *Disproportionation of Bisborates and Bisborinates.*

By Arthur Finch, P. J. Gardner, and J. C. Lockhart.

Ethylene bis(dichloroborinate) (I; $n = 2$, $X = Cl$) has been shown [1] to possess considerable stability at room temperature, and the derived ester, ethylene bis(dibutyl borate) (I; $n = 2$, $X = OBu^n$), to be stable to repeated distillation.[1, 2] We have attempted to prepare the corresponding trimethylene systems (I; $n = 3$, $X = Cl$, NCS, or OBu^n) and have found a striking difference in thermal stability.

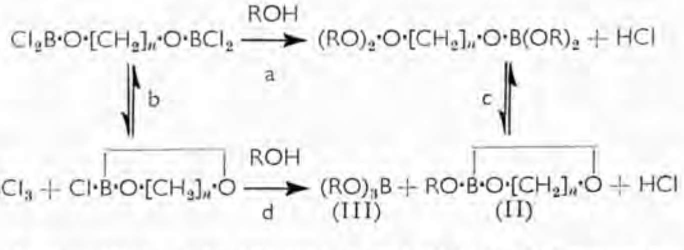
$X_2B{\cdot}O{\cdot}[CH_2]_n{\cdot}O{\cdot}BX_2$ (I)

Although the infrared spectrum of the product of reaction of appropriate quantities of boron trichloride and trimethylene glycol indicated formation of the discrete compound trimethylene bisdichloroborinate (I; $n = 3$, $X = Cl$), decomposition into 2-chloro-1,3,2-dioxaborinan and boron trichloride proceeded rapidly at room temperature, possibly as indicated in scheme (1). Trimethylene bisdi-isothiocyanatoborinate (I; $n = 3$, $X = SCN$) appeared to disproportionate similarly.



....(1)

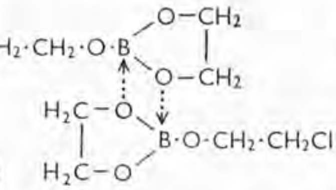
We attempted to make trimethylene bis(di-2-chloroethyl borate) by condensation of the trimethylene bisdichloroborinate (I; $n = 3$, $X = Cl$) with 2-chloroethanol. The infrared spectrum and refractive index of the product were identical with those of an equimolar mixture of 2-2′-chloroethoxy-1,3,2-dioxaborinan and tris-2-chloroethyl borate. On distillation these were separated and identified as the sole products. Reaction of the trimethylene bis(dichloroborinate) and butan-1-ol likewise yielded the corresponding cyclic ester (II; $R = Bu^n$). We cannot distinguish between the two reaction paths shown in (2); either or both of them may be operative.



. . . . . . (2)

This instability of trimethylene bis(dialkyl borates) is in sharp contrast to the behaviour of the ethylene compound (I; $n = 2$, $X = OBu^n$). That thermal stability is not a simple function of chain-length was shown by the attempted preparation of the ethylene bis(di-2-chloroethyl borate) (I; $n = 2$, $X = O{\cdot}[CH_2]_2{\cdot}Cl$). Tris-2-chloroethyl borate and 2-2′-chloroethoxy-1,3,2-dioxaborolan were the only products. Tetramethylene bisdichloroborinate was not thermally stable, and disproportionation as in (1) is assumed.

The disproportionation product 2-2′-chloroethoxy-1,3,2-dioxaborolan (IV), synthesised by an independent method, was shown by cryoscopic measurements in benzene solution (0·1—0·25M) to be a dimer. Chloroethyl and chloropropyl boronates and borinates are known to possess greater thermal stability than esters with no terminal chlorine. Thus 2-ethoxy-1,3,2-dioxaborinan could not be obtained pure, whilst 2-2′-chloroethoxy-1,3,2-dioxaborinan was stable on distillation.[3, 4] It has been suggested that this may be due in part to chelation, with back-donation from chlorine to boron. This is unlikely in ester (IV) where association presumably results as shown, from boron–oxygen bonding. Infrared examination of associated molecules of this type is in progress.


(IV)

Experimental.—Trimethylene bisdichloroborinate. Propane-1,3-diol (3·3 g.) was added dropwise to boron trichloride (10·3 g.) at −80° under a condenser cooled to −80°. Hydrogen chloride evolved (100%) was estimated volumetrically. The *compound* was stored at −80° (Found: B, 9·1; Cl, 58·3. $C_3H_6B_2Cl_4O_2$ requires B, 9·1; Cl, 59·7%) and had n_D^{25} 1·4418. The infrared spectrum differed from those of the disproportionation products, dioxaborinan [4] and boron trichloride, there being intensity changes and frequency shifts near 780, 1025, and 1100 cm.$^{-1}$.

Attempted preparation of trimethylene bis(di-2-chloroethyl borate). 2-Chloroethanol (7·15 ml.) was added dropwise to trimethylene bisdichloroborinate (6·4 g.) at −80° under a condenser cooled to −80°. Hydrogen chloride evolved was estimated volumetrically (84%). The liquid product, n_D^{25} 1·4500, was analysed before distillation (Found: B, 5·3. $C_{11}H_{22}B_2Cl_4O_6$ requires B, 5·2%). The infrared spectrum (0·125M-solution in CCl_4) was quantitatively similar to the superimposed spectra of the disproportionation products. The product was distilled under reduced pressure, boiling over the range 25—75°/0·1 mm., and the centre fraction was refluxed at 180° for 5 hr. After several refractionations, the centre fraction distilled over the same range, leaving no residue. The lowest-boiling fraction, n_D^{25} 1·4481, b. p. 48—50°/0·07 mm., was shown to be principally 2-2′-chloroethoxy-1,3,2-dioxaborinan [4] by analysis (Found: B, 6·2. Calc. for $C_5H_{10}BClO_3$: B, 6·6%) and comparison of its infrared spectrum with that of an authentic sample. The highest-boiling fraction, b. p. 70—80°/0·1 mm., n_D^{25} 1·4520, was identified as tris-2-chloroethyl borate [5] by analysis (Found: B, 4·8. Calc. for $C_6H_{12}BCl_3O_3$: B, 4·3%) and by its infrared spectrum. 83% of the theoretical quantity of tris-2-chloroethyl borate (calc. on reaction 2c) was recovered.

Attempted preparation of trimethylene bis(di-n-butyl borate). The reaction was conducted in a similar manner with butan-1-ol (15·4 ml.) and trimethylene bisdichloroborinate (8·7 g.). Hydrogen chloride (78%) was evolved. Repeated refractionation under reduced pressure effected separation into tri-n-butyl borate, n_D^{25} 1·4079, b. p. 48—52°/0·1 mm. (lit.,[5] n_D^{25} 1·4070) (infrared spectrum identical with that of an authentic sample, which boiled at 50—52°/0·1 mm.), and 2-n-butoxy-1,3,2-dioxaborinan, b. p. 34—37°/0·06 mm. (lit.,[4] b. p. 36—38°/0·12 mm. (infrared spectrum identical with that of an authentic sample).

Trimethylene bis(di-isothiocyanatoborinate). Trimethylene bisdichloroborinate (3·9 g.) was run into a solution of potassium thiocyanate (6·4 g.) in 1,2-dimethoxyethane (100 ml.). Precipitated potassium chloride was filtered off and the solvent evaporated from the filtrate. The residue was distilled into four fractions, the highest of which was 2-isothiocyanato-1,3,2-dioxaborinan, b. p. 55—65/0·05 mm., which had an infrared spectrum identical with that of an authentic sample.[3] Boron tri-isothiocyanate has only very recently been described.[6]

Ethylene bis[di-(2-chloroethyl) borate]. Ethylene bisdichloroborinate (Found: B, 9·3, Cl, 61·5. Calc. for $C_2H_4B_2Cl_4O_2$: B, 9·7; Cl, 63·6%) was esterified with 2-chloroethanol as before; hydrogen chloride (93%) was evolved. Successive fractionation yielded 2-2′-chloroethoxy-1,3,2-dioxaborolan, b. p. 52—56°/0·02 mm., n_D^{25} 1·4565, identical in infrared spectrum with that obtained by another route (below), followed by tris-2-chloroethyl borate, b. p. 68°/0·05 mm., n_D^{25} 1·4520 (lit., b. p. 70°/0·01 mm., n_D^{25} 1·4530) (Found: B, 4·3. Calc.: B, 4·6%).

2-2′-Chloroethoxy-1,3,2-dioxaborolan.—Prepared from 2-chloro-1,3,2-dioxaborolan and 2-chloroethanol by a standard method, this *ester* was a colourless viscous liquid, b. p. 52—58°/

0·02 mm., n_D^{25} 1·4554 (Found: C, 31·9; H, 5·7; B, 7·05; Cl, 24·75%; *M*, 290. $C_4H_8BO_2Cl$ requires C, 31·95; H, 5·4; B, 7·2, Cl, 23·6%; *M*, 150).

Tetramethylene bisdichloroborinate. Butane-1,4-diol (3·0 ml.) was added to boron trichloride (8·1 g.) at −80° under a condenser cooled to −80°. Hydrogen chloride (84%) was evolved and the residual *ester*, a white amorphous fuming solid, darkened rapidly at room temperature (Found: B, 8·7; Cl, 53·9. $C_4H_8B_2Cl_4O_2$ requires B, 8·6; Cl, 56·3%).

Physical constants. Molecular weights were determined cryoscopically in benzene, and infrared spectra were investigated between 3000 and 700 cm.$^{-1}$ on a Perkin-Elmer model 137 spectrometer.

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ASSOCIATION IN CYCLIC BORONATES AND BORATES

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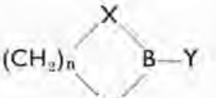
Abstract—The molecular weights of some cyclic boron compounds have been studied over a wide concentration range. Olan derivatives were far more associated than their inan analogues. The degree of association of some inans was concentration-independent. Modes of association are proposed.

SEVERAL references to molecular weight determinations of cyclic boron compounds at isolated concentrations are to be found in the literature.(1,2) There are also many reports of anomalous physical properties (e.g., boiling point, viscosity) of cyclic derivaties relative to their acyclic analogues.(1,3,4,5)

Investigation of a series of compounds of the type:



n = 2, 3
Y = Cl, ϕ, OR
X = O, s
R = alkyl

indicates two distinct modes of association: (a) concentration-dependent association and (b) concentration-independent association, with the occasional possibility of both. The results confirm the predictions of DALE(6) on the relative stabilities of trigonal and tetrahedral boron in five- and six-membered rings. It is clear, from this work, that any molecular weight datum obtained at an isolated concentration should be accepted with reservation.

EXPERIMENTAL

General procedure. Compounds ($X = S$, $Y = \phi$) were prepared by condensing phenyl boron dichloride with the appropriate dithiol. All others were prepared by condensing boron trichloride with the appropriate diol followed by alcholysis for the ester derivatives. The majority of the derivatives, being moisture-sensitive, were handled in a dry-box; they were distilled under reduced pressure immediately prior to use. Precautionary measures were taken to ensure the absence of pyrolysis or hydrolysis throughout cryoscopic measurements. The benzene solvent, of specially purified cryoscopic grade (B. D. H.) was stored over sodium.

Apparatus. The cryoscopic cell was of all glass construction and similar to that of ZEMANY(7). Agitation was effected by means of a chromium-plated stirrer actuated by an external solenoid. The intermittent pulse to the solenoid was supplied by a slowly-rotating cam operating a micro-switch. The temperature-sensitive element was a thermistor (F2311/300, Standard Telephone and Cables Ltd.) incorporated in a Wheatstone bridge.

Calibration and errors. Using the described equipment, differential temperature measurement was

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(1) R. J. BROTHERTON and A. L. MCCLOSKEY, *J. Org. Chem.* **26**, 1668 (1960).

(2) E. W. ABEL, S. H. DANDEGAONKER, W. GERRARD and M. F. LAPPERT, *J. Chem. Soc.* 4697 (1956).

(3) J. A. BLAU, W. GERRARD and M. F. LAPPERT, *J. Chem. Soc.* 4116 (1957).

(4) J. A. BLAU, W. GERRARD, M. F. LAPPERT and B. A. MOUNTFIELD and H. PYSZORA, *J. Chem. Soc.* 380 (1960).

(5) S. H. ROSE, *Diss. Abs.* **22**, 2185 (1962).

(6) J. DALE, B. HARGITAY and A. J. HUBERT, *J. Chem. Soc.* 910, 922 and 931 (1961).

(7) P. D. ZEMANY, *Analyt. Chem.* **24**, 348 (1952).

accurate to ±0·002°C. Assuming the resistance/temperature relation[8,9] for a thermistor to be $R = A \exp [B/T]$, the constants (A, B) were obtained by comparison with a platinum resistance thermometer (Degussa Hanau) over the range 0–6°C coupled to a six-inch potentiometric recorder sensitive to 0·02°C. The thermistor was also directly calibrated by determining the constant C in the standard form of the depression equation $M_2 = Cm_2/\Delta R$, where M_2 = molecular weight of solute, m_2 = mass of solute, and ΔR = freezing-point depression in ohms. The value of this constant was found to be within ±1 per cent of that calculated from the approximate expression $C = M_1 \underline{R}\, R_0 B/Hm_1$, where $\underline{R}$ = gas constant, R_0 = resistance at T_0, ΔH latent heat of fusion of the solvent and T_0 = freezing point of pure solvent. Since the benzene/naphthalene system is ideal to almost eutectic concentrations[10] it is legitimate to use the experimental value of C in computing molecular weights, cryoscopically determined in benzene.

Values of the cryoscopic constant K_f, derived from the equation $K_f = m_1 C T_0^2/R_0 B$ were: 5123 ± 100 for benzene (Lit.[11] 5120), and 7161 ± 100 for nitrobenzene (lit.[11] 7200). Test runs over the concentration range 0·01–0·6 M on phenyl boron dichloride and tri-n-butyl borate were made, giving molecular weights of 161 (calculated 158·8) and 226 (calculated 232·2) respectively. The reproducibility of individual runs was *ca.* 0·3 per cent.

The reproducibility of runs on the compounds studied varied between ±0·3 and ±2 per cent, dependent on their stability. The approximations involved in using the standard colligative depression equation were estimated for a hypothetical compound of molecular weight 150 ideally dissolved in benzene and amounted to 0·4, 1·5 and 3·7 per cent at the concentrations 0·05, 0·2 and 0·5 M respectively. The accuracy of the experimental data hence depends largely on the purity and stability of the compounds, rather than the precision or accuracy of the experimental method.

RESULTS AND DISCUSSION

Molecular weights at 0·5M, 0·2M and 0·5M concentrations are listed in the Table and the variation of cryoscopic depression with concentration for several compounds is shown in Fig. 1.

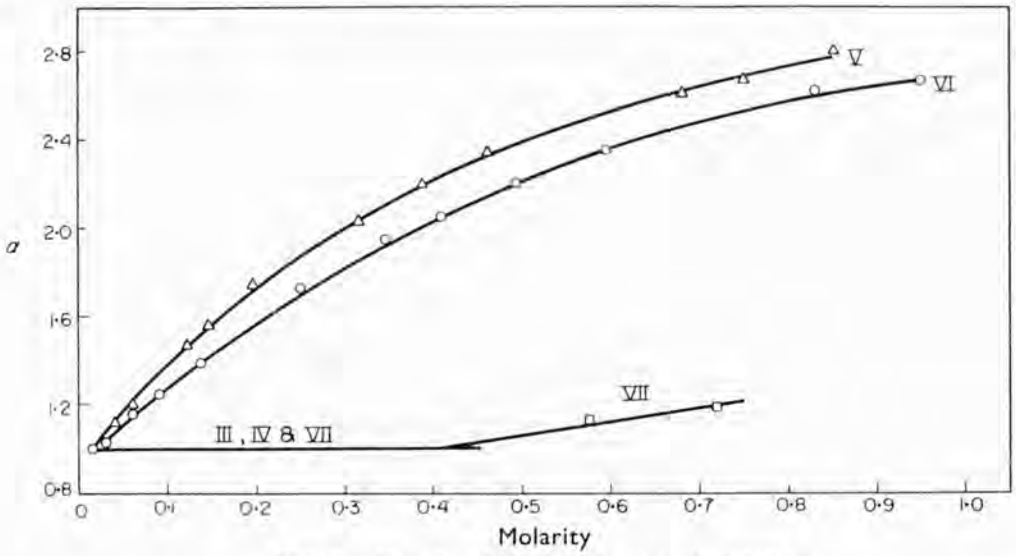

FIG. 1.—Graphs of degree of association (α) vs.
Molarity III Phenyl boron dichloride IV Tri-n-butyl borate
V 2-(2′-chloroethoxy) 1,3,2-dioxaborolan VI 2-(n-butoxy) 1,3,2-dioxaborolan
VII 2-(2′-chloroethoxy) 1,3,2-dioxaborinan
(experimental points for III, IV and VII are omitted between 0·0 and 0·45 molar)

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(8) J. A. BECKER, C. B. GREEN and G. L. PEARSON, *Bell Syst. Tech. J.* **26**, 170 (1947).

(9) H. A. SKINNER (Editor), *Experimental Thermochemistry*, Vol. 2, p. 168, Interscience, New York (1962).

(10) R. K. MCKULLAN and J. D. CORBETT, *J. Chem. Educ.* **33**, 313 (1956).

(11) WEISSBERGER (Editor) *Techniques of Organic Chemistry Vol.* 7. Organic Solvents. Interscience, New York (1955).

MOLECULAR WEIGHTS AT THREE MOLARITIES

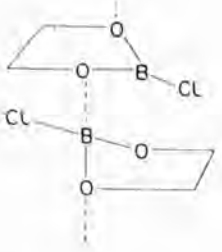
	Compound	b.p. (°C/mm)	Molecular weight (Degree of Association) 0·05M	0·2M	0·5M	Calcd. Mol. wt.
			130(1·22)	200(1·88)	260(2·44)	
I	$\overline{\text{OCH}_2\text{CH}_2\text{OB}}\text{Cl}$	35–40/0·05	130(1·22)*	168(1·58)*	220(2·07)*	106·3
			135(1·12)	133(1·12)	135(1·12)	
II	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{Cl}$	22–24/0·05	130(1·08)*	130(1·08)*	130(1·08)*	120·3
III	ϕBCl_2	66/18	161(1·01)	161(1·01)	—	158·8
IV	$(\text{Bu}^n\text{O})_3\text{B}$	232/760	226(0·98)	226(0·98)	—	230·2
V	$\overline{\text{OCH}_2\text{CH}_2\text{OB}}\text{OCH}_2\text{CH}_2\text{Cl}$	59–60/0·05	152(1·01)	305(2·03)	274(2·49)	150·4
VI	$\overline{\text{OCH}_2\text{CH}_2\text{OB}}\text{OBu}^n$	58–60/0·05	146(1·01)	233(1·62)	346(2·40)	144·0
VII	$\overline{\text{OCH}_2\text{CH}_2\text{CH}_2\text{OB}}\text{OCH}_2\text{CH}_2\text{Cl}$	57–58/0·05	169(1·03)	169(1·03)	189(1·15)	164·4
VIII(12)	$\overline{\text{SCH}_2\text{CH}_2\text{SB}}\text{Cl}$	24–25/0·05	141(1·02)	141(1·02)	—	138·5
IX(12)	$\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{SB}}\text{Cl}$	52/0·1	165(1·08)	165(1·08)	—	152·5
X(12)	$\overline{\text{SCH}_2\text{CH}_2\text{SB}}\phi$	90–92/0·05	179(0·99)	179(0·99)	—	180·1
XI(12)	$\overline{\text{SCH}_2\text{CH}_2\text{CH}_2\text{SB}}\phi$	110–111/0·05	196(1·01)	196(1·01)	—	194·1

* in nitrobenzene solvent: all others in benzene

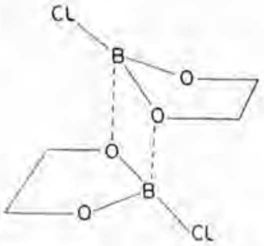
(12) A. FINCH and E. J. PEARN, Unpublished work.

The acyclic compounds phenyl boron dichloride and tributyl borate (III, IV) and the sulphur compounds (VIII, X, XI) are monomeric at all concentrations studied. All others show association, the effect being especially marked and concentration-dependent in the five-membered (olan) structures. Considering these first, four models for association may be examined:

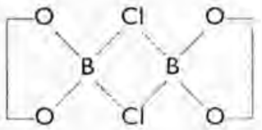
(1) Boron-oxygen bridging: (x = cl)



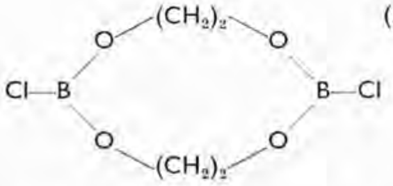
(2) Four-centre interaction: (x = cl)



(3) Chlorine bridging ($X = Cl$):



(4) Ten-membered ring formation: ($X = Cl$)



or combinations of these.

Large-ring formation (4) may be dismissed, since, as seen in the Figure, the degree of association is strongly concentration-dependent, and the energy required for breaking a B—O bond (*ca.* 110 kcal./mole[(13)]) is not available on dilution. In this model alone the boron retains the sp^2 (trigonal) configuration, hence nuclear magnetic resonance measurements might be of value. Molecular models show that the ten-membered system is strain-free; hence its independent existence is not precluded.

Since the olan esters (V) and (VI), like the parent compound (I), show similar strongly concentration-dependent association, it is reasonable to ascribe this primarily to (1). From the physical properties, e.g. viscosity, vapour-pressure, boiling point, of the pure phases, as well as by extrapolation of the molecular weight *vs.* concentration data, it is obvious that these compounds are associated considerably beyond the dimer ($\alpha = 2$) stage. However, the inapplicability of colligative-property equations to these

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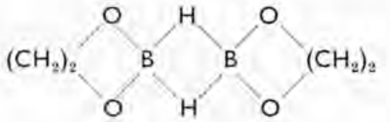
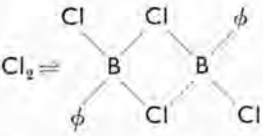
(13) T. CHARNLEY, H. A. SKINNER and N. B. SMITH, *J. Chem. Soc.* 2288 (1952).

conditions prevents the precise estimation by the usual techniques. This suggests that some form of stacking, as in (1), is operative. As expected from its higher dielectric constant, the use of nitrobenzene as solvent reduced the degree of association.

Compound (II) is of special interest since the six-membered (inan) skeleton, unlike the olan analogue, is relatively strain-free, and hence less tendency for change to the tetrahedral sp^3 configuration ($sp^2 \rightarrow sp^3$) would be predicted. The comparatively small association observed ($\alpha = 1\cdot1$ in both benzene and nitrobenzene) is well outside experimental error and independent of concentration; this is in direct contrast with the behaviour of the olan system. It is possible, therefore, that a different mechanism, e.g. chlorine bridging (2) is now operative. Similarly, the dithioborinan is also slightly associated in a concentration-independent manner. If it is assumed that a degree of association of 1·1 represents a monomer-dimer equilibrium, $2A \rightleftharpoons A_2$, it is difficult to understand why this should not be dependent on concentration. This form of bridging is formally similar to the hydrogen bridging proposed in a recent dissertation(5) for 1,3,2-dioxaborolan:



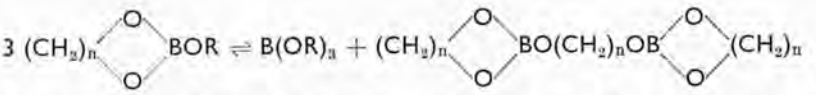
No evidence for stable chlorine bridging in boron compounds could be found in the literature, though the phenomenon is well established for other elements. In this connexion the molecular weight of phenyl boron dichloride was measured under comparable conditions, and a strictly monomeric solution was found at all concentrations. This confirms a previously reported value(2) at a single concentration. This does not preclude chlorine bridging in the inan derivatives. The difference in energy between trigonal and tetrahedral boron configurations is very much greater in the cyclic than the acyclic system. Further, the extent of dimerisation



might be expected to be small under ambient conditions.

Association of the inan ester (VII) cannot occur via chlorine bridging: it is slightly concentration-dependent and presumably due to boron-oxygen interaction.

The n-butyl and 2-chlorethyl esters were selected as being of known stability.(14) The apparent high molecular weight of some esters may be due to disproportionation.(6)



The possibility that solvent-solute interaction, i.e. weak π-bonding, occurred was also considered. The ultraviolet spectrum of solutions of benzene, of (II) and of an equimolar mixture of both, all in cyclohexane, were measured in the range 220–290 mμ. No changes in the characteristic B-band at 255 mμ., loss of fine structure or change in band envelope were observed.

(14) A. Finch, P. J. Gardner, J. C. Lockhart and E. J. Pearn, *J. Chem. Soc.* 1428 (1962).

In principle this association should be reflected by the appearance in the infra-red spectra of bands associated with $\nu_{B-X\,(\mathrm{bridge})}$ and with corresponding changes in the frequency of ν_{B-X} in the monomeric molecule. However, the assignment of ν_{B-Cl} in (1) is equivocal(15) and the region in which boron-oxygen stretching modes are expected to absorb (ca. 1300–1440 cm^{-1}.) is complex. Hence as yet this method has not been successful in distinguishing between the two forms of association.

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(15) A. FINCH, P. J. HENDRA and E. J. PEARN, *Spectrochim. Acta*, **18**, 51 (1962).