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A STUDY OF SOME MOLECULAR ADDITION COMPOUNDS OF ZIRCONIUM AND HAFNIUM TETRAHALIDES

By

F. M. Chung

This Thesis is Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science at the Department of Chemistry, University of Ottawa

December, 1967

A. D. Westland
Associate Professor of Chemistry
Research Supervisor

F. M. Chung
Candidate

PREFACE

Since Sidgwick (1) summarised in 1941 the then available data on the relative affinities of the commoner ligand atoms for various acceptor molecules and ions, coordination chemistry in this respect has been a field of increased interest. However, direct thermochemical studies have not been widely conducted due, at least in part, to chemical and technical difficulties. Nevertheless, thermochemical research provides some of the most basic of all chemical information. Such information is independent of any other theories although it may support some correct ones.

Among various thermochemical methods, solution calorimetry is widely adopted and was chosen in the studies reported here. There are difficulties in dealing with air sensitive molecular addition compounds and in finding proper solvents for solution calorimetry. For the compounds whose thermal data are not directly obtainable, research has been done otherwise and considered to be supplemental.

The thesis presents first the methods used and the basic theories behind them. The experimental results and the discussion then follow. All should be self-explanatory in the respective chapters.

ACKNOWLEDGEMENTS

Thanks first go to Dr. A. D. Westland of Department of Chemistry of University of Ottawa. He has supervised the whole work with a spirit of conscientious scientist and great teacher. His well-rounded knowledge in chemistry and other fields as well, his readiness and patience in guidance and discussion have always been the main sources of inspiration and encouragement. Without any of these, the work and the thesis for this research would not have been possible. To him, the author wishes to express his heartfelt gratitude.

Also to Mrs. A. Phillips, Mr. C. Reyes-Zamora, Mr. R. Swingle, and Mr. P. Coulombe, the author is grateful for their assistance in providing some of the ligands, in taking NMR measurements, and in preparing figures and calculating some of the results. He thanks not the least his wife for her understanding and cooperation during the entire period of research.

Finally, financial assistance in the form of research grant under the name of Dr. A. D. Westland given by National Research Council of Canada is acknowledged.

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ABSTRACT

Addition complexes MX_4-2L, where M is Zr or Hf, X is Cl or Br, and L is tetrahydrofuran or tetrahydrothiophene have been prepared. Thermochemical data have been obtained and the results are interpreted. The enthalpies of reaction of $MX_4(c) - 2L \longrightarrow MX_4$-2L(c) was measured calorimetrically and the values converted to gas phase and correlated in terms of polarizability and steric effects. The compounds MX_4 appear to be on the borderline between class a and class b behaviour with hafnium showing a very slightly greater tendency toward class b behaviour.

The nuclear magnetic resonance spectra have been obtained for these complexes and the internal chemical shifts determined. The order of the increasing internal shift correlates satisfactorily with the order of thermal stability of the complexes.

Triphenyl phosphine oxide and triphenyl arsine oxide complexes of zirconium tetrachloride and hafnium tetrachloride have been prepared. They are 1:2 addition complexes except $ZrCl_4$-$3Ph_3AsO$ which is a 1:3 addition complex. They are insoluble in common solvents tested, hence neither the thermal measurements nor the n. m. r. spectrometry was carried out. Instead, their

infrared spectra were studied with those of corresponding niobium complexes which have also been prepared as 1:2 addition compounds. The analyses of the shifts of the P-O and the As-O stretching frequencies confirm the relative hardness of zirconium(IV) chloride and hafnium(IV) chloride as Lewis acids, hence the relative tendency toward class b behaviour thermochemically observed for zirconium and hafnium.

INTRODUCTION

Until about the year 1950, workers in the field of coordination chemistry were concerned almost exclusively with the stereochemistry of complex compounds and with the preparation of complexes of new types or containing new ligands. (2) In recent years, other physicochemical principles involved in complex formation have received increased attention. Efforts are currently being made to obtain quantitative information concerning the influence of the ligand on the properties of the complexes formed by a particular metal, or how the properties of the complexes containing the same ligand depend upon the position of the metal in the Periodic Table. (3)

Studies of the affinity and enthalpy of formation of complex compounds afford very interesting information regarding the energetic phenomena involved in the formation of molecular compounds from their molecular constituents. (4) It has also been pointed out that with suitably chosen donors and acceptors, both free energy and enthalpy changes in donor-acceptor reactions give affinity orders which are similar and the thermal stabilities of similar complexes thus give some idea about the strength of the donor-acceptor interaction. (5,6)

Of special interest in this respect are the different thermal properties of aluminium and gallium (7,8) which, with similar atomic radii -- 1.18 A and 1.26 A respectively -- differ in their electronic configurations only in that as an ion the former has a rare gas configuration while the latter has a pseudo-rare gas one with a filled 3d subshell. Since zirconium, atomic radius 1.45 A, differs from hafnium, atomic radius 1.44 A, only in that the former has an empty 4f subshell while in the latter this subshell is filled, the two elements exhibit qualitatively very similar behavior. It was of interest to obtain a quantitative measure of the acceptor ability of their respective anhydrous halides.

Zirconium and hafnium are more alike than any other pair of congeneric elements known. (9) This is due to the fact that both the atomic radii of zirconium and hafnium and the radii of the Zr^{4+} -- 0.79 A -- and Hf^{4+} -- 0.78 A -- are very similar and nearly identical, (10) and, presumably, because highly ionic behaviour prevails in the chemistry of both elements. The chemistry of hafnium has been studied much less than that of zirconium, but so far as it has been examined it differs very little from that of zirconium. In most cases, it is assumed that it is generally comparable to that of zirconium, the small

differences being in volatilities or solubilities of compounds.

The principal purpose of this research is to determine the enthalpies of complex formation between some zirconium(IV) halides, i.e., chloride and bromide, hafnium(IV) chloride and the ligands, tetrahydrofuran, THF, and tetrahydrothiophene, THT. These two ligands are chosen for the reason that they are structurally similar, differing only in the heteroatom. Oxygen is more basic towards the proton than sulfur while sulfur is more polarizable than oxygen. Using the popular terminology of Pearson (11), the oxygen compound is a harder base than the sulfur analogue. Since hafnium has a filled 4f subshell while zirconium has not; $HfCl_4$, for example, might be expected to be a softer acid than $ZrCl_4$ according to the π-bonding theory of hard and soft acids and bases and bind more strongly to the sulfur donor than to oxygen. This may be further comfirmed if, on the other hand, $ZrCl_4$ is proved to bind more strongly to the oxygen donor than $HfCl_4$ does. Our thermal studies do not bear these all out, but $HfCl_4$ is proved to be softer, though only slightly, than $ZrCl_4$.

Complexes containing triphenyl phosphine oxide and triphenyl arsine oxide as ligands have also been prepared, but their enthalpies of complex formation are not obtainable by

solution calorimetry due to the poor solubilities of the complexes in the solvents tested. Their infrared spectra, however, are discussed in the present work.

Certain aliphatic amines and thioethers have also been tried as ligands in conjunction with $ZrCl_4$. The only compound to be obtained in a well-defined state is that containing tetrahydrothiophene.

CHAPTER I BASIC THEORIES

SECTION I THERMOCHEMISTRY OF COMPLEX COMPOUNDS

The thermochemical studies of complex compounds may be considered under two catagories; first, those being carried out in the aqueous solution; and second, those studies of addition compounds which are prepared and handled in non-aqueous systems.

From the thermochemistry of aqueous solution, comparable metals have been correlated through the knowledge of their water-solvated states. Thus a series of enthalpies of hydration are found to be correlated with their corresponding ionization potentials in a linear relationship.

This indicates that ligands in a complex act more or less electrostatically just like the electrons in an atom. This is thought to be reasonable since the addition of ligands (the water molecule in this case) is analogous to the addition of electrons as such and the important influences here are size and effective charge of the positive central ion.

The thermochemical studies of addition compounds have been for the most part directed toward an understanding of acceptor and

donor relationships which are highly important features of coordination compounds. This type of study is concerned essentially with the enthalpy of the reaction

$$AX_n + BY_m = X_nA{-}BY_m$$

where AX_n is a Lewis acid or acceptor and BY_m a Lewis base or donor.

For this reaction, as in other chemical reactions as well, the most significant thermodynamic value is of course the Gibbs' free energy change. Free energies are not easy to measure for the complex compounds unless a measurable equilibrium can be set up. However, since we are interested in the relative accepting or/and donating abilities of similar systems, the enthalpy changes nearly parallel the free energy changes, i.e., the entropy effects have more or less constant influence.

$$\Delta H_2 - \Delta H_1 = (\Delta G_2 - T\Delta S_2) - (\Delta G_1 - T\Delta S_1) = \Delta G_2 - \Delta G_1$$

since $\Delta S_1 = \Delta S_2$

It has been pointed out (5) that in most cases studied, both free energy and enthalpy changes in donor-acceptor reactions give affinity orders which are similar. Thus the thermal stabilities of similar adducts give some idea about the donor-acceptor interaction. For example, consideration of thermal stabilities has been used to estimate the relative acceptor strengths of $ZrCl_4$, $ZrCl_3(OC_2H_5)$,

$ZrCl_2(OC_2H_5)_2$, and $ZrCl(OC_2H_5)_3$ toward $CH_3COOC_2H_5$ (4,12). These compounds will be referred to in the discussion.

In some ideal situations, interesting numerical data can be obtained from gas-phase equilibrium studies (13,14). For example, the enthalpy of dissociation of the adduct $(CH_3)_3B-N(CH_3)_3$ has been found to be 17.6 Kcal/mole. The corresponding value for $F_3B-N(CH_3)_3$ is 28.9 Kcal/mole. Work in the gaseous state is possible only in minority of cases, however. The values so obtained are enthalpies of formation of the complex compounds which are closely related to the dative-bond strength. The corresponding enthalpy of formation of a complex compound in solution may sometimes be used to calculate the same dative-bond strength provided that other data, e.g. enthalpies of sublimation, vaporization or solution are available. It has been found, however, that the enthalpies of formation of addition compounds in solution are nearly the same as the enthalpies of dissociation in the vapor phase (15,16). There are some instances where the enthalpies of reaction have been found to differ by a somewhat larger amount. (17) Such differences are unlikely to be large enough to affect orders of stabilities for a series of closely related addition compounds.

To appreciate the meaning of the above mentioned thermal data, an understanding of the relationship of various free energy

states is essential. This is also true in designing or carrying out any thermochemical study. This may be qualitatively demonstrated in terms of an energy cycle of formation (18).

For an adduct AX_n-BY_m formed from a donor BY_m and an acceptor AX_n, the various energy steps shown on page 17 should be considered. The quantity ΔG_f refers to the difference between the corresponding states of reactants and products. This is usually a practical indication of the coordinate bond strength though it is sometimes complicated by crystal field energy and reorganization energy, etc. Hence, if the acceptor and the complex are both soluble in excess of the donor compound, one can measure both the enthalpy of complex formation (in solution) and the enthalpy of solution of the complex and get their difference as ΔH_f, the standard enthalpy of complex formation.

The most recent example in adapting this cycle to coordinate compounds similar to those of interest in the present thesis are the works of N. L. Richards and A. Thompson (19,20), and of N. N. Greenwood and T. S. Srivastava (7). These authors note that if the enthalpy of reaction for the process

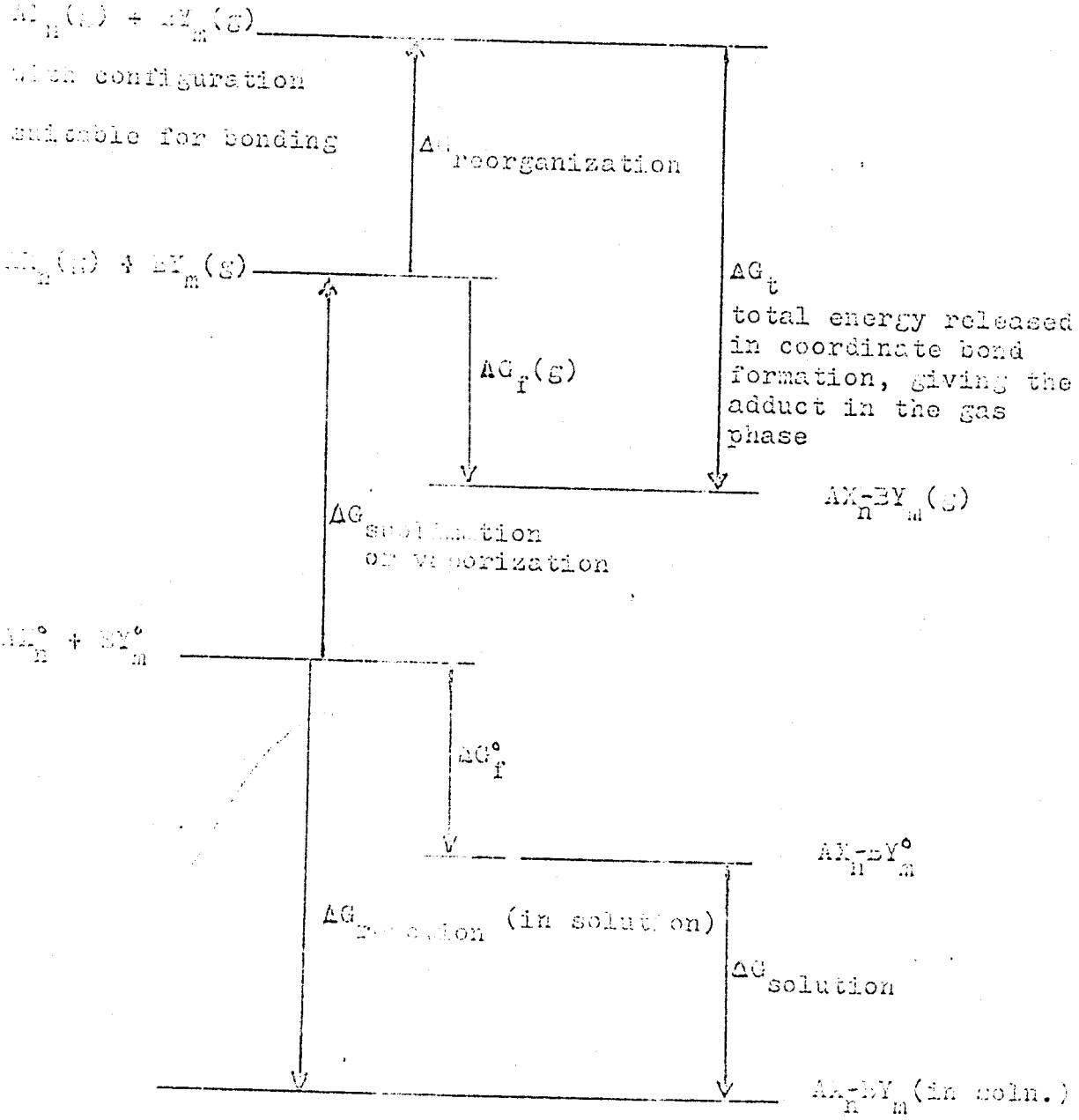
$$MX_3(c) + (n + x)L(l) = MX_3\text{-}L_x \text{ in } nL$$

is $-\Delta H_1$ and that of the process

$$MX_3\text{-}L_x(c \text{ or } l) + nL(l) = MX_3\text{-}L_x \text{ in } nL$$

ENERGY CYCLE IN THE FORMATION OF

MOLECULAR ADDITION COMPOUNDS



is $-\Delta H_2$, then for the adduct formation

$$MX_3(c) + xL(l) = MX_3{\cdot}L_x(l \text{ or } c)$$

the enthalpy of complex formation is $-\Delta H_f = \Delta H_2 - \Delta H_1$.

This kind of adaptation has resulted in an accumulation of data to the extent that some thermochemically qualitative understanding of coordinate bonds in adduct compounds is now possible. This is illustrated by the following discussions.

Collected data (6,15) show that the enthalpies of complex formation of $AX_n{\cdot}BY_m$ in the reaction

$$\underset{\text{acceptor}}{AX_n} + \underset{\text{donor}}{BY_m} = \underset{\text{adduct complex compound}}{AX_n{\cdot}BY_m}$$

for the series $(CH_3)_3N{\cdot}BF_3$, $(CH_3)_3N{\cdot}BF_2CH_3$, $(CH_3)_3N{\cdot}BF(CH_3)_2$ and $(CH_3)_3N{\cdot}B(CH_3)_3$ are 26.6-30.9, 25.1, 18.3 and 17.6 Kcal/mole respectively. This was thought to indicate that the highly electronegative fluoride atom attached to boron increased its electron accepting power (21,22,23,24,25). This was supported by the fact that $H_3P{\cdot}BF_3$ was known but $Cl_3P{\cdot}BF_3$ and $F_3P{\cdot}BF_3$ were unknown (26, 27,28). Here the more electronegative chlorine and fluorine atoms attached to phosphorus presumably decreased its electron donating power.

These evidences would lead us to think that the acceptor power of boron halides are in the order of

$$BF_3 \rangle BCl_3 \rangle BBr_3$$

However, additional information shows that the enthalpies of complex formation of the indicated reactions of other boron complexes in Kcal/mole are (29,30) as follows:

$C_5H_5N(*) + BX_3(*) =$	$C_5H_5NBF_3(*)$ 25.0	$C_5H_5NBCl_3(*)$ 30.8	$C_5H_5NBBr_3(*)$ 32.8
$C_5H_5N(l) + BX_3(l) =$	$C_5H_5NBF_3(*)$ 31.7	$C_5H_5NBCl_3(*)$ 39.5	$C_5H_5NBBr_3(*)$ 44.5
$C_5H_5N(l) + BX_3(l) =$		$C_5H_5NBCl_3(c)$ 40.6	$C_5H_5NBBr_3(c)$ 45.5
$C_5H_5N(g) + BX_3(g) =$		$C_5H_5NBCl_3(g)$ 37.9	$C_5H_5NBBr_3(g)$ 43.5
$C_5H_{11}N(l) + BX_3(l) =$		$C_5H_{11}NBCl_3(c)$ 84.4	$C_5H_{11}NBBr_3(c)$ 114.5
$C_5H_{11}N(g) + BX_3(g) =$		$C_5H_{11}NBCl_3(g)$ 80.6	$C_5H_{11}NBBr_3(g)$ 111.6
$C_6H_5NO_2(l) + BX_3(l) =$	$C_6H_5NO_2BF_3(*)$ 6.7	$C_6H_5NO_2BCl_3(*)$ 8.7	$C_6H_5NO_2BBr_3(*)$ 12.5

(*) = (soln.)

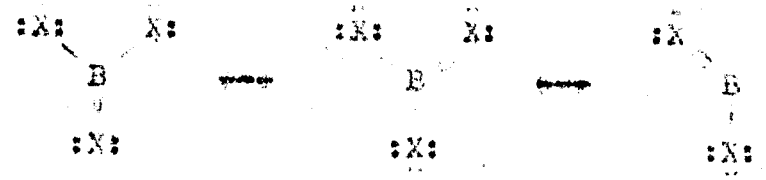
The accepting power order is therefore actually

$$BBr_3 \rangle BCl_3 \rangle BF_3$$

with only a few exceptions such as those previously mentioned. The same trend, though developed to a milder extent, is followed by the aluminium halides (31,32,33,34,35,36,37). This trend which is contrary to the order of electronegativity was thought to be due

to two reasons: (29,30,38)

1. From fluoride, chloride, bromide to iodide, there is a decreasing tendency to form resonance π-bonds by back donation from the halogen atom into the vacant boron or aluminium orbitals, eg.



Since resonance structures of this kind are not possible in the molecular addition compounds, such resonance will tend to reduce the tendency of adduct formation.

2. There is, in the complexes of the same halide sequence, a decrease in the electrostatic repulsion between the B-X or Al-X bond electrons and the lone-pair electrons on the ligand due to the increase in the radii of the halogen atoms.

These factors are revealed in the large difference in the reorganization energies which are required to break the resonance π-bond and to change the halides from planar to tetrahedral shape as the trihalide molecules form coordinate bonds. The pertinent reorganization energies have been estimated elsewhere (7,32,39) as listed below. The large differences of the reorganization energies among boron and aluminium halides should be high enough to outweigh, at least in part, the effect of electronegativity and to reverse the order of the acceptor strength of the halides.

Estimated Reorganization Energies (from planar to tetrahydral)
unit: Kcal/mole

Compound	BF_3	BCl_3	BBr_3	$AlCl_3$	$AlBr_3$	AlI_3	$GaCl_3$	$GaBr_3$	GaI_3
Cotton & Leto(39)	48.3,	30.3,	26.2,	31.6,	27.9,	18.7,			
Eley & Watts (32)	79.5,	65.7,	39.7,						
Perkins (7)									24.1, 25.9, 17.8.

The differences in the reorganization energies between the various gallium halides are much smaller. This may be the reason why the enthalpy data of gallium halide adducts shown below indicate that the electronegativity effect is playing an important role again (7,40).

Some Enthalpy of Complex Formation Data for Gallium Halide Adducts
unit: Kcal/mole

Acceptor	Donor						
	C_5H_5N	$2C_5H_5N$	Et_3N	H_3N	Et_2O	Et_2S	$(CH_3)_2S$
$GaCl_3$	35.1	21.3	34.4	28.7	26.6	32.1	30.1
$GaBr_3$	33.7	14.6	10.0	25.4	23.5	27.9	26.7
GaI_3	28.7	---	1.7	18.9	15.6	23.0	22.4

The above mentioned enthalpy data show the steric effect in various ways. Thus, the progressive decrease in acceptor strength toward piperidine is greater than that toward pyridine and it is greater for the complexes of triethylamine which are the most sterically hindered of all the related examples. The effect of steric strains have been reviewed (41) and additional discussion

can be found elsewhere (15,40,42).

With $AlCl_3$, $AlBr_3$, and $GaCl_3$ as reference acceptors, the relative donating powers for ethers and thioethers all show that Et_2O < THF and Et_2S < THT. These are thought to be the result of the steric effect (19,20). The steric effect may also be one of the reasons why the order of acceptor strength $ZrCl_4$ > $ZrCl_3(OC_2H_5)$ > $ZrCl_2(OC_2H_5)_2$ > $ZrCl(OC_2H_5)_3$ is observed toward the donor $CH_3COOC_2H_5$ (5,12).

Researches such as these have established that the strength of the coordinate bond in complex compounds is largely, if not entirely, determined by the competing factors of (I) steric effect, (II) electronegativity and polarity effect, and (III) reorganization energy.

In the experiments described in this thesis, the steric effect due to the ligand size was minimized by choosing tetrahydrofuran (THF) and tetrahydrothiophene (THT) as reference donors in studying the relative acceptor strength of sterically similar zirconium (IV) chloride and hafnium (IV) chloride. The ligands are both very compact molecules. The information obtained should be of interest in comparing the bonding abilities of zirconium and hafnium and give us some idea of how the electronegativity and

polarity effect influences the complex formation in the system chosen. When these are compared with the enthalpy data of zirconium bromide, however, the steric effect is seen to be important.

Data for enthalpy of complex formation with zirconium and hafnium are not sufficient to illustrate the relationship between the enthalpies of the complex formation and the electronegativities. However, all the enthalpies of formation for the halides and oxides of hafnium, zirconium, and titanium (included for comparative purposes) show an increase down the group as shown by the data listed.

ENTHALPIES OF FORMATION OF TITANIUM, ZIRCONIUM, AND HAFNIUM COMPOUNDS FROM THEIR STANDARD STATE, $-\Delta H$ (25°C, Kcal/mole)

$TiF_4(s)$	$TiCl_4(l)$	$TiCl_4(g)$	$TiCl_3(s)$	$TiCl_2(s)$	$TiO_2(s)$
394.2[a]	192.3[c]	182.4[c]	170.7[d]	123.0[g]	225.8[c]
$ZrF_4(s)$	$ZrCl_4(s)$		$ZrCl_3(s)$	$ZrCl_2(s)$	$ZrO_2(s)$
458.8[b]	233[c]		178.6[e]	124.3[e]	261.5[c]
$HfF_4(s)$	$HfCl_4(s)$		$HfCl_3(s)$	$HfCl_2(s)$	$HfO_2(s)$
461.4[a]	237[c]		195[f]	130.[e]	266.1[c]

a. E. Greenberg, J. L. Settle, and W. N. Hubbard, J. Phys. Chem., 66, 1345, 1962

b. E. Greenberg, J. L. Settle, H. M. Feder, and W. N. Hubbard, J. Phys. Chem., 65, 1168, 1961.

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e. S. N. Lungu, Acad. Rep. Populare Romine, Studii Cercetari Fiz., 13, No. 1, 29, 1962, through Chem. Abstr., 57, 9297, 1962.

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g. L. Brewer, G. R. Somayajulu, and E. Brackett, Chem. Rev., 63, 111, 1963.

The promotion energies probably do not account for the order. It has been pointed out (43) that among the $TiCl_4$ valence-states, a state derived from the configuration d^3s with tetrahedral symmetry is likely to be preferred to one derived from configuration sp^3, although a hybrid involving both d^3s and sp^3 configurations is more satisfactory than either separately. If the separation between the ground state (d^2s^2) level and the lowest-lying level of the excited d^3s configuration of the gas-phase atom can be taken as a relative measure of the $d^2s^2 \longrightarrow d^3s$ promotion energy, then the values of this separation for Ti, Zr, and Hf, taken from Moore (44) and tabulated below, suggest a slightly more ready promotion in Zr, but a considerably more endothermic process for Hf.

$d^2s^2 \longrightarrow d^3s$ SEPARATION

	cm^{-1}	e.v.	kcal/mole
Ti	6[illegible]7	[illegible].01	1[illegible].7
Zr	4871	0.60	13.9
Hf	14092	1.74	40.3

The actual trend therefore was explained (45) by (a) the larger differences in lattice enthalpies of the compounds and (b) in differences in the ionization of the metals. The formation of hafnium compounds relative to zirconium analogues was favoured by (a) and zirconium compounds were favoured over titanium analogues by (b). The result is that the enthalpies of formation increase down the group in spite of the increasing electronegativities.

An ionic-cycle enthalpy cycle for the chlorides $TiCl_2$, $ZrCl_2$, and $HfCl_2$ was used to illustrate this (45), using the following data.

Ionization potentials, e.v. (kcal/mole)

Ti Zr Hf

21.10 (2101), 22.42 (1765), 23.4 (1891).

Calculated lattice enthalpies, 25°C, kcal/mole

$TiCl_2$ $ZrCl_2$ $HfCl_2$

2879 2632 2705

The results were presented graphically as shown in Figure 1.

The enthalpy of complex formation would be independent of the values of the enthalpy of sublimation of metal, the enthalpy of atomization and the electron affinity of individual elements. Nor would the ionization potential influences fit in the above manner. The data for enthalpies of complex formation in the condensed phase obtained in the present work, however, correlated with the increasing electronegativity from Ar to Kr. A further analysis of the bonding is attempted in the discussion later.

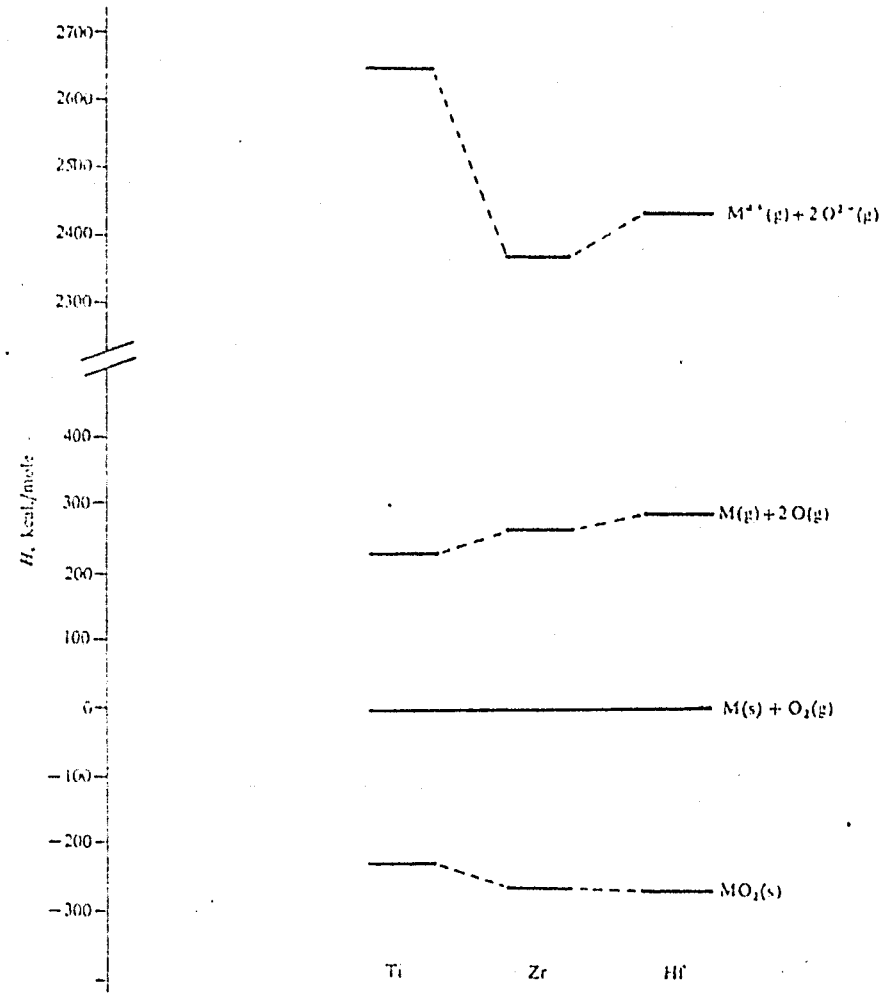


Figure 1. [illegible] relationships between [illegible] of Ti, Zr, and Hf.

SECTION II SPECTROSCOPIC STUDIES OF COMPLEXED LIGANDS

1. INFRARED STUDIES

Adduct formation at the oxygen atom in R_3PO or R_3AsO, where R is either an alkyl or a phenyl group, always leads to a change in the strength of the bond between the oxygen atom and the rest of the donor molecule. A decrease of this kind is associated with a decrease in the frequency of the vibrational mode assumed to be characteristic of stretching of the bond(s). Thus the P-O and As-O stretching frequencies may be used as indicators of acceptor strength. Changes in adjacent bonds have also been considered to some extent (5,42). It has been pointed out that purely kinematic effects would lead to an increase in the frequency, so that the actual decrease due to bond weakening is, in fact, larger than that measured directly by the frequency shift (46,47).

Structure determinations show that oxygen is the donor atom not only in adducts with phosphine oxides such as $SbCl_5(CH_3)_3PO$ but also in adducts with phosphoryl halides such as $SbCl_5POCl_3$, $NbCl_5POCl_3$, $TaCl_5POCl_3$, $SnCl_4{\cdot}2POCl_3$, $TiCl_4{\cdot}2POCl_3$ and $(TiCl_4POCl_3)_2$. The negative shift of the P-O vibration frequency in adducts with phosphine oxides has been extensively verified (48-56).

Adducts containing Ph_3PO and Ph_3AsO have been prepared and the complex formation effect on the P-O and As-O stretching frequencies investigated.

The P-O and As-O stretching frequencies of the complexes discussed in the present work containing triphenyl phosphine oxide, Ph_3PO, or triphenyl arsine oxide, Ph_3AsO, are interpreted in the light of information in the literature.

2. NUCLEAR MAGNETIC RESONANCE STUDIES

The origin and the principle of the application of n.m.r. in connection with the study of relative donor and acceptor strengths can be understood by starting with a quotation from T.D. Coyle and F. G. A. Stone (57).

"The simple qualitative description of the formation of molecular addition compounds by electron donor-acceptor interactions implies that the electron-attracting power of the donor and the acceptor atoms in an adduct will be somewhat different from that in the free Lewis base and acid, and will depend in part upon the strength of the coordinate bond. On these grounds, the empirical relationship between the electronegativity of substituents and the chemical internal shifts in ethyl derivatives was applied

recently to an investigation of the triethyl derivatives of aluminium and gallium and their diethyl etherates. The results of that study indicated that the apparent electronegativity of the Group III acceptor atom is diminished by complex formation and that the electronegativity of the donor atom is increased with increasingly strong coordination ... Furthermore, the relation between electronegativity and chemical shifts in methyl derivatives might provide a similar means of evaluating relative stabilities in methyl-substituted addition compounds."

The same results, however, havenot been confirmed uniformly in their attempt to correlate the separation of the chemical shifts due to the methylene and methyl protons of the ethyl groups with the stability of some of the boron-containing addition compounds.

R. L. Richards and A. Thompson (19,20) applied this same idea in their studies on the metal-oxygen and metal-sulfur bonds in some addition compounds of aluminium and gallium trihalides with ethers and thioethers, along with their thermal studies on the same subject. These authors showed that chemical shifts and thermochemical data correlate well if all measurements are made on systems which are in the same state. We may conclude that when all relevent factors have been considered, n.m.r. data may give a guide to the condensed-phase order of stability in a closely related series of complexes, but the difficulty of choosing the

correct parameters and the anomalies which occur (1,19,20) show that corrected thermochemical measurements, although considerably more tedious, are far more reliable when discussing relative bond strengths.

CHAPTER II EXPERIMENTAL WORK

SECTION I EXPERIMENTAL METHODS

1. CONSTRUCTION OF CALORIMETER

THE THERMOSTAT The vessel is illustrated in Figure 2. A glass jar of 13 inches high and 9 inches in diameter was used as a thermobath container. It was matched with an outer metal container. These two vessels were assembled with Vermiculite in between them which served as a heat insulator. This insulator liner was covered with a wooden ring and sealed in place with No. 30 Sternson High Temperature Cement.

Inside the thermostat, a Dewar flask was situated at a convenient position. The outer metal shell of the Dewar flask was suitably cut and arranged to house an all-glass calorimeter. The Dewar flask was itself held in position with aquarium cement. The calorimeter was suspended inside the Dewar flask with a fibre supporting ring as shown in Figure 3.

THE THERMOSTAT COVER A water-filled brass cover for the thermostat was constructed. Ports were provided for the calorimeter, the thermostat heater, the cooling coils, the thermoregulator,

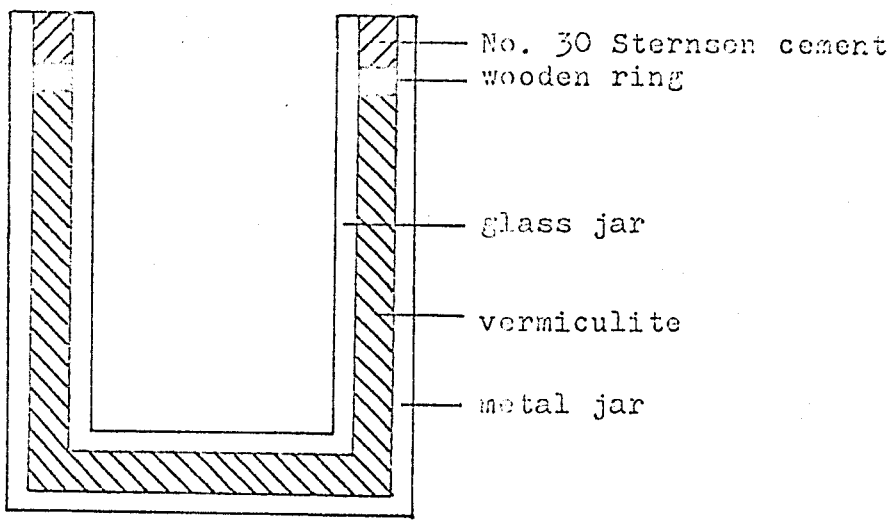


Figure 2. The thermostat.

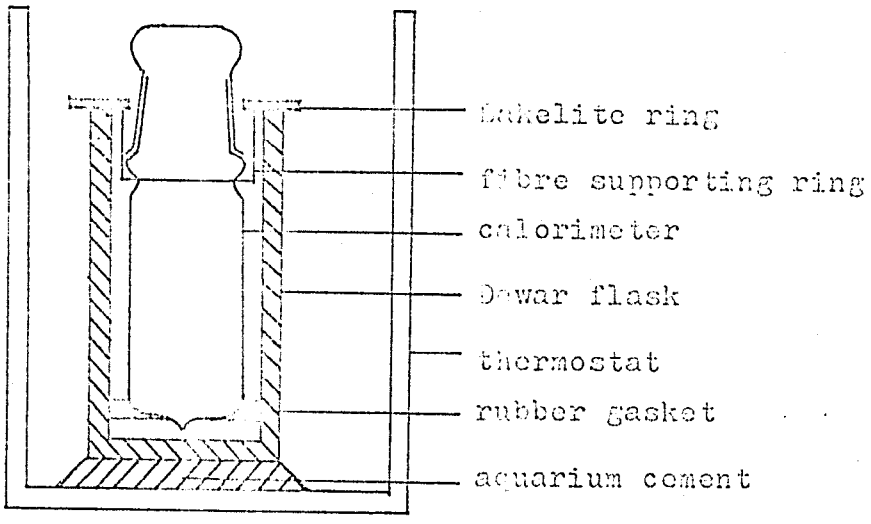


Figure 3. Dewar flask assembly.

the thermometer, the thermostat stirrer, the water inlet and the water outlet.

The size of the brass cover and its water inlet and water outlet were so designed that, with proper pumping, the water in the top would come to a certain equilibrium level without overflowing when in operation. The cover is as shown in Figure 4.

The water inlet was put as far from the water outlet as possible to help water circulation. The brass cover and the brass tubes therein were all soldered into a whole piece. The cooling coil, made from one quarter inch copper tubing, was also soldered to the top.

THE TEMPERATURE CONTROL SYSTEM An electronic relay, 115 V and 50-60 cyc., Precision Scientific Co., Chicago, supplied electric power for the thermostat stirrer and the calorimeter stirrer which were geared with the driving motor such that the thermostat stirrer had the highest speed while the calorimeter was driven at 160 r.p.m.. The bath temperature was controlled by a mercury contact thermoregulator. The controlled temperature could be set at will within the range, -35°F--- 135°F. The thermostat temperature was controlled at 25.0°C ± 0.1.

A rotatory water pump was used for the circulation of the water through the thermostat cover.

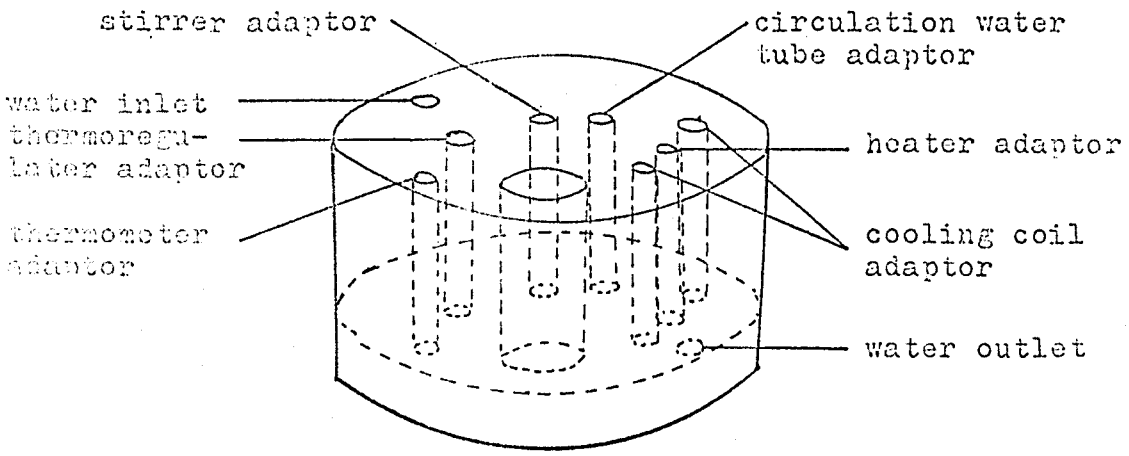


Figure 4. The thermostat cover.

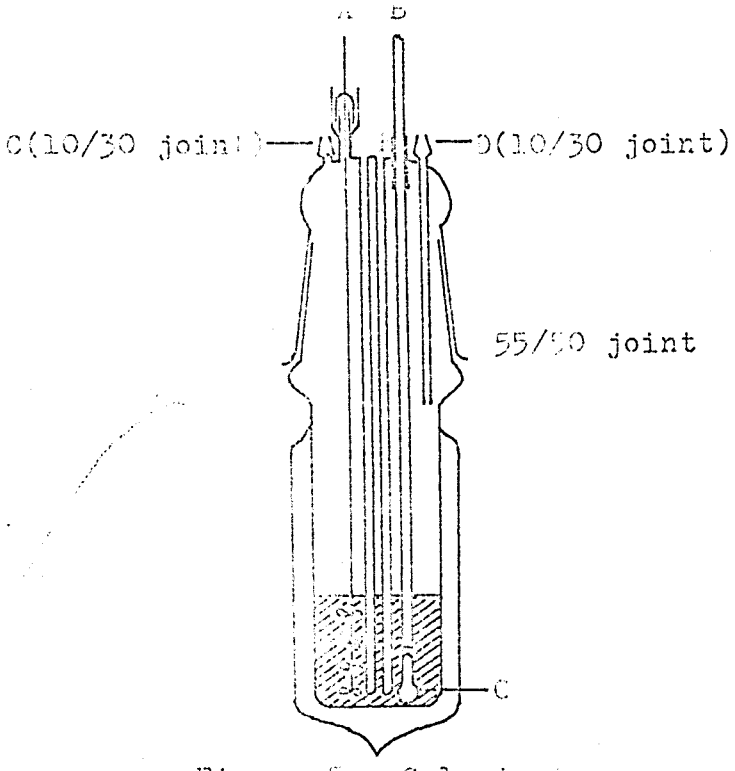


Figure 5. Calorimeter

To assemble and disassemble the thermostat and calorimeter, the calorimeter stirrer was disconnected from the driving wheel and the calorimeter heater and the thermocouple taken out from the wells. The operation was facilitated by use of a jacking system. When the jacks were lowered, the thermostat vessel was lowered so that the calorimeter could easily be taken out, using the ring support.

THE CALORIMETER The all-glass calorimeter was fashioned after that used by N. N. Greenwood and F. G. Perkins (58). The distilling device originally designed was not adopted, however, since it was not needed. One of the mercury seals, for attachment b, was also replaced with a precision ground glass rod which just fitted in the attachment B and which had a sample bulb adaptor at one end. The diagram on Figure 5 shows the construction of the calorimeter.

The calorimeter head was a 55/50 joint rounded off about 2 cm. from the grinding; it carried six attachments A-F. A refers to a mercury-sealed inlet carrying the stirrer. B is a glass rod held in position with a guide tube. This was kept air tight by means of silicone grease. The sample adaptor was situated at the lower end to hold the sample bulb G. C and D are 10/30 cones, one of which (D) carried a feed-in to admit in dry nitrogen and the

other for allowing the gas to escape. E and F are wells of specially thinned glass for containing the calibration heater and the thermocouple.

THE THERMOCOUPLE. Temperatures were measured by means of an eight-junction thermocouple made from No. 30 Constantan and copper wires. The hot junctions were immersed in mineral oil in one of the thin glass wells in the calorimeter. The reference junctions were contained in a distilled water-ice bath. Potentials were measured by means of a potentiometer, type 4025, manufactured by H. Tinsley & Co. Limited, which read to 1 μV. By interpolation, the galvanometer deflection gave thermo-emf values precise to less than 0.5 μV.

THE CALORIMETER CALIBRATION HEATER. The calorimeter heater coil, made from No. 30 Constantan wire and having a total resistance of about 5 ohms, was standardized with a resistance thermometer bridge, type J-1003, H. Tinsley & Co. Limited. Current was taken from three large-capacity 2V batteries connected in parallel. In order to achieve a steady current, it was passed through a dummy heater of 5 ohms resistance for at least three hours before a run. The current drawn was about 0.3 A. The duration of electrical heating was timed by means of an electric timer, reading to 0.1 second, which was synchronized with the heater by a double pole double throw (D.P.D.T.) switch as shown

in Figure 6.

The current was measured by means of a potentiometer of Diesselhorst pattern, type 3589-H, H. Tinsley & Co. Limited, using the potential drop across five 1-ohm standard resistors connected in parallel. Currents were measured with a precision of ±5 μA.

2. CALORIMETRIC MEASUREMENTS

PREPARING THE SAMPLE BULB A sample filling tube and the sample bulbs were assembled, as shown in Figure 7 and connected to a vacuum line and outgassed. Dried nitrogen was then let in. The 24/40 joint was disconnected while nitrogen was passing through, and a nitrogen filled tube containing the sample was broken over the opening and the sample poured in. The 24/40 joint was reconnected and the assembly outgassed again. The stopcock was closed and the 14/35 joint was disconnected from the vacuum line. The sample was then transferred to the sample bulb which was subsequently sealed off at the point indicated in Figure 7.

PREPARING THE CALORIMETER The prepared sample bulb was placed in the rod 5 adaptor shown in Figure 5. This was done when the calorimeter head was not on the body. The head and the body were then assembled as shown in Figure 5. The calorimeter stirrer

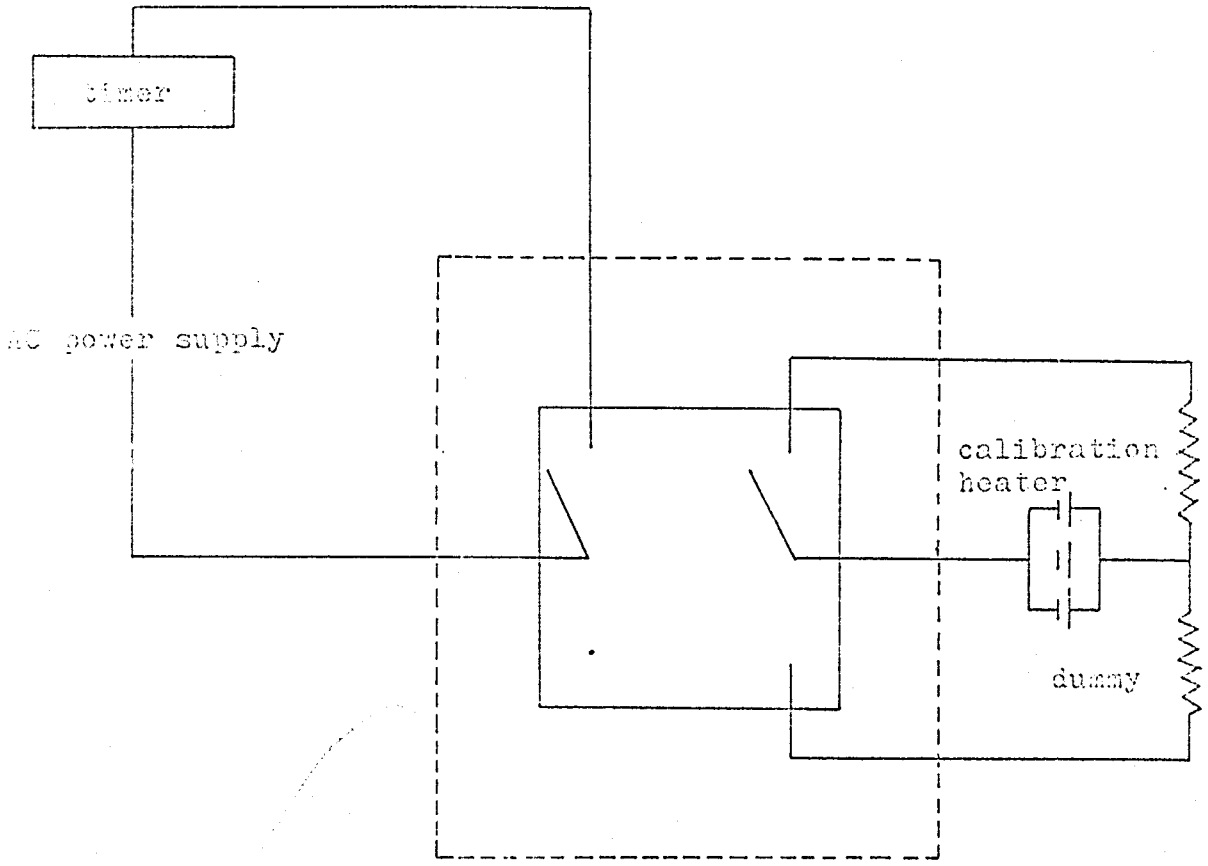


Figure 6. Synchronization of heater and timer.

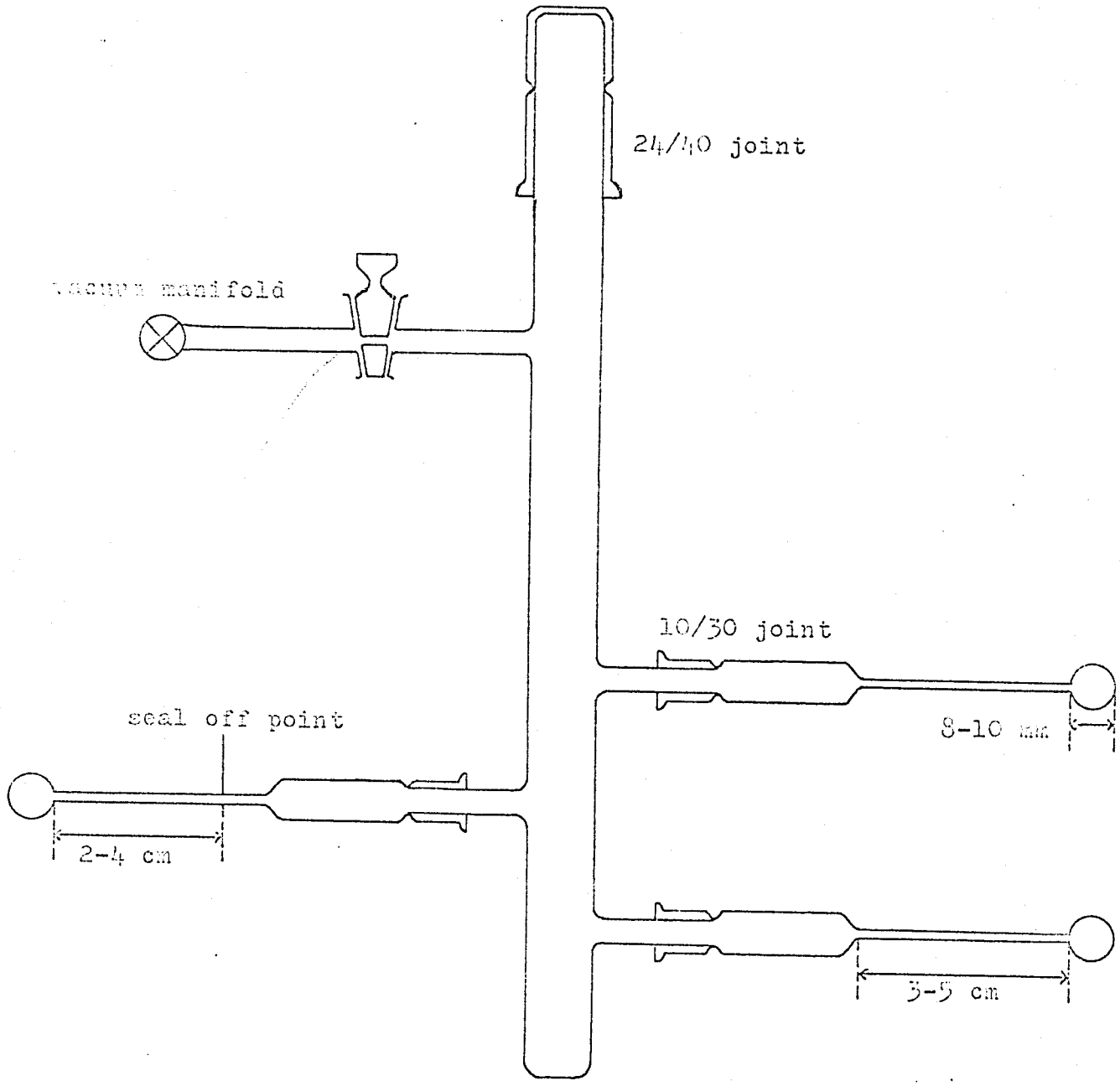
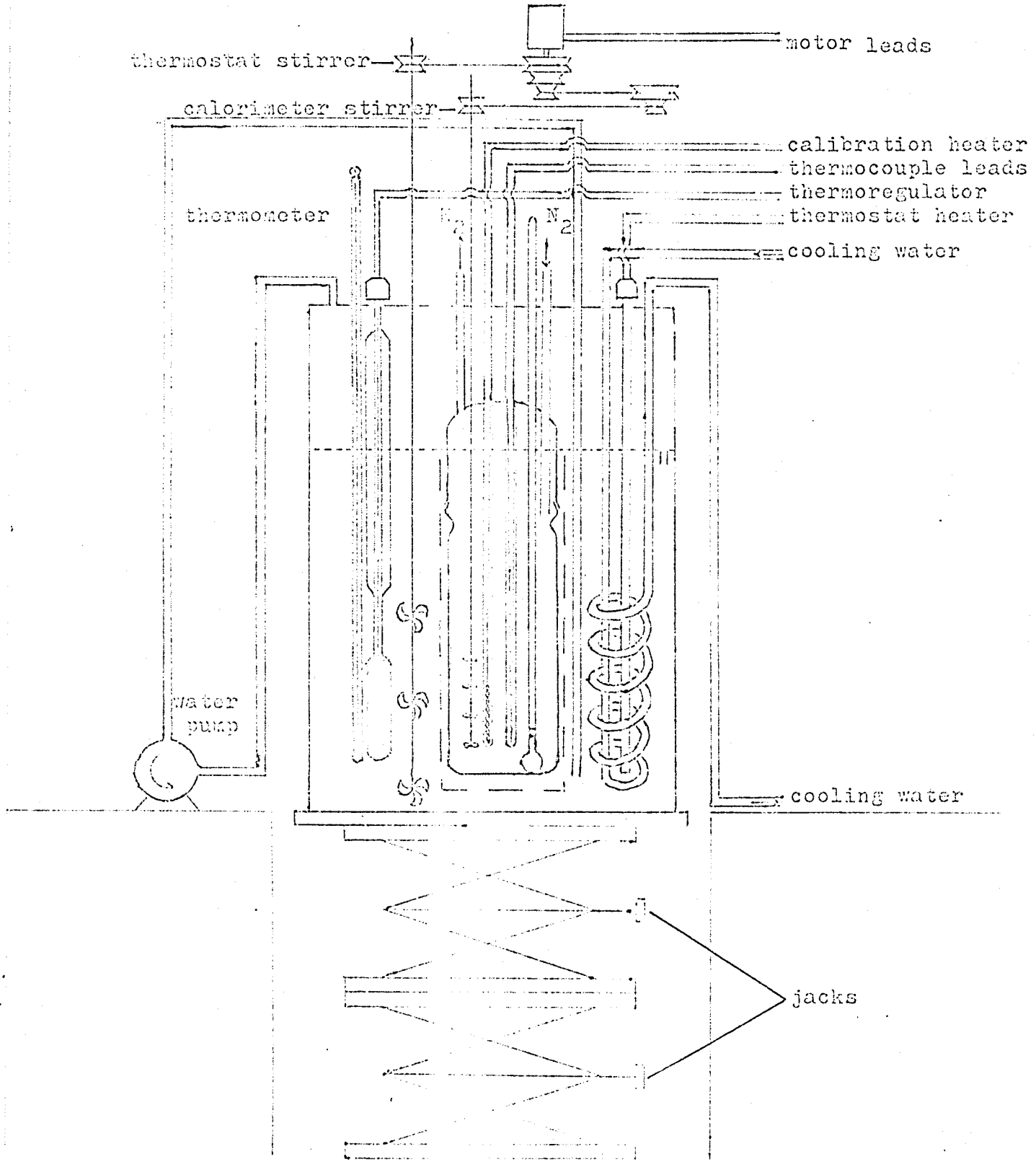


Figure 7. The sample filling tube and the sample bulbs.

inlet A was filled with mercury and the wells E and F two-thirds filled with mineral oil. The whole calorimeter was then introduced into the Dewar flask as shown in Figure 3, the thermostat filled with water up to a level about 1 cm. below the lid of the Dewar flask with the two jacks shown in Figure 8 at the lowest position, by operating the jacks. The calorimeter stirrer was screwed into position, and the calorimeter heater and the hot junctions of the thermocouple inserted into the wells E and F. Nitrogen was led in through the feed-in D and out through C (see Figure 5) for at least one hour before 100 ml. of freshly distilled ligand liquid was introduced through C into the calorimeter body using a small tipped funnel while nitrogen was still flowing. C was then covered and the nitrogen flow stopped. The calorimeter inlet on the brass cover was covered with glass wool further to prevent heat loss. Tap water was passed through the cooling coil and the reference junctions of thermocouple put into the distilled water-ice bath. The power supply switch on the electric relay and all the batteries were turned on, with the heater switch shown in Figure 6 in the dummy position. The apparatus was allowed to reach a steady state before calibration was begun.

CALORIMETRIC CALIBRATION AND MEASUREMENT

a. FORE-PERIOD CALIBRATION When the calorimeter was prepared, the calorimeter temperature, i.e. the potential of the thermocouple, was taken every minute for at least 15 minutes. The


motor leads
thermostat stirrer
calorimeter stirrer
calibration heater
thermocouple leads
thermoregulator
thermometer
thermostat heater
N_2
N_2
cooling water
water pump
cooling water
jacks

heater switch was then turned to the calorimeter position and the current measured at least five times in about 300 seconds heating period. The heater switch was turned back to the dummy position when the heating was stopped and the calorimeter temperature recorded every minute till the temperature changed linearly.

b. [illegible] The calorimeter was allowed to come to a steady state after the fore-period calibration. The calorimeter temperature was then recorded every minute for at least 15 minutes. The sample bulb was then broken by thrusting the adaptor rod against the calorimeter wall. The temperature was recorded every 15-30 seconds for about 5-10 minutes and then every minute till the temperature changed linearly.

c. AFTER-PERIOD CALIBRATION The calorimeter was allowed to come to a steady state after the measurement and the calorimeter prepared again. The same procedure as in a was followed to carry out the after-period calibration.

DATA EVALUATION AND CALCULATION

a. The Calibration The energy in calories supplied by the calibration heater was determined using the equation

$$W = I^2Rt/4.1840$$

where the symbols have their usual significance in electrical theory. When I varied slightly during the heating time, I^2R values were plotted against t and W in joules is the area under the curve.

The calorimeter temperature rise ΔT was determined graphically by plotting the recorded temperature-emf, in uV unit, against the recorded time, extrapolating linear portions before and after heating to the middle point of the heating period and taking the difference there.

The calibration C was calculated as

$$C = \frac{W}{\Delta T} \text{ cal/uV}$$

for the fore- and the after- period calibration respectively. They were in agreement with one another to within 3%. The average of the two was taken as the calibration for the measurement.

b. The Measurement The molar enthalpy of reaction or the molar enthalpy of solution described in the last chapter was calculated using the equation

$$\Delta H = C.x\ \Delta T \times f.w. / W_{sample} \text{ cal/mole}$$

where f.w. is the formula weight of the sample and W_{sample} is the weight of the sample used.

3. INFRARED SPECTRA

Infrared spectra were recorded using a Beckmann IR-8 or a Perkin-Elmer model 137 spectrometer with sodium chloride or cesium iodide plates. Samples were prepared in the form of Nujol mulls in a glove box and held between salt plates, the edges of which were greased to prevent ingress of moisture.

4. N. M. R. SPECTRA

Proton nuclear magnetic resonance spectra were recorded on a Varian V-4302 spectrometer at 60 mc/s.

The sample was introduced into a tube which had been connected to the vacuum line, outgassed and flushed with dry nitrogen. The solvent, purified benzene in our work, was then added. The saturated solution so formed was transferred to an n.m.r. spectrum tube which had been connected to the above-mentioned tube. It was frozen with liquid nitrogen and the spectrum tube sealed off under reduced pressure.

5. PREPARATION OF SAMPLES

Zirconium (IV) chloride and hafnium (IV) chloride, supplied by A. D. Mackey Inc., were purified by sublimation in an atmosphere of dry nitrogen in a sealed tube at 280°C and 275°C respectively.

The sublimation tube shown in Figure 9 consisting of 3-4

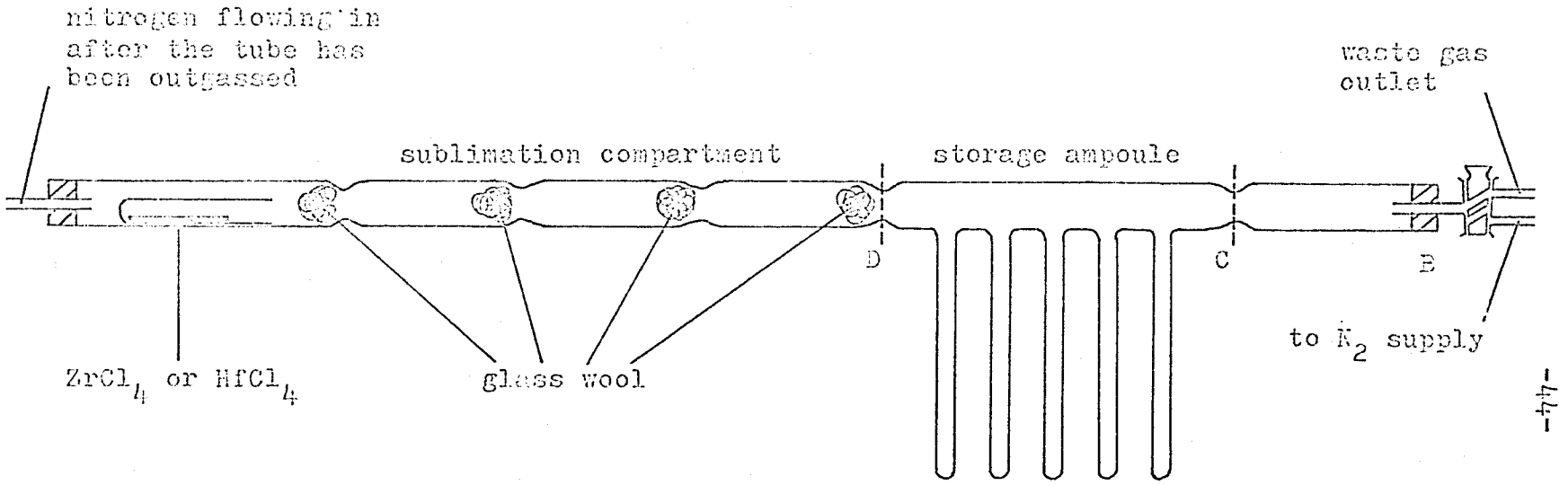


Figure 9. The Sublimation tube.

sublimation compartments and storage ampoules was originally open at end A but closed at end B. A was connected to a vacuum line and the whole sublimation tube outgassed. Dried nitrogen was then passed through A and B which was now opened to the atmosphere. A tube filled in a glove box with zirconium (IV) tetrachloride or hafnium (IV) tetrachloride was inserted through A while nitrogen was flowing through B. Nitrogen was then admitted through A while B was connected to a tube leading to a fume hood. The tetrachloride was heated with a flame and sublimed from one compartment to another till it reached the storage ampoules. These were then sealed off at C and D.

Zirconium (IV) bromide was prepared using a procedure similar to that described by Ray and Westland (59) as follows:

a. Distillation of Bromine: Bromine which had been allowed to stand over P_2O_5 was introduced into container A of the distilling apparatus shown in Figure 10. The tube was outgassed while bromine in A was frozen with liquid nitrogen. C was then closed and the bromine distilled into the thin-walled tube, B, until the tube below the lower constriction was about 80% full. The sample tube B was sealed off at D.

b. Preparing the Reaction Tube: The appararus shown in Figure 11 was assembled containing nuclear grade zirconium sponge. The bromine ampoule was scratched with a file before assembling. The ampoule was shattered by means of a rod passed in at E while

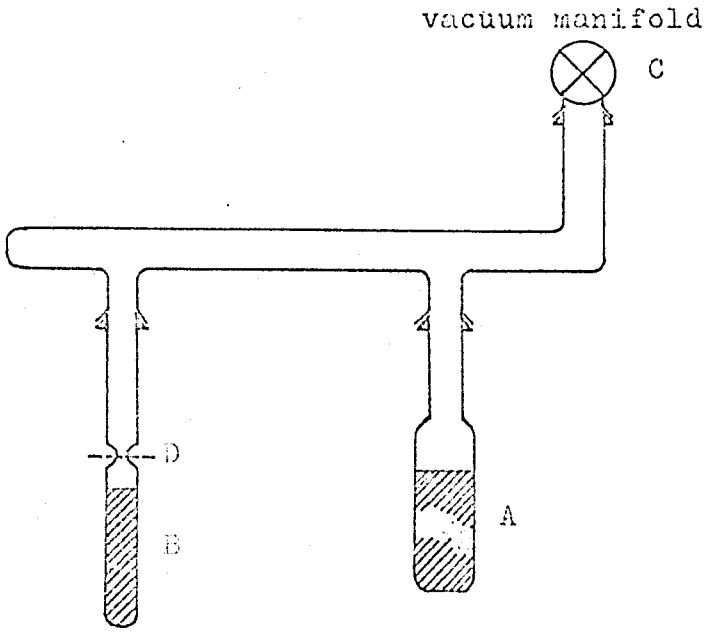


Figure 10. The bromine distillation tube.

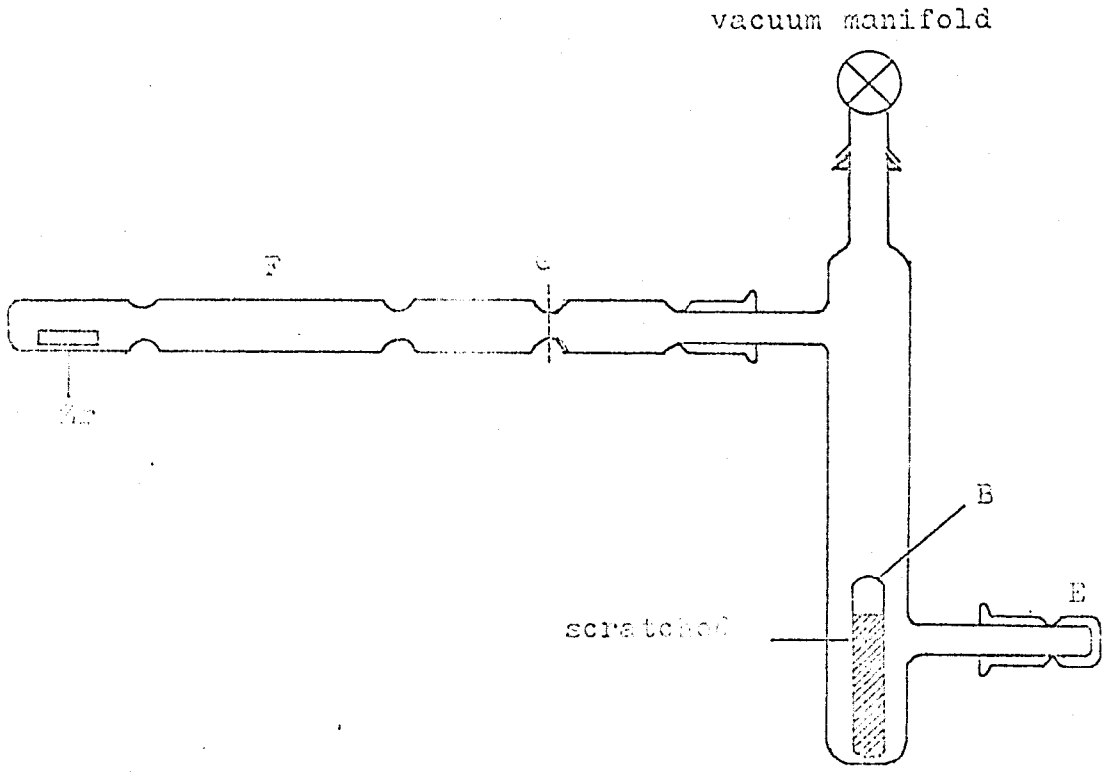


Figure [illegible] The sample transferring tube.

nitrogen was flowing out of the opening. E was then covered and bromine from D was decanted into the reaction tube F. The transferring of bromine was completed by cooling F in liquid nitrogen. The whole transferring tube was then outgassed and the reaction tube sealed off at G under vacuum.

c. Formation of Zirconium Tetrabromide: The reaction tube from b was heated in an aluminium block furnace at 350°C with one end containing liquid bromine kept at room temperature. The pressure of the bromine was sufficient for the reaction to proceed. The apparatus was assembled as shown in Figure 12 and heating continued for two days. Crude zirconium tetrabromide, thus produced in the middle part of the reaction tube, was transferred into a test tube in a glove box. The tube was then inserted into the dried sublimation train as shown in Figure 9. The sublimation of zirconium tetrabromide was carried out, using the same procedure as for the sublimation of zirconium tetrachloride previously described. The finely powdered, white zirconium tetrabromide was stored in an ampoule under nitrogen. Anal.: Calc. Br 22.20, Zr 77.80; Found Br 22.22, Zr 77.04.

Tetrahydrofuran (Fisher Certified Reagent) and tetrahydrothiophene (Aldrich) were freshly purified by distillation, the middle portion being collected.

Triphenyl phosphine oxide and triphenyl arsine oxide were

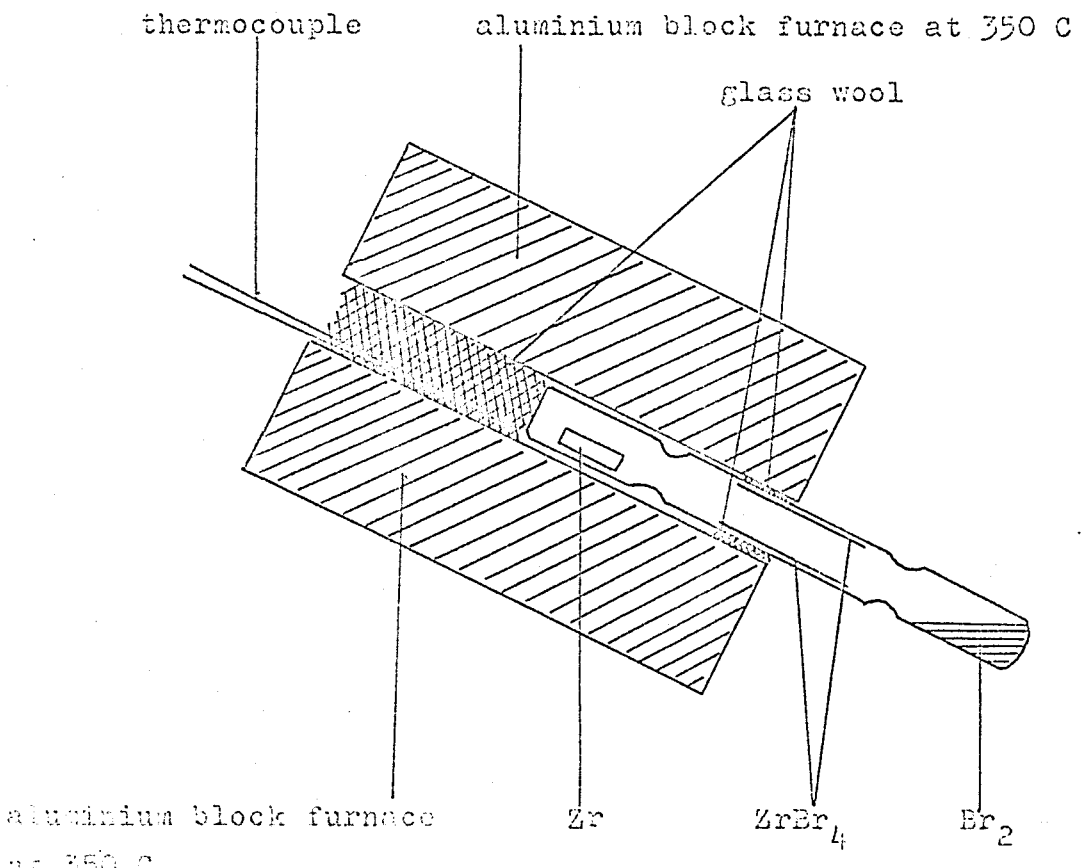


Figure 12. Apparatus for the preparation for the $ZrBr_4$

prepared and furnished by Mrs. Phillips of this laboratory and used without further purification.

Niobium tetrachloride was prepared in two steps using a procedure described by Fair (60) as follows:

Niobium metal was first chlorinated to give niobium pentachloride by passing dried chlorine gas from a cylinder over metal heated to 250°C. The yellow pentachloride was then reduced to niobium tetrachloride by metallic niobium. These two steps were carried out in a simple single system, thus avoiding transference from one system to another at any stage. The reduction of the pentachloride by the metal was achieved by placing the aluminum block furnaces end to end, one set for higher temperature and the other for the lower one. The products were transferred to storage ampoules in a glove box and stored under nitrogen. These procedures are modifications of those described by McCarley and Torp (61), McCarley and Boatman (62), and Schafer and Kahlenberg (63).

All the complexes were prepared using a procedure essentially the same as that described by Kay and Rosotzand (59) as follows:

About one liter of benzene was refluxed with a few ml. of concentrated H_2SO_4 and formalin, extracted with water, dried over $CaCl_2$, and distilled. The distillate was refluxed with benzophenone ketyl, redistilled, and finally stored over sodium.

The purified benzene was distilled at reduced pressure from sodium metal into a Schlenk tube immersed in liquid nitrogen. The distillate (about 50 ml.) was allowed to attain room temperature, after which dry nitrogen was admitted. The content of an ampoule of metal halide (1-5 g.) was introduced into the tube and to this suspension was added about 1.05 times the stoichiometric amount of ligand. Vigorous stirring for 1-3 hrs. produced a heavy white or yellow precipitate but stirring was continued for a further 24 hrs. or longer to ensure complete reaction. The solvent volume was then reduced to one-third by pumping before the solid material was separated in a filtering apparatus similar to that described by Fritz and co-workers (64). The product was washed with benzene before drying under vacuum at room temperature. As the complexes were air-sensitive, they were stored in ampoules under nitrogen.

6. Analytical Analysis

Analyses for chlorine and bromine in complexes were carried out by Volhard titration or potentiometrically following the preparation of the sample by Parr bomb combustion (65).

In the Parr bomb combustion, about 0.200 gram sample was put into a 22 ml. bomb and immediately mixed with 0.3 gram powdered lactose and one dipper (15 grams) of sodium peroxide.

This was mixed thoroughly and ignited with a small hot flame. After igniting the charge, the bomb was cooled rapidly to room temperature and opened. The melt was dissolved with 100 ml. of distilled water and neutralized by adding 50 ml. of dilute(1:1) nitric acid slowly with constant stirring. Halides were then determined volumetrically.

To determine the chlorine and the bromine contents of the tetrahalides, the samples were first dissolved in 10% sodium hydroxide solution, oxidized with hydrogen peroxide and then neutralized with nitric acid and distilled ammonia. Halide was titrated volumetrically.

Analyses for sulfur in complexes were carried out gravimetrically following the preparation of the sample by Parr bomb combustion.

The charge and the ignition were the same as above-mentioned. After igniting the charge and the bomb was cooled and opened, however, the melt was made just faintly acidic with concentrated hydrochloric acid. The solution was filtered through a qualitative filter paper into a 600 ml. beaker. The ash residue was washed with distilled water. The combined filtrate was diluted to approximately 400 ml., added with about 10 ml. saturated bromine water and boiled to expel the liberated bromine. It was made just

neutral to methyl orange using sodium hydroxide, then added with exactly 1 ml. of 1 N hydrochloric acid. Sulphate was then determined gravimetrically.

The analyses of metal in both the tetrahalides and the complexes were done gravimetrically. A sample in a tared crucible was moistened with water and ignited in a muffle furnace to constant weight at 1000°C.

SECTION II EXPERIMENTAL RESULTS

1. PREPARATION OF COMPLEXES

Table 1 lists the conditions of preparation for the various complexes. The general procedure described in the last section was used in each case.

Table 1. Preparation of complexes

Reactants	Wt. of MX_4 (gm.)	Period of stirring	Color of product
$ZrCl_4$ & THF	0.73	40 hours	white
$ZrCl_4$ & THT	1.61	48 hours	yellow
$ZrCl_4$ & Ph_3PO	1.43	72 hours	white
$ZrCl_4$ & Ph_3AsO	1.86	72 hours	white
$HfCl_4$ & THF	3.53	36 hours	white
$HfCl_4$ & THT	1.93	36 hours	yellow
$ZrBr_4$ & THF	3.70	50 hours	white
$ZrBr_4$ & THT	4.69	48 hours	yellow
$NbCl_4$ & Ph_3PO	0.45	108 hours	yellow
$NbCl_4$ & Ph_3AsO	0.42	96 hours	white

THF, tetrahydrofuran; THT, tetrahydrothiophene; Ph, phenyl.

2. ANALYSES OF METAL HALIDES AND COMPLEXES

The complexes indicated above, together with the metal halides used as one of the reactants, were analyzed following

the procedure described in the last section. The results are shown in Table 2.

Table 2. Analysis figures for halides and complexes

Compound	% found			% calculated		
	Zr(Hf,Nb)	X	S	Zr(Hf,Nb)	X	S
$ZrCl_4$	38.83	60.95		39.14	60.86	
$ZrCl_4$-2THF	25.90	36.32		24.18	37.59	
$ZrCl_4$-2THT	23.40	35.58	14.48	22.28	34.65	15.67
$ZrCl_4$-2Ph_3PO	13.65	17.65		11.56	17.96	
$ZrCl_4$-3Ph_3AsO	6.86	12.02		7.60	11.82	
$HfCl_4$	54.48	44.88		55.73	44.27	
$HfCl_4$-2THF	39.47	29.61		38.42	30.53	
$HfCl_4$-2THT	35.65	28.45	12.02	35.94	28.56	12.91
$ZrBr_4$	22.23	77.04		22.20	77.80	
$ZrBr_4$-2THF	17.49	57.96		16.43	57.59	
$ZrBr_4$-2THT	14.98	54.32	9.71	15.54	54.43	10.92
$NbCl_4$	40.24	60.40		39.59	60.41	
$NbCl_4$-2Ph_3PO	9.00	15.49		8.69	13.26	
NbCl -2Ph AsO	10.81	16.80		10.59	16.13	

THF, tetrahydrofuran; THT, tetrahydrothiophene; Ph, phenyl.

3. THERMAL MEASUREMENTS AND CALCULATIONS

The enthalpies of reaction, $-\Delta H_r$, of zirconium (IV) chloride, zirconium (IV) bromide, and hafnium (IV) chloride with tetrahydrofuran, THF, and tetrahydrothiophene, THT, the enthalpies of solution, $-\Delta H_s$, of the complexes containing THF

Table 3. Calorimetrical measurement data.

Compound	W_{sample} (g)	Ligand or/and solvent	Calibration (cal/u)	$-\Delta H_s$ (kcal/mole)	$-\Delta H_s$
$ZrCl_4$	0.45081	THF	0.1881	39.8	
	0.31405		0.1793	40.6	
$ZrCl_4$-2THF	0.15528	THF	0.1683		6.7
	0.20461		0.1678		6.5
$ZrCl_4$	0.45886	THT	0.1748	42.9	
	0.29833		0.1748	41.1	
$ZrCl_4$-2THT	0.15238	THT	0.1679		12.2
	0.16020		0.1714		12.2
$HfCl_4$	0.47994	THF	0.1596	41.0	
	0.42326		0.1300	41.0	
$HfCl_4$-2THF	0.21343	THF	0.1780		6.2
	0.14863		0.1667		6.5
$HfCl_4$	0.46013	THT	0.1664	40.3	
	0.22388		0.1674	40.1	
$HfCl_4$-2THT	0.16076	THT	0.1896		6.9
	0.06776		0.1589		7.2
$ZrBr_4$	0.74752	THF	0.1720	51.8	
	0.19950		0.1680	52.4	
$ZrBr_4$-2THF	0.44611	THF	0.1702		16.4
	0.11409		0.1764		15.5
$ZrBr_4$	2.23855	THT	0.1814	29.4	
	0.28337		0.1659	30.1	
$ZrBr_4$-2THT	0.25768	THT	0.1782		21.1
	0.22353		0.1724		21.1

THF, tetrahydrofuran; THT, tetrahydrothiophene.

and THT listed in Tables 1 and 2 in THF and THT respectively were measured calorimetrically. The enthalpy values obtained are listed

in Table 3. From these results, the enthalpies of complex formation were calculated and are shown in Table 4.

Table 4. Enthalpies of complex formation in kcal/mole.

Donor	Acceptor		
	$ZrCl_4$	$HfCl_4$	$ZrBr_4$
THF, tetrahydrofuran	33.6	34.6	36.2
THT, tetrahydrothiophene	29.8	33.1	8.7

Table 5. Nuclear magnetic resonance correlations.

Compound	Solv.	Proton shift relative to TMS(τ)		Internal shift	$-\Delta H_r$	$-\Delta H_f$	$-\Delta H_g + V_c - F$	$-\Delta H_g + V_c - F - S$
		α-CH_2	β-CH_2					
THF	C_6H_6	6.72	8.78	2.06				
$ZrCl_4$-2THF	C_6H_6	6.24	9.14	2.90	40.2	33.6	76.3	47.8
$HfCl_4$-2THF	C_6H_6	5.76	8.83	3.07	41.0	34.6	73.4	48.8
$ZrBr_4$-2THF	C_6H_6	5.96	9.31	3.35	52.1	36.2		50.4
THT	C_6H_6	7.47	8.45	0.98				
$ZrCl_4$-2THT	C_6H_6	7.44	9.01	1.57	42.0	29.8	77.1	48.6
$HfCl_4$-2THT	C_6H_6	7.22	8.77	1.55	40.2	33.1	76.9	51.9
$ZrBr_4$-2THT	C_6H_6	7.84	9.27	1.42	29.8	8.7		27.5

THF, tetrahydrofuran; THT, tetrahydrothiophene.

4. N. M. R. SPECTRA

The same series of complexes containing THF and THT were examined for their N. M. R. spectra. They all showed absorptions

for α- and β- protons of the heterocyclic ligands. The internal shifts were calculated therefrom and correlated with thermal data as it was recently done by R. L. Richards and A. Thompson (19,20) and others before them. The results are listed in Table 5.

5. INFRARED SPECTRA

Those complexes whose solubilities are too low to permit thermal measurement were examined by means of I. R. spectrometry. The procedure is described in the last section and the results for Nujol mulls are given in Table 6.

Table 6. P-O or As-O stretching in Ph_3PO or Ph_3AsO and their complexes.

Compound	P-O or As-O stretching (cm^{-1})	Shift	Compound	P-O or As-O stretching (cm^{-1})	Shift
Ph_3PO	1175		Ph_3AsO	870	
$ZrCl_4$-$2Ph_3PO$	1117	-58	$ZrCl_4$-$3Ph_3AsO$	860	-10
$HfCl_4$-$2Ph_3PO$	1120	-55	$HfCl_4$-$2Ph_3AsO$	873	+ 3
$NbCl_4$-$2Ph_3PO$	1113	-62	$NbCl_4$-$2Ph_3AsO$	852	-18

Ph, phenyl.

CHAPTER III DISCUSSION

1. THERMOCHEMISTRY OF THE COMPLEXES MX_4-2L WHERE M IS Zr OR Hf; X, Cl OR Br; AND L, THF OR THT

All the complexes containing THF or THT listed in Table 1 are soluble in excess of the corresponding organic ligand. Hence the energies involved in these comparable electron donor-acceptor reactions or the enthalpies of formation of these addition compounds can be measured by using the scheme described in Chapter I.

Let us define the following heat quantities:

$A(\text{acceptor},c) + (x+2)L(\text{ligand},l) = AL_2(\text{dissolved in } xL), -\Delta H_r$

$AL_2(c) + xL(l) = AL_2(\text{dissolved in } xL), -\Delta H_s$

and $A(c) + 2L(l) = AL_2(c), \quad -\Delta H_f = -\Delta H_r + \Delta H_s$

The quantity $-\Delta H_f$ is the enthalpy of formation of the complex in the condensed phase; the cycle below was used to calculate the enthalpy of formation from gaseous reactants.

CYCLE

$$\begin{array}{ccccc} MX_4(g) & + 2L\ (g) & \xrightarrow{\Delta H_g} & MX_4\text{-}2L\ (g) & \\ \uparrow S & \uparrow V_l & & \uparrow V_c & \\ & & & MX_4\text{-}2L\ (l) & \\ & & & \uparrow F & \\ MX_4(c) & + 2L\ (l) & \xrightarrow{\Delta H_f} & MX_4\text{-}2L\ (c) & \end{array}$$

Thus $-\Delta H_G = -V_c - F + S + V_1 - \Delta H_f$

or $-\Delta H_G + (V_c + F) = S + V_1 - \Delta H_f$

or $-\Delta H_G + (V_c + F - S) = V_1 - \Delta H_f$

where $-\Delta H_G$ is the enthalpy of formation of complex, gas phase,

V_c is the heat of vaporisation of complex,

V_1 is the heat of vaporisation of ligand,

S is the sublimation energy of halide,

F is the heat of fusion of complex.

From the results listed in Table 4 and literature data available, the revised enthalpies of formation listed in Table 7 were obtained.

Table 7. Computed thermochemical data (kcal/mole)

Complex	$-\Delta H_f$	S	V_1	$-\Delta H_G + V_c + F$	$-\Delta H_G + V_c + F - S$
$ZrCl_4$-2THF	33.6	28.5[a]	2(7.1)[b]	76.9	47.8
$ZrCl_4$-2THT	29.3	28.5[a]	2(9.4)[c]	77.1	48.6
$HfCl_4$-2THF	34.6	24.6[a]	2(7.1)[b]	73.4	48.8
$HfCl_4$-2THT	33.1	24.6[a]	2(9.4)[c]	76.5	51.9
$ZrBr_4$-2THF	36.2		2(7.1)[b]		30.4
$ZrBr_4$-2THT	8.7		2(9.4)[c]		27.5

a. W. E. Dasent, Nonexistent Compounds, 125, Marcel Dekker Inc., N. Y.

b. Estimated from Trouton's Rule.

c. J. V. Davies and S. Sumner, Acta Chem. Scand., 1962, 16, 1870.

No attempt was made to determine V_c and P for these complexes. It is assumed that these values are equal for such a closely related series of compounds (19). The lack of a value of S for $ZrBr_4$ would not affect the relative thermal stabilities of $ZrBr_4$-2THF and $ZrBr_4$-2THT which provide the only comparison we wish to make on the basis of the corrected enthalpy values. However, the values of ($-\Delta H_g + V_c + P - S$) were calculated and listed together for comparative purpose.

1a. THERMAL STABILITIES OF THE COMPLEXES OF $ZrCl_4$ & $HfCl_4$

Comparing the enthalpies of complex formation ($-\Delta H_g + V_c + P$)'s from the gas phase for $ZrCl_4$ and $HfCl_4$ complexes, it is seen that both THF complexes are formed more exothermically than their THT counterparts. This is comparable with the relative thermal stabilities of corresponding or similar gallium complexes (19,20), namely,

$GaCl_3$-C_4H_8O	<	$GaCl_3$-C_4H_8S
47.5 kcal/mole		49.5 kcal/mole
$GaCl_3$-Et_2O	<	$GaCl_3$-Et_2S
39.6-40.8 kcal/mole		45.1 kcal/mole

These gallium values had been compared with their aluminium counterparts and explained in terms of hardness of acceptor acids and the donor bases (7,20) following Pearson's terminology (11). Gallium was thus said to be a softer acid than aluminium chloride

due to the presence of the filled 3d- orbitals in the central gallium(III) atom. The filled d shells on the metal may form d_π-d_π bonds with the vacant 3d orbitals of sulphur. This situation can occur neither with aluminium(III) where there are no filled d shells nor with oxygen donors where the d orbitals are not of suitable energy to allow for the π-bonding. Hence, aluminium chloride forms thermally more stable complexes with oxygen-containing ligands than with sulphur-containing ones, i.e.

$AlCl_3$-C_4H_8O	>	$AlCl_3$-C_4H_8S
57.1 kcal/mole		46.7 kcal/mole
$AlCl_3$-Et_2O	>	$AlCl_3$-Et_2S
55.0 kcal/mole		44.0 kcal/mole

For the complexes of zirconium tetrachloride and hafnium tetrachloride in this work, there is no non-bonding d electron available for π-bonding to the ligand. The fact that their THT complexes are thermally more stable than the corresponding complexes of THF should be due largelt to the difference in the polarisation of the ligands. Sulphur is much more polarisable than oxygen. In addition, the dipole moment of THT, 1.90 D in benzene at 25°C, is greater than that of THF, 1.75 D under the same conditions(66). In a polarising field such as that exerted by the poorly shielded zirconium or hafnium nucleus, the thio-ligand would be more polarised and consequently the covalent σ ligand-metal bond strength would be enhanced. This explains also

why ether was found to be readily displaced from the complexes $NbCl_5$-Et_2O, $TaCl_5$-Et_2O and $NbCl_5$-n-Pr_2O by the corresponding dialkyl sulphide (67), why sulphide ligands appeared to be the stronger donors for complexes of titanium(IV) tetrahalides (68), and why TiX_4-$2C_4H_8OS$ where X is Cl or Br was found to have coordinate bonding through sulphur (69).

In any case, the presence of inner d- or/and f- orbitals increases the softness of the metal as an acid, due to either π-bonding or polarisation effects, and this makes it a better acceptor for sulphur than for oxygen. When the thio- and oxo-adducts of $SnCl_4$ and $SbCl_5$ are considered, the thio-complexes are more stable than the oxo- complexes. It is likely that both π-bonding and polarisation effects occur together and the metal-ligand bond is strengthened by a synergic type of effect. Hence, although the great contrast between the gallium and aluminium series is not observed with zirconium and hafnium, the enthalpy increase from the THF complex to the THT analogue is seen to be larger for the hafnium series than for the zirconium counterparts. The presence of filled 4f orbitals in hafnium(IV) should make it, as an acid, softer than zirconium(IV) which has no such filled 4f orbitals and which is therefore better shielded than hafnium(IV). However, zirconium(IV), being a little larger in size, 0.79 Å, than hafnium, 0.78 Å, is , according to Allred and Rochow, a

little less electronegative than hafnium (χ- values are 1.32 and 1.23 respectively). This may be the reason why the enthalpies of the zirconium complexes in this work are a little larger than hafnium analogues in spite of the size difference.

1b. THERMAL STABILITY AND IONIC FUNCTION

It has long been pointed out (70,71,72) that enthalpies of hydration and similar stability values are linearly related to the ionic function which is the ratio of the valence, Z, and the ionic radius, r, in Å of the central ion for the complex. This correlation is considered to indicate electrostatic bonding and the positive deviations are attributed to covalent bonding.

When we plot the above mentioned gas phase enthalpy data against ionic function as shown in Figure 13, we note that the oxygen- and the sulphur- containing complexes of aluminium(III) chloride and gallium(III) chloride can be divided into two groups. The oxygen- containing compounds are in the group with a pair of approximately parallel lines having positive slopes. The sulphur-containing compounds are in the group with a similar pair of lines having much smaller positive or even negative slopes. This may be interpreted as an indication that the sulphur-containing complexes of gallium chloride have a more covalent nature than the oxygen

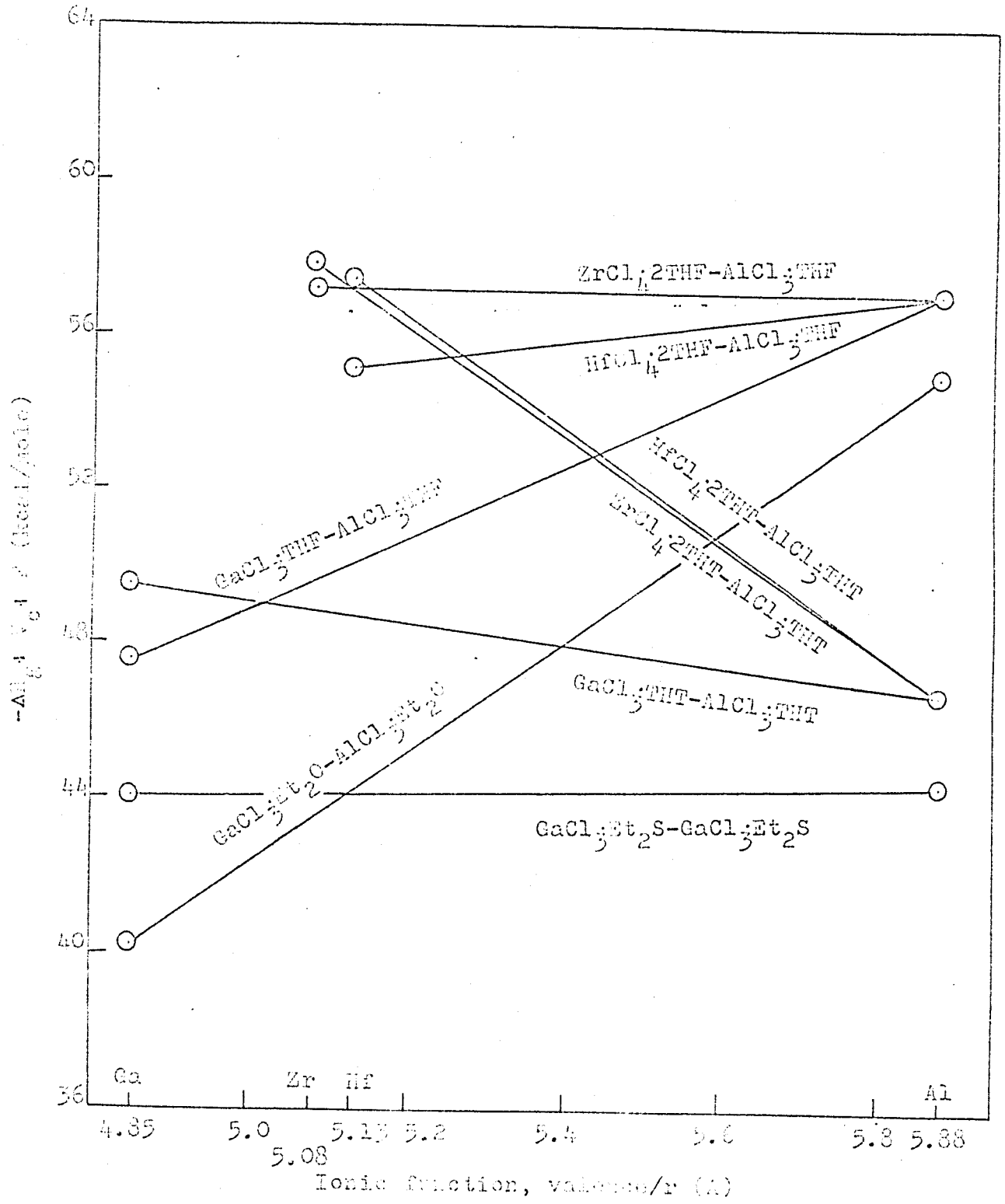


Figure 13. Ionic function and crystallography correlation.

analogues. According to the covalent-ionic bonding theory of hard and soft acids and bases, this would mean that either thioethers or gallium(III) chloride is, or both of them are, softer in the Pearson sense, than the corresponding ethers or aluminium(III) chlorides.

To compare the similar gas phase enthalpy data of zirconium(IV) chloride and hafnium(IV) chloride complexes with aluminium(III) chloride and gallium(III) chloride complexes in the ionic function-enthalpy relationship, one should compare the enthalpy data of complex formation with the same number of donors and acceptors. It has been established that the enthalpy of addition of the second molecule of the ligand is considerably less than that of the first (19,73,74). From the gas phase enthalpy data of $AlCl_3$-C_4H_8O, $AlCl_3$-$2C_4H_8O$, $GaCl_3$-C_4H_8O, and $GaCl_3$-$2C_4H_8O$ (19), it is found that the enthalpy of 1:1 addition complexes in the gas phase is about three quarters of that of 1:2 addition complexes. Assuming that this may be applied to estimate the gas phase enthalpies of 1:1 addition in complex formation for our complexes, the gas phase values for the addition of a single ligand are estimated and listed with those for the aluminium(III) chloride complexes and the gallium(III) chloride complexes in Table 8, and are plotted together in Figure 13. Also listed in the table are the slopes of the lines connecting the points plotted for the aluminium complexes and the others with the same

ligand. This was done on the assumption that aluminium(III) chloride, gallium(III) chloride and diethyl ether form the most ionic bonds among the complexes listed. Any value for an ether complex which might lie above the straight line passing through the points for $AlCl_3$-Et_2O and $GaCl_3$-Et_2O would indicate a coordinate bond more covalent than weighed average of the coordinate bonds of $AlCl_3$-Et_2O and $GaCl_3$-Et_2O. The relative differences of the slopes of the straight lines then should be a measure of the covalent deviation from the average.

Table 8. Ionic function and enthalpy, $-\Delta H_S+V_c+F$, in kcal/M.

Complex	Metal atom, M	Ga	Zr	Hf	Al
	Ionic radius in A	0.62	0.79	0.78	0.51
	Ionic function	4.85	5.08	5.13	5.88
MCl_3-C_4H_8O or	a. Enthalpy, adding 1 ligand	47.5	57.2	55.1	57.1
MCl_4-$2C_4H_8O$	b. Slope, M-Al line	9.32	-0.25	2.67	
MCl_3-C_4H_8S or	a. Enthalpy, adding 1 ligand	49.5	57.8	57.4	46.7
MCl_4-$2C_4H_8S$	b. Slope, M-Al line	-2.72	-13.88	-14.27	
MCl_3-Et_2O	a. Enthalpy, adding 1 ligand	40.2			55.0
	b. Slope, M-Al line	14.37			
MCl_3-Et_2S	a. Enthalpy, adding 1 ligand	44.0			44.3
	b. Slope, M-Al line	0.29			

The function Z^2/r is sometimes used in stead of Z/r in

correlating stability data. The use of the former function makes no substantial difference in the present instance, however.

The conclusions drawn above from the plots of the enthapy data against the ionic functions must not be taken too seriously because, although the method provides satisfactory correlations for complexes formed in aqueous solutions, it is easily upset by unforseen factors such as steric hindrance. Moreover, it has not, to our knowledge, been applied to ions with charges greater than +3.

1c. THERMAL STABILITY AND ELECTRIC AND STERIC EFFECTS

A comparison between the enthalpies of complex formation of zirconium(IV) bromide complexes and zirconium(IV) chloride complexes can be made with only about the same degree of significance in the gas phase as in the condensed phase due to the lack of further information. The data on hand, however, show that for complexes of THF the following relation holds:

$ZrBr_4$-2THF	>	$ZrCl_4$-2THF
50.4 kcal/mole		47.8 kcal/mole.

This is the same trend as those for most boron and especially aluminium complexes. The same reasoning therefore

can probably be applied as follows: (a). There is a decrease in the electrostatic repulsion between Zr-X bond electrons and the lone-pair electrons on the ligand due to the increase of radii of halogen atoms from chloride to bromide acceptors. (b). There is a decrease of reorganization energy from $ZrCl_4$ to $ZrBr_4$. Most of the halides investigated show this tendency of diminishing reorganization energy (7,11,32,39) though no investigation has been actually done for zirconium halides so far.

The enthalpy value for the THF complex of zirconium(IV) bromide is particularly low compared to that of the complex of zirconium(IV) chloride and THF. The steric effect should play an important role. It has been found (5,12) that using $CH_3COOC_2H_5$ as the donor the order of acceptor strength is $ZrCl_4$ > $ZrCl_3(OC_2H_5)$ > $ZrCl_2(OC_2H_5)_2$ > $ZrCl(OC_2H_5)_3$. It therefore should not be a surprise to see that using C_4H_8S as the donor the acceptor strength of $ZrBr_4$ should be smaller than that of $ZrCl_4$.

2. CORRELATION BETWEEN NUCLEAR MAGNETIC RESONANCE DATA AND THERMOCHEMICAL DATA.

Ligands like ether, thioether, ethyl derivatives, tetrahydrofuran and tetrahydrothiophene which contain both methyl and methylene groups or both α- and β- CH_2 groups in complex formation

show a change in the separation of the methyl and the methylene resonances or the separation of the resonances due to the α- and the β-CH_2 groups relative to the separation in the free ligands. These changes of seperation are often referred to as internal shifts or internal chemical shifts (19,20,75,76). The formation of molecular addition compounds by electron donor-acceptor interactions implies that the electron attracting power of the donor and acceptor atoms in an adduct will be somewhat different from that in the free Lewis base and acid. The electron attracting power will depend in part upon the strength of the coordinate bond, the empirical relationship between the internal shifts and the electronegativity of substituents. However, due to the many factors known to influence proton chemical shifts, a direct correlation between chemical shifts and electron attracting power of the acceptor as indicated by adduct stabilities has not been established. Nevertheless, it is found (20) that when all relevant factors have been considered, n.m.r. data give a guide to the condensed phase order of stability in closely related series of complexes. The data listed in Table 5 show a good correlation between internal shifts and enthalpies of reaction in solution, $-\Delta H_r$. The correlation between internal shifts and enthalpies of formation, $-\Delta H_f$, is also satisfactory, though somewhat poorer. Since the n.m.r. data were obtained in solution and the enthalpies of reaction measured in excess ligand, it may mean that good corre-

lation may be expected only under similar conditions.

3. EFFECT OF COMPLEX FORMATION ON P-O AND As-O STRETCHING FREQUENCIES FOR THE COMPLEXES MCl_4-2L WHERE M IS Zr, Hf, OR Nb; L IS TPPO, TRIPHENYL PHOSPHINE OXIDE OR TPAsO, TRIPHENYL ARSINE OXIDE

These complexes also are 1:2 addition compounds except $ZrCl_4$-3TPAsO. They are, however, insoluble in the organic solvents tested, eg. C_6H_6, CH_3CN, hence no solution calorimetric measurement could be made. In stead, their infrared spectra were obtained and a discussion of these follow:

Sheldon and Tyree (48) found P-O stretching bands at 1125 cm^{-1} for $(Ph_3PO)_2SnCl_4$, $(Ph_3PO)_2SnBr_4$, and $(Ph_3PO)_2FeBr_2$, at 1130 cm^{-1} for $(Ph_3PO)_2TiCl_4$ and at 1180 cm^{-1} for Ph_3PO; all in Nujol. Cotton, Barnes, and Bannister (47) found the P-O stretch for Ph_3PO to be at 1195 cm^{-1} and for various Ph_3PO complexes of halides and perchlorates of the first transition series elements to lie between 1125 cm^{-1} and 1170 cm^{-1}. Halman and Pinchas (77) reported also the P-O stretching frequency for Ph_3PO at 1190 cm^{-1}. In spite of the differences in the reported TPPO frequencies, they all showed a lowering of the corresponding frequencies on complex formation. Cotton, Barnes and Bannister (47) proposed that the P-O bond has

at least partial muliple bond character and there are three effects of complex formation upon the P-O bond order and hence on the bond-stretching force constant.

a. When the oxygen atom is placed close to the positively charged metal ion, to which it may, to some extent, also form an actual covalent bond, an enhancement of the $\overset{+}{P}\rightarrow\overset{-}{O}$ σ-bond will be expected. The effect tends to raise k_{PO}.

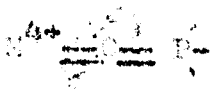
b. At the same time the $p\pi\rightarrow d\pi$ back bonding $\overset{-}{O}\rightarrow\overset{+}{P}$ will tend to be decreased, thus lowering k_{PO}.

c. Conceivably, for transition metal ions where there are low-energy filled d orbitals, there may be a drift of metal $d\pi$-electrons toward oxygen $p\pi$-orbitals, displacing the oxygen $p\pi$-electrons toward $d\pi$-orbitals of phosphorus. This would probably tend to increase k_{PO}.

While the second effect must be dominant, the consolidated result is the lowering of k_{PO} and thus the P-O stretching. This proposal has also been applied implicitly by Goodgame and Cotton (51) for the similar lowering of As-O stretching in the complex formation of $Cu(Ph_3AsO)_2Cl_2$ and $Cu(Ph_3AsO)_2Br_2$.

Comparison with our data as shown in Table 6 shows that while the uniform lowering occurs in the TPPO series, different results arise in the TPAsO analogues. Further, in the TPPO complexes, all three have approximately equal shifts. However, the shift for $NbCl_4$-2TPPO is larger than that for $ZrCl_4$-2TPPO and the

smallest shift is observed for the $HfCl_4$-2TPO. Hafnium(IV), due to the corresponding increase of effective nuclear charge with the inclusion of an extra proton in the nucleus, should give less $p\pi$--$d\pi$ bonding $O \rightarrow P$ and thus lower the P-O stretching to a greater extent by the mechanism



The greater lowering of the P-O stretching frequency in the zirconium complex relative to the hafnium complex parallels the relative thermal stabilities as found among the THF and the THT complexes. It is possible that in TPPO complexes also, the coordinate bonding between zirconium and the ligand is stronger than that between hafnium and the ligand. The smaller lowering or positive shift of As-O stretching compared with analogous shifts in P-O stretching can be accounted for by the greater π-acceptor character of As relative to P (73).

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