QUANTITATIVE ASPECTS OF LEWIS ACIDITY

[Interaction of Germanium tetrachloride with nitrogen bases in aprotic media]

A Thesis presented

for

The Degree

of

DOCTOR OF PHILOSOPHY

in

The Faculty of Science

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UNIVERSITY OF THE PUNJAB

by

FAKHRA IDREES QURESHI

Institute of Chemistry
University of the Punjab
Lahore-1 (Pakistan)

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"ALL PRAISES FOR GOD, THE BENIFICENT, THE MERCIFUL, WHO GUIDES US IN DARKNESS AND HELPS US IN DIFFICULTIES"
DEDICATED

TO MY HONOURABLE

MOTHER
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FAKHIRA IDREES QURESHI
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INTRODUCTION
Acids and bases are regarded as mutual opposites which in general lose their defining properties when brought in contact with each other. The word acid belongs to Latin word 'acidus' that means sour. Acids have been characterized by their tastes, by their effects upon indicators and their catalytic effects upon certain reactions.

A substance opposite in properties to an acid is a base. The main characteristic of a base is its ability to destroy the effects of an acid. In 1680, R. Boyle defined acids as substances dissolving many other substances.

The concepts about acids, in the eighteenth century, were centered around their sour taste, reactions with lime-stone, turning of syrup of violet to red, and production of neutral materials with alkalies as the characteristic properties of acids. In 1774, Rouelle extended the acid-base concept by defining a base as any substance which reacts with an acid to form a salt. In 1787, Lavoisier stated that acids are binary compounds containing oxygen as an essential constituent. He proved experimentally that a number of elements, such as carbon, nitrogen and sulphur burned in oxygen to give compounds which acted as acids in aqueous solutions. In 1787, Berthole on the other hand, offered experimental evidence that certain acids contained no oxygen but showed the properties of an acid.
The acidifying character of oxygen was accepted until Davy. In 1810, Davy produced convincing proof\textsuperscript{1,3} against oxygen-theory that hydrochloric acid contained no oxygen. His conclusion was that acidic character was due to hydrogen. Later on, in 1814, Davy further stated\textsuperscript{1} that acidity did not depend upon any one element but rather upon a peculiar combination of various elements. Thus Gay-Lussac, in 1814, explained\textsuperscript{4} that an acid was a species neutralizing alkalinity and acids and bases could be defined only in terms of each other. Soon Davy's concept of an acid was discarded. Thus the early hydrogen theory of acids may be stated as 'All acids contain hydrogen but all hydrogen compounds are not acids'.

In 1838, Leibig supported\textsuperscript{5} the hydrogen theory of acidity and considered acids as compounds containing hydrogen which could be replaced by metals. The character of such hydrogen was acceptable as a criterion for acidity for many subsequent years. At the same time, in 1834, Faraday said\textsuperscript{5} that electrolytic conductance is due to charged particles (ions) and he characterized acids, bases and salts as electrolytes.

MODERN CONCEPTS OF ACIDS AND BASES

The modern concepts of acids and bases are derived from the theory of electrolytic dissociation, by Svante Arrhenius in 1884, and was further developed\textsuperscript{5} by Ostwald.
Modern concepts have developed directly from Arrhenius theory to include more types of materials as acids and bases.

1. Arrhenius Concept of Acids and Bases
   (Water Ion System)

   In 1887, Arrhenius working on the conductance of acid solutions advanced the theory of ionization. According to Arrhenius "an acid is defined as a hydrogen compound which in water solution gives hydrogen ions and base is a compound having hydroxylic groups; which in aqueous solution yields hydroxide ions". The process of neutralization results from the combination of hydrogen ions with hydroxide ions to form water molecules. The Arrhenius was criticized as follows:

   (a) The theory defines acids and bases in terms of aqueous solutions and not in terms of the substances themselves. For example hydrochloric acid should be considered as an acid only when dissolved in water, while in solvents like benzene or in the gaseous state it should not be considered as an acid. While process of neutralization can take place in many other solvents and even in the absence of solvents as well.

   (b) Basic and amphoteric characters are limited to hydroxy compounds, although many ions possess basic properties comparable to those of hydroxyl ions and amphoteri:
is characterized among many oxides, sulphides, halides etc., as well as among hydroxides.

(c) According to the theory, ammonia must react with water to produce ammonium hydroxide, which, in turn, ionizes to give hydroxide ions.

\[ \text{NH}_3 + \text{HOH} \rightleftharpoons \text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- \]

There is no proof for the existence of ammonium hydroxide, and the assumption of such an ionization could be misleading.

(d) Arrhenius theory does not satisfy the idea of acidity of certain salts such as aluminium chloride (AlCl\(_3\)).

(e) The objection that hydrogen ions can not exist\(^8\) as such in aqueous solutions because of their high hydrational energy (250 K Cal/Mole) is not so serious.

In spite of many objections, to the Arrhenius concept of acids and bases the theory is enough for elementary approach.

2. Franklin Concept  
(Theory of Solvent System)

In 1905, E.C. Franklin\(^9\) extended the Arrhenius view of acids and bases in aqueous solution to liquid ammonia. He argued that if water ionizes into hydronium ion and hydroxide ion, liquid ammonia should ionize in a similar way into ammonium and amide ions.
\[ 2H_2O \rightleftharpoons H_3O^+ + OH^- \]
\[ 2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \]

Generally, if hydronium ion concentration increases in aqueous solution, the hydroxide ion concentration decreases. If the hydroxide ion concentration increases, it shifts the equilibrium in the opposite direction. In the same way, on addition of ammonium ions in the form of ammonium salt to liquid ammonia shifts the ammonia equilibrium to decrease the amide-ion concentration. The addition of amide compounds produces an opposite effect upon the equilibrium. Therefore, just as the hydronium ion is an acid and hydroxide ion is a base in aqueous solution, in the same way ammonium ion would act as an acid and amide ion as a base in liquid ammonia solution. Further more the ammonium and amide ions may be titrated with phenolphthalein as an indicator, just like acids and bases in aqueous solutions. The neutralization reaction can be written as:

\[ \text{NH}_4^+ + \text{NH}_2^- \rightleftharpoons 2\text{NH}_3 \]

\[ \text{NH}_4\text{Cl} + \text{NaNH}_2 \rightleftharpoons \text{NaCl} + 2\text{NH}_3 \]

**Acid**  **Base**  **Salt**  **Solvent**

Certain metals cause evolution of hydrogen when reacting with either hydronium ions in water or ammonium
ions in ammonia. This indicates acidic properties of both the hydronium ions and ammonium ions which carry protons. These ions are either hydrated protons or ammoniated proton and for that reason both ions behave as acids.

In view of above discussion about the theory of solvent system, an acid may be defined as a solute which imparts a cationic characteristic to the solvent, and a base as a solute which gives rise to an anionic characteristic in the solvent. The process of neutralization, in terms of the solvent system, is due to the combination of the solvent cation with solvent anion to produce solvent. This theory has the advantage of explaining the acid-base interaction of substances in non-aqueous media too. The typical example of this type is the behaviour of liquid sulphur dioxide as solvent. The slightly ionizable pure liquid sulphur dioxide probably produces thionyl and sulphite ions according to the following equation:

\[ 2\text{SO}_2 \rightleftharpoons \text{SO}^{++} + \text{SO}_3^- \]

The solute which would increase the cation concentration of the solvent is considered to behave as an acid. Thus sulphur trioxide is an acid in sulphur dioxide as solvent, as the cation concentration is increased in the presence of sulphur dioxide as shown by the following equation:

\[ \text{SO}_2 + \text{SO}_3 \rightleftharpoons \text{SO}^{++} + \text{SO}_4^{--} \]
The effective bases in liquid sulphur dioxide are sulphites of organic amines, e.g., tetramethyl ammonium sulphite. When we increase the anion activity in liquid sulphur dioxide, with tetramethyl ammonium sulphite as solute, the reaction may be shown as follows:

\[ \text{SO}_2 + [(\text{CH}_3)_4\text{N}]_2\text{SO}_3 \rightleftharpoons \text{SO}_3^- + [(\text{CH}_3)_4\text{N}]_2\text{SO}_2^{2+} \]

The neutralization phenomenon would involve union of the acidic solute and the basic solute producing a salt solute which may be regarded as a part of the neutralization. The reaction in liquid sulphur dioxide can be shown as given below:

\[ \text{SO}_3 + [(\text{CH}_3)_4\text{N}]_2\text{SO}_3 \rightleftharpoons [(\text{CH}_3)_4\text{N}]_2\text{SO}_2^{2+}\text{SO}_4^- + \text{SO}_2 \]

Acid   Base   Salt   Solvent

3. **Bronsted - Lowry Concept**
(Proton Donor-Acceptor System)

In 1923, Bronsted and Lowry defined an acid as a substance having a tendency to lose one or more protons and a base is a substance having a tendency to add protons. By definition, acids and bases are thus made independent of a solvent and there exists no relationship of the salts formed during a neutralization reaction. Salts are to be regarded as aggregations of positive and negative ions which may be indirectly related to acids and bases.
The basic relationship between an acid and a base is indicated by following equations:

$$\text{Acid}_1 \rightleftharpoons \text{H}^+ + \text{Base}_1 \quad \ldots \ (1)$$

$$\text{Base}_2 + \text{H}^+ \rightleftharpoons \text{Acid}_2 \quad \ldots \ (2)$$

the overall reaction for these two equilibria is:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Base}_1 + \text{Acid}_2 \quad \ldots \ (3)$$

Therefore, any acid-base reaction involves two acids and two bases. These acids and bases are called conjugate pairs. In the above equation (3) Acid$_1$, Base$_1$, and Base$_2$, Acid$_2$ form conjugate pairs.

**ACID-BASE BEHAVIOUR IN AQUEOUS SOLUTION**

Water plays a dual character in acid-base system. Water can function as an acid in the presence of bases stronger than itself. For example, water can donate protons to bases such as ammonia and carbonate ions.

$$\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$$

$$\text{H}_2\text{O}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{OH}^-$$

Moreover, water can function as a base in the presence of acids stronger than itself. For example the acceptance of protons from acids as in the case of hydrogen chloride and
bisulphate ion reactions.

\[
\text{Acid}_1 + \text{Base}_2 \leftrightarrow \text{Acid}_2 + \text{Base}_1 \\
\text{HCl} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{HSO}_4^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{SO}_4^{2-}
\]

Ions can also act as an acids e.g., the ammonium ion is an acid in aqueous solution:

\[
\text{Acid}_1 + \text{Base}_2 \leftrightarrow \text{Acid}_2 + \text{Base}_1 \\
\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NH}_3
\]

However, the ammonium ion is a weak acid and few hydronium ions are produced in aqueous solution. According to Bronsted\textsuperscript{10} theory all negative ions (the anions) are classified as bases, since they can combine with protons, anions, which form slightly dissociated species with protons are considered as strong bases and those which form weak linkages with protons are termed as weak bases. Thus in aqueous solution, the hydroxide ion is the strongest base and chloride ion is the weakest one.

**ACID AND BASES IN NON-AQUEOUS MEDIA**

Acidic and basic properties of solutes are markedly influenced by the relative proton donor and acceptor properties of the solvent itself. On the basis of such characteristics, a number of types of solvents are distinguished\textsuperscript{12}, the most important\textsuperscript{13} of different types
of solvents are given as below:

<table>
<thead>
<tr>
<th>Solvent type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic solvents</td>
<td>HF, H₂SO₄, CH₃COOH, HCOOH, HCN, C₆H₅OH</td>
</tr>
<tr>
<td>Basic solvents</td>
<td>NH₃, N₂H₄, NH₂OH and Amines.</td>
</tr>
<tr>
<td>Amphiprotic solvents</td>
<td>Alcohols</td>
</tr>
<tr>
<td>Aprotic solvents</td>
<td>C₆H₆, CHCl₃, C₂H₄Cl₂, o-dichlorobenzene, ether.</td>
</tr>
</tbody>
</table>

The type of solvent greatly effects the acid-base interactions of the solute, i.e. Urea behaves as an acid when dissolved in liquid ammonia (a basic solvent) but as a strong base in anhydrous formic acid (as acidic solvent). The following reaction takes place:

\[
\begin{align*}
\text{NH}_2 & \quad \text{CO} \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{NH}_3 \quad \leftrightarrow \quad \text{CO} \quad \text{NH}_4^+ \\
\text{Urea} & \quad \text{Liquid Ammonia} & \quad \text{Base} \quad \text{Acid}
\end{align*}
\]

\[
\begin{align*}
\text{NH}_2 & \quad \text{CO} \quad \text{NH}_2 \\
\text{NH}_2 & \quad \text{HCOOH} \quad \leftrightarrow \quad \text{CO} \quad \text{HCOO}^- \\
\text{Formic Acid} & \quad \text{Urea} & \quad \text{Base} \quad \text{Acid}
\end{align*}
\]
Another example may be quoted that of the behaviour of nitric acid in aqueous solution. Apparently it behaves as proton acceptor in liquid hydrogen fluoride.

\[ \text{HNO}_3 + \text{HF} \quad \overset{\text{Base}}{\underset{\text{Acid}}{\longrightarrow}} \quad \text{H}_2\text{NO}_3^+ + \text{F}^- \]

Generally, materials, which are weakly basic in an amphiprotic solvent (water), become strongly basic in highly acidic solvent.

In the light of Bronsted-Lowry concept, quantitatively speaking, the strength of an acid can be measured by the extent to which protons are released and the base strength is a measure of the extent to which they are accepted. The conjugate base of strong acid is weak and a conjugate base of a weak acid is strong. Moreover, strengths can be expressed in terms of equilibrium constant. According to this concept an acid base reaction can be considered as:

\[ \text{Acid}_1 \quad \overset{\text{Base}_1 + \text{Proton}}{\underset{\text{A}}{\longrightarrow}} \quad \text{B} + \text{H}^+ \quad \ldots \quad (1) \]

\[ \text{Base}_2 + \text{Proton} \quad \overset{\text{Acid}_2}{\underset{\text{B}}{\longrightarrow}} \quad \ldots \quad (2) \]

\[ K_A = \frac{a_B \cdot a_{H^+}}{a_A} \quad \ldots \quad (3) \]

\[ K_B = \frac{a_A}{a_B \cdot a_{H^+}} \quad (4) \]
For the equilibria of the type as:

\[ \text{A}_1 + \text{B}_2 \underset{\text{K}}{\overset{\text{K}}{\rightleftharpoons}} \text{A}_2 + \text{B}_1 \] ... (5)

and \[ K = \frac{a_{A_2}a_{B_1}}{a_{A_1}a_{B_2}} \] ... (6)

Such equilibria as these can be used for evolution of relative acid and base strengths in a series of materials if one acid-base pair is common to all the equilibria. For comparison in water solution, such a condition is maintained and we may write:

\[ \text{A} + \text{H}_2\text{O} \underset{\text{K'}}{\overset{\text{K'}}{\rightleftharpoons}} \text{H}_3\text{O}^+ + \text{B} \] ... (7)

\[ K' = \frac{a_{\text{H}_3\text{O}^+}a_{\text{B}}}{a_{\text{A}}} \] ... (8)

Since activity of water in dilute solutions is constant, then employing a new constant which includes the activity of the water, we get:

\[ K'_{\text{A}} = \frac{a_{\text{H}_3\text{O}^+}a_{\text{B}}}{a_{\text{A}}} \] ... (9)

and \[ K'_{\text{B}} = \frac{a_{\text{A}}}{a_{\text{H}_3\text{O}^+}a_{\text{B}}} \] ... (10)

where magnitudes of \( K'_{\text{A}} \) and \( K'_{\text{B}} \) indicate the strengths of the acid \( \text{A} \) and the base \( \text{B} \) respectively. All strong acids appear\(^2\) to be about the same strength in aqueous solutions and, to somewhat lesser extent, the same is true of the strongest bases. Water, therefore, may be regarded as exerting a leveling effect upon acidic and
basic strengths. In a similar manner, any solvent with basic properties will level the strengths of acids, and any solvent with acidic properties will level the strengths of bases.

A true acid or base strength can be evaluated by using differentiating solvents. The most useful solvents, for differentiation, are those which are aprotic, as they can impose no limitation upon acidic or basic properties through their tendencies towards proton loss or gain.

4. The Lux-Flood Concept

Since the protonic concept failed to explain the acid-base behaviour to oxide system. Lux suggested that in such systems a base is any material which gains oxide ions like:

\[
\begin{align*}
\text{Base} & \iff \text{Acid} + \text{XO}^{-2} \\
\text{CaO} & \iff \text{Ca}^{+2} + \text{O}^{-2} \\
\text{SO}_{4}^{-2} & \iff \text{SO}_{3} + \text{O}^{-2}
\end{align*}
\]

The Lux concept had certain limitations and could not be applied for the explaining the acid-base behaviour. Later on Flood and his Coworkers have extended the Lux concept to number of systems and have pointed out that in such systems acid strength may be compared by comparing the magnitudes of equilibrium constants as defined by the following equation:
\[ K = a_{\text{acid}} \cdot a_{\text{O}^-}^2 / a_{\text{base}} \] 

Thus acid strength was found\(^2^7\) to increase in the series \( \text{TiO}_3^- , \text{SiO}_3^- , \text{BO}_2^- , \text{PO}_3^- \).

5. **The General Theory of Solvent System**

Several definitions for acids and bases have been advanced in terms of a parent solvent\(^2^8,2^9,3^0,3^1\). They may be combined to provide a general definition of an acid to be any material giving either by direct dissociation or by interaction with the solvent, the cationic character, and a base, any material giving anionic character, while salt is regarded as material giving solutions of greater conductivity than the pure solvent and yielding at least one ion different from those characterizing the solvent.

6. **Usanovich Concept**

A Russian Scientist, Usanovich\(^3^2\) gave most comprehensive concept of acids and bases. According to his theory an acid is any substance that produces cations, combines with anions or electrons and forms salts with bases in the course of neutralization. Similarly, base is any material which produces anion or electrons and combines with cations, and forms salts with acids in the process of neutralization.

According to the Usanovich\(^3^3\) the acidic or basic property of a molecule is dependent upon the valence of the
atom with which it combines. Usually, the effect of an atom, having the highest valence, is the most prominent. This explanation is related back to the periodic function of the elements, that the acidic character increases from left to right in Mendeleev's periodic table; and the basic character increases from top to bottom of the periodic table. Therefore, according to this theory, 'The higher valence of an element produces a more acidic molecule than a lower valence'. Usanovich also emphasized the importance of 'Coordination Unsaturation' by which he means the ability of an atom to increase its covalence. To him the acidic function within a molecule depends upon the presence of a coordinately unsaturated positive atom and the basic property depend upon the presence of a negative unsaturated atom. Examples of neutralization in terms of Usanovich concept are given as follows:

\[
\text{Acid} + \text{Base} \quad \xrightarrow{\text{Salt}} \quad \text{Salt}
\]

\[
\text{SO}_3 + \text{Na}_2\text{O} \quad \xrightarrow{\text{Na}_2\text{SO}_4} \quad \text{Na}_2\text{SO}_4
\]

\[
\text{Sb}_2\text{S}_5^+ + 3\text{(NH}_4\text{)}_2\text{S} \quad \xrightarrow{2\text{(NH}_4\text{)}_3\text{SbS}_4} \quad 2\text{(NH}_4\text{)}_3\text{SbS}_4
\]

\[
\text{Cl}_2 + 2\text{Na} \quad \xrightarrow{2\text{NaCl}} \quad 2\text{NaCl}
\]

\[
\text{Fe(CN)}_3^+3\text{KCN} \quad \xrightarrow{\text{K}_3[\text{Fe(CN)}_6]} \quad \text{K}_3[\text{Fe(CN)}_6]
\]

All the previously described acid-base concepts, as described above, place restrictions for the presence of
particular atom, ion or other species. Thus, a particular definition is only valuable for a particular system. Therefore, a definition which is true for one system is not applicable to another system. The concepts of acids and bases remained limited to the systems defined by various definition. In the field, a concept was needed that could be applied, in general, to all systems. In other words, a broad definitions was required to generalize the concepts about acidity and basicity.

7. The Lewis Electronic Theory  
(The Electron Donor-Acceptor System)

In 1923 G.N. Lewis\(^{34}\) stated the fundamental concept of the theory and was later extended and reviewed by Luder\(^{35}\). A Lewis acid is defined as any radical, molecule or ion which is electron deficit due to incomplete electronic arrangement. It is capable of binding to another species by accepting an electron pair from that species. On the other hand a Lewis base is molecule, ion or radical capable of donating an electron pair to a Lewis acid. The Lewis\(^{34}\) acid-base definition is a broad based generalization. It supercedes the definition of an acid or a base as given by Bronsted and Lowry\(^{10,37}\). It covers the previous definitions. Thus, Bronsted and Lowry acid-base concept as represented by a proton is the simplest Lewis acid. It took many years before the Lewis concept gained a general acceptance. Ingold\(^{38,39}\) used the term electrophile for a Lewis acid where as the term nucleophile for a Lewis base. In organic
Chemistry it is more accepted. The Lewis concept was introduced in co-ordination chemistry by Sidgwick\textsuperscript{40} who used the term electron acceptor or acceptor for a Lewis acid and Electron donor or donor for a Lewis base. The reaction between ammonia and boron trifluoride is a typical example of an acid-base reaction:

\[
\begin{align*}
\text{H} & \quad \text{F} \\
\text{H} & \quad \text{N} : \quad \text{→} \quad \text{B} & \quad \text{F} \\
\text{H} & \quad \text{F}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Lewis</th>
<th>Base</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sidgwick</td>
<td>Donor</td>
<td>Acceptor</td>
</tr>
<tr>
<td>Ingold</td>
<td>Nucleophile</td>
<td>Electrophile</td>
</tr>
</tbody>
</table>

The Lewis concept is applicable, in addition to acid-base chemistry, to co-ordination chemistry, substitution, displacement, group transfer and redox phenomenon. An oxidizing agent is acceptor of Electrons and a reducing agent is a donor of electrons according to Usanovich\textsuperscript{41} concept. Therefore, the Lewis acid-base concept is extremely useful in understanding the chemical behaviour and for explaining and predicting various chemical phenomenon. The concept emphasises the structural variability of a molecule on co-ordination. The Lewis concept represents an interpretation of experimental facts rather than the mere theoretical approach. From many examples and illustrations which have been given\textsuperscript{35,36,42,43,44}.
TYPES OF LEWIS ACIDS

The Lewis acids can be classified into three main types of ions. Molecules or Species.

1. Cations

All metal cations can behave as Lewis acids. The acidic strength of a cation would be greater, the greater the positive charge on the ion. The electronegativity of the metal would thus also affect the acidic character of the metal ion. The hydration of Lithium and ferric ions are the examples for the cations which show acidic properties:

\[ \text{Li}^+ + 4\text{H}_2\text{O} \rightarrow \text{Li} \ (\text{H}_2\text{O})_4^+ \]
\[ \text{Fe}^{+++} + 6\text{H}_2\text{O} \rightarrow \text{Fe} \ (\text{H}_2\text{O})_6^{3+} \]

The positively charged heavy metal ions which behave as Lewis acids, have incomplete stable orbitals. For example, silver and copper ions, have incompletely filled d-orbitals. Neutralization, according to the theory results in the formation of co-ordinate bonds. The reactions for such positive ions are shown as below:

\[ \text{Ag}^+ + 2(\text{NH}_3) \rightarrow \text{Ag} \ (\text{NH}_3)_2^+ \]
\[ \text{Cu}^{++} + 4(\text{OH}_2) \rightarrow \text{Cu} \ (\text{OH}_2)_4^{++} \]

Acid Base Co-ordinate bond formed
In addition to stable metal cations, other less stable positive ions such as $^{46}$Br$^+$, I$^+$, Carbonium R$^+$ and acylum R CO$^+$, are also of considerable importance as Lewis acids.

Generally cations have vacant orbitals and have tendency to accept one or more electron pairs from donor molecules. For instance Lithium ion has vacant 2S and 2P orbitals. Aluminium ion has vacant 3S, 3P and 3d orbitals and brominium ion has vacant 4P orbitals. While cations like, nitronium ion, can only have vacant orbital available, when a reagent approaches it.

$$0\longrightarrow N^+\longrightarrow O + X^- \longrightarrow X\longrightarrow N^+\longrightarrow 0^-$$

Similar behaviour is shown by more stable carbonium ions such as triphenyl carbonium:

2. Molecules (MX$_n$)having Vacant Orbitals on a Central Atom

The majority of the covalent compounds of the elements of group-III are acceptor molecules, e.g., BF$_3$, BCl$_3$, AlCl$_3$, ...
B(CH\textsubscript{3})\textsubscript{3}, GaCl\textsubscript{3}, BeCl\textsubscript{2}, and ZnCl\textsubscript{2}. These molecules are covalent and have one or more vacant orbitals on the central atom, which is occupied by non-bonding electrons on adjacent atoms. For example, in boron trifluoride, the 2\textit{p} orbital of boron is vacant which is occupied by non-bonding electrons of the fluorine atom.

![Diagram of boron trifluoride](image)

Typical examples of this class of Lewis acids are boron tri-chloride and sulphur tri-oxide and the reaction between these Lewis acids with bases are given in the following equations:

\[
\begin{align*}
\vdots & : F & \text{H} & : F & \text{H} \\
\vdots & : F & \text{B} + & \vdots & : N & \text{H} \\
\vdots & : F & \text{H} & \leftrightarrow & : F & \text{B} : \vdots & : N & \text{H} \\
\vdots & : F & \text{H} & \leftrightarrow & : F & \text{B} & \vdots & : N & \text{H} \\
\vdots & : O & \leftrightarrow & : O \\
\vdots & : O & \leftrightarrow & : O & \vdots & : S & \vdots & : O & \text{H} \\
\vdots & : O & \vdots & : O & \text{H} & \leftrightarrow & : O & \vdots & : O & \text{H} \\
\vdots & : O & \text{H} & \leftrightarrow & : O & \text{H}
\end{align*}
\]

Acid Base Co-ordinate bond

The halides of second and subsequent period elements, including transition elements having vacant d-orbitals, are
also included in this class of Lewis acids. Generally, the second and third row elements of the periodic table have the availability of d-orbitals and the acceptor molecules combine with one or at the most two donor molecules or ions e.g.,

\[
\begin{align*}
\text{FeBr}_3 + \text{Br}^- & \rightarrow \text{FeBr}_4^- \\
\text{SbF}_5 + \text{F}^- & \rightarrow \text{SbF}_6^- \\
\text{I}_2 + \text{I}^- & \rightarrow \text{I}_3^-
\end{align*}
\]

Acid Base Complex ion

Elements in the later periods of the periodic table can make use of their two or more orbitals and are capable of forming higher co-ordination numbers, e.g.,

\[
\begin{align*}
\text{Zr F}_4 + 3\text{F}^- & \rightarrow \text{Zr F}_7^{-3}
\end{align*}
\]

This class of Lewis acids may be represented by a general formula, MX_{x}, where M is a metal or metalloid and 'X' is normally electronegative ion or group. This type of Lewis acid is very important in their action as catalysts for various reactions. Under anhydrous conditions, the covalent character is prominent and the electronegative nature of 'X' brings about an electron deficiency on metal atom, M, which becomes an electrophilic centre. The present work is an extension of studies of this type of Lewis acids. Germanium tetrachloride (GeCl₄) belongs to
this type of Lewis acids. Its property as Lewis acid is known\textsuperscript{48,49} but studies on its quantitative strength, as Lewis acid are rare. Therefore, the present work involved the study of interactions of GeCl\textsubscript{4} as Lewis acid with donor bases in non-aqueous medium.

3. Molecules having Double Bonds

In molecules having double bonds, a pair of electrons is transferred to make the orbital available for an incoming electron pair from a donor molecule. For example

\[
\begin{align*}
O &= C = O + OH^- &\rightarrow O &= C \quad OH^-
\end{align*}
\]

\[
\begin{align*}
O &= S + N &\rightarrow O^- &= S - N^+
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} &\quad \text{C} = O + \text{CN}^- &\rightarrow \quad \text{H}_3\text{C} &\quad \text{O}^-
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} &\quad \text{C} \quad \text{CN} &\rightarrow \quad \text{H}_3\text{C} &\quad \text{CN}
\end{align*}
\]

Acid Base

Aromatic electrophilic substitution may be regarded as an acid-base reaction\textsuperscript{48} in the Lewis sense. The Lewis
acids, in nitration and sulphonation, provide a vacant orbital by an electron pair shift in a double bond and the aromatic molecule behaves as a base. The acid-base interaction results in the formation of an unstable transition state, A strong acid can lose a proton to the medium to give the substituted aromatic compounds; e.g.,

\[
\begin{align*}
\text{ benzene } + \text{ O} & \quad \rightarrow \quad \text{[structure]} \quad \rightarrow \quad \text{[structure]} + \text{H}^+
\end{align*}
\]

**STRENGTH OF LEWIS ACIDS**

As explained earlier, the acids could be protonic or non-protonic compounds. The solvent in which they are dissolved are also classified in the same way. According to Lewis theory, acids are electron pair acceptors and may be non-protonic in nature, the neutralization, according to Lewis concept results in a co-ordinate bond formation. It is not necessary that a proton must participate in the neutralization reaction. The acid molecule, ion or species may show variable strength, while interacting with bases. The strength of an acid as an electron acceptor will however depend upon the following factors:
a) Electronic configuration of the acid  
b) The strength of the base with which it reacts  
c) The solvent in which reaction takes place

The strength of protonic acids depends upon the nature of the solvent in which the acid is dissolved. In aqueous solutions the acids such as $\text{HClO}_4$, $\text{HCl}$, $\text{HBr}$, and $\text{HNO}_3$ show little difference in their acidic strengths. These compounds react completely with the solvents in dilute aqueous solutions. For example, hydrogen chloride reacts with water as shown below:

$$\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$$

In this reaction water molecule is much stronger base as compared with chloride ion. Thus the acid, in solution exists in the form of hydronium ion, rather than simple protons. The other protonic acids as mentioned above, behave similarly. Thus the protonic acids exhibit similar strength. This phenomenon is known as leveling effect of the solvent. In the same way, other solvents, more basic than water, would show a similar leveling effect upon the various acids. Therefore, in liquid ammonia, acetic acid seems to be as strong as hydrochloric acid or nitric acid. Since ammonia has levelled the strength of these acids so they appear to be 100 percent ionized. The
ionization reaction of $\text{CH}_3\text{COOH}$ and $\text{HCl}$, in liquid ammonia may be shown as follows:

$$
\text{H}_3\text{C} - \text{C} - \text{OH} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_3\text{C} - \text{C} - \text{O}^-
$$

and

$$
\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-
$$

Ammonia molecule being a much stronger base than acetate or chloride ion displaces these ions from their hydrogen compounds.

A solvent more acidic than water has a poor leveling effect. For example strength of hydrogen chloride, when dissolved in water and when dissolved in acetic acid differ appreciably. In aqueous solution, complete reaction occurs while in acetic acid the solute dissolved shows a reversible equilibrium; as a partial conversion of $\text{HCl}$ takes place into the products.

$$
\text{HCl} + \text{H}_3\text{C} - \text{C} - \text{OH} \rightleftharpoons \text{H}_2\text{C}_2\text{H}_3\text{O}^+ + \text{Cl}^-
$$

Acetic acid appears to be a weak base. There is a little scope for the reaction to proceed towards the right hand side completely. Therefore, it is possible to compare the strength of the various acids.

Some generalization may as well be considered regarding
the strength of an acid.

1) The strength of an acid decreases as the oxidation number (charge) of the central atom decreases, e.g., the smaller size of sulphur makes sulphurous acid slightly stronger acid than the selenic acid. The order of the acidic strength of some protonic acids may be shown as given below:

\[ \text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3 > \text{H}_2\text{SeO}_3 > \text{H}_3\text{ASO}_3 \]

2) According to Pauling's rule, the charged oxygen acids with all oxygens attached to some central atom, relates the strength of such acids to the number of non-hydrogenated oxygen atoms present in a molecule. If no non-hydrogenated oxygen atom is attached with an acid e.g., B(OH)_2 or Cl(OH), its ionization constant is roughly \(10^{-9}\); if only one non-hydrogenated oxygen atom is attached, e.g., (OH)_3PO the ionization constant is \(10^{-2}\). Acids with two or three non-hydrogenated oxygens e.g., (OH)_2SO_2 or HOCIO_3, the acid should be very strong. Ricci's \(^5^1\) expresses the above idea mathematically as follows:

\[ -\log K = 8 - 9m + 4n \]

- \(K\) = Ionization constant
- \(m\) = Formula charge on central atom
- \(n\) = Number of non-hydrogenated oxygens.
Just to judge the strength of an acid (or base), solvents used should be aprotic solvents as they are useful in differentiating solvents, and they impose no limitations upon acidic or basic properties for donation or acceptance of protons. In such solvents, acid-base system was studied by adding second base or acid, that can act as an indicator. If HA and B represent respectively an acid and an indicator, the equilibrium:

\[ \text{HA} + \text{B} \rightarrow \text{BH} + \text{A} \] ...

will be established between acid and the indicator. For this equilibrium, \(^{52}\)

\[ K = \frac{K_{\text{HA}}}{K_{\text{HB}}} = \frac{C_{\text{HB}}}{C_{\text{B}}} \cdot \frac{C_{\text{A}}}{C_{\text{HA}}} \] ...

\( K \) = Measures acidity and depends upon the comparative strengths of two acids HA and HB

\( C \) = Concentrations

B and BH are two forms of indicator.

Evaluation of the ratio, of \( C_{\text{A}} \) to \( C_{\text{HA}} \) gives a measure of acid strength of HA as compared with indicator. Bronsted\(^{1}\) determined the relative strengths of acids. The order of acid strength be the same as in water, with HCl being the strongest, others\(^{53,54}\) have extended these observations and the whole subject has been discussed by Hall\(^{13}\). Hantzsch
and Voigt\textsuperscript{55} determined the relative acid strength in chloroform and ether, using equi-molar solutions of dimethyl yellow salts of a number of acids, and also investigate the dilutions (with solvent) to cause the indicator to change colour. At these dilutions, the reactions as:

$$\text{BH}^+ + \text{X}^- \rightarrow \text{B} + \text{BX} \quad \ldots (13)$$

salt \hspace{2cm} Indicator Acid

were assumed to be complete.

A charged atom at one point is an ion and can effect the reactivity at another point in the same ion, such an effect is called Inductive effect\textsuperscript{51} for example inductive effect makes $\text{HSO}_3^-$ a weaker acid than $\text{H}_2\text{SO}_4$, $\text{HO} - \text{C} - \text{C} - \text{O}^-$ a weaker acid than $\text{HO} - \text{C} - \text{C} - \text{OH}$, $\text{NaNH}_3^+$ a weaker base than $\text{NaNH}_2$. So the conclusion comes out to be if a molecule has more than one acidic or basic site, reaction at one of these makes, reaction at the remaining site less favourable. The inductive effect is basically electrostatic effect. The influence of one reaction site on another decreases when the distance between the two sites increases.

The inductive effect may operate, even though there is no net change on the molecule. $\text{HCl}$ is a stronger acid than $\text{H} = \text{H}$, because of electronegativity. Similarly $\text{Cl} - \text{O} - \text{H}$
is a stronger acid than \( H - O - H \), as substitution of chlorine for hydrogen has caused a shift in electron density toward chlorine and away from hydrogen. In another example, if one of the hydrogens in acetic acid \( CH_3COOH \), be replaced by chlorine, forming \( CH_2ClCOOH \), the electronic charge will be pulled away from the \( O - H \) bond, making chloroacetic acid a stronger acid than acetic acid. Dichloro acetic acid should be still stronger:

\[
\begin{align*}
\text{Weak} &\quad H &\quad O &\quad H - C - C - &\quad O - H, \quad Cl - C - C &\quad: O &\quad H, \quad Cl &\quad C &\quad C &\quad: O &\quad H \\
&\quad H &\quad &\quad H &\quad &\quad &\quad &\quad &\quad &\quad &\quad &\quad Cl
\end{align*}
\]

The general subject of acid strength among protonic acids has been discussed by Hammett\(^{56}\) comparisons of acidities or basicities among several solvents should consider differences in both solvent basicity and dielectric behaviour, that is why Universal strength scale is doubtful.

**LEWIS ACIDS AS CATALYSTS**

The catalytic properties of acids and bases represent an important aspect of acid-base behaviour\(^{57}\). The importance of acid-base catalysis may be concluded from the extensive literature available which has been collected over the years\(^{38,40,42,43,58-64}\).
The Bronsted-Lowry\textsuperscript{11,10} definitions have served to emphasize the importance of protonic materials as acid catalysts in both aqueous and non-aqueous media (for example, the hydrolysis of esters as catalyzed by acids such as hydrochloric acid in aqueous medium with the ammonolysis of esters as catalyzed by ammonium salts in liquid ammonia). The most fruitful generalization has come from the application of Lewis electronic theory. In terms of this theory it is possible to show how acid or base catalyst may form an unstable intermediate by acceptance or donation of an electron pair.

Lewis acid catalysts have been studied in a variety of solvents\textsuperscript{65,66} most of which are aprotic having medium dielectric constants and having reasonable or large degree of donor properties. The dielectric constant will allow ionization to take place to some extent while the donor properties lead to exothermic reactions with the acceptor halide and allow the dissolution of even halides that are associated in the solid state.

The behaviour of Lewis acid catalysts are mostly related with chlorides. The Lewis acid catalyst reactions may be classified\textsuperscript{67} as:

1. Solvation \\
\textit{(Solvation Strength)}

Lewis acid catalyst when dissolved in an aprotic solvent
by the reaction between solute and solvent, the donor-acceptor bonds are formed. The strength of donor-acceptor bonds are shown by the heat of dissolution.

The donor strength decreases from chloride to bromide to iodide. Donor strength is larger in compounds containing oxygen as donor atom and still larger with nitrogen as the donor atom in the molecule.

Another factor affecting the donor property is the presence of other atoms or groups in the donor molecule. The donor properties of inorganic chloride are weak. The donor-properties are not only related with the dipole moments but also with Lewis base strengths. The availability of electrons at the donor atom is more important for the donor properties than the electrostatic properties of donor molecule. In general steric hinderance, on the base reduces its basic strength enormously.

The acceptor strength of group-III chloride decreases from boron to aluminium and then to gallium; while acceptor strength of the corresponding bromides is smaller for aluminium than for boron and gallium.

2. Ionization

The ionization of halides in a solvent may occur in three different ways.
a) **Ionization by Halide-Ion Transfer**

Lewis acid catalyst can accept an anion from a polar solvent with the formation of halometallate ion:

\[
\text{Me}X_n + YY \rightarrow [\text{Me}X_{n+1}]^- + Y^+
\]

This type of ionization is possible with halides or oxyhalides as solvents. It occurs in halide solvents, whenever halide co-ordination take place. Alkyl Halides show considerable conductivities with aluminium halides, apparently due to this type of ionization\(^{69,70}\).

b) **Ionization of a Solvate Complex**

The catalysts can donate a halide ion with simultaneous solvation. In such cases metal-halide bond will ionize

\[
\text{MeCl}_n + m S_v \rightarrow [\text{MeCl}_{n-1} S_v_m]^+ + Cl^-
\]

Thus heat of solvation can enhance ionization, and will depend upon donor strength of the solvent. A solvent possess poor co-ordinating power, weak ionization will take place, when the Cl\(^-\) acceptor properties of the Lewis acid catalysts are more pronounced than Cl\(^-\) donor properties.

The solvent having medium donor properties, ionization of the Lewis acid may take place for example, in solutions of aluminium chloride or zinc chloride, in either phosphorus...
oxygen chloride or phenyl phosphonic dichloride, show ionization due to interactions between the solute and the solvent.

c) **Ionization with Formation of Autocomplex ion**

For ionization a combination of (A) and (B) is possible. The solute is capable of both donating halide ions under the influence of solvation (B) and accepting halide ions (A) formed by reaction (B), leading to the formation of autocomplex compounds. For example

\[ 2 \text{M Cl}_n + m \text{SV} \rightarrow [\text{MCl}_{n-1} \text{SV}_m]^+ [\text{MCl}_{n+1}]^- \]

Autocomplex formation occurs in solutions of antimony (V) chloride in acetonitrile\(^ {71} \), ferric chloride in tri ethyl phosphate and aluminium chloride in phosphorous oxychloride.

3. **Dissociation**

Addition of a halide ion to the co-ordination sphere of a metal atom present in a Lewis acid catalyst or replacement of a halogen atom by a solvent molecule does not always lead\(^ {72} \) to the formation of free ions, since the dielectric properties of the solvent, will have an important effect. Dissociation will be complete in a solvent of high dielectric constant, such as anhydrous hydrogen fluoride, or dimethyl sulphoxide where electrostatic dissociation equilibria can be distinguished from chemical equilibria. Dissociation
will be favoured by increasing size and decreasing charge on ions.

4. **Association**

Chemical reactions in terms of association of single molecule or single ion of Lewis acid catalyst in non-aqueous solution with formation of halide bridges is known to occur with chlorides which are associated in pure solid or liquid state. Examples are zinc chloride, aluminium halides or ferric chloride in solvents of low co-ordination affinity. The halide bridges will remain in solution and the dissociation of the ion pairs formed will occur only to a limited extent. Acetic acid, chloro benzene and benzene are also examples in which chemical association of Lewis acid catalyst is indicated.

**TYPES OF LEWIS BASES**

Bronsted and Lowry considered bases as compounds capable of forming a protonated entity, then the Lewis defined the base as a compound capable of donating an electron pair. The electron pairs donated by bases are usually represented as unshared electron pairs. $\pi$ electrons can also be used for donating electrons as well. Lewis bases can be classified into various types as given below:
1. **Negatively Charged Ions**

Almost all negative ions can act as Lewis bases. For example, reactions of fluoride, hydride and iodide ions as Lewis bases are well known:

(i) \[ [:\cdot F:]^- + B \cdot F \rightarrow [F \cdot B \cdot F]^- \]

(ii) \[ H^- + H - C = O \rightarrow H - C = O \rightarrow H - C \cdot O^- \]

(formaldehyde) \hspace{1cm} (methoxide ion)

(iii) \[ [:\cdot I:]^- + I : I : I \rightarrow [I : I : I : I : I : I]^- \]

(base) \hspace{1cm} (acid) \hspace{1cm} (tri-iodide ion)

In reaction (i) the fluoride ion acts as a base and is donating its electron pair to an acid having a sextet of electrons. In reaction (ii), the base hydride is donating its electron pair to a C = O double bond. In reaction (iii), the base iodide is donating its electron pair to the acidic iodine molecule with expanded octets around the iodine atoms.
2. **Molecules having Unshared Electron Pairs**

Neutral molecules can behave as Lewis bases if they contain fifth and sixth group atoms with unshared electron pairs. Therefore, both water and ammonia react vigorously with the Lewis acid, as shown below:

\[
\begin{align*}
\text{H}_2\text{O} & : + \text{BF}_3 \quad \rightarrow \quad \text{H}_2\text{O} : \text{BF}_3 \\
\text{H}_3\text{N} & : + \text{BF}_3 \quad \rightarrow \quad \text{H}_3\text{N} : \text{BF}_3
\end{align*}
\]

**Base**  **Acid**  **Addition compound**

3. **Compounds with Double Bonds**

Molecules containing carbon-carbon double bond can act as Lewis bases as well; high solubilities of the inorganic Lewis acids, e.g., boron trifluoride, aluminium bromide and silver perchlorate, in benzene derivatives and in olefinic compounds suggest acid-base interactions. Addition compounds formed from silver perchlorate and number of such hydrocarbons (having double bond) are well known. But in such addition compounds silver ion is not bonded to any of the carbon atom of double bond but sits astride the two \( \bar{\pi} \) -electrons. This type of adducts are known as \( \bar{\pi} \) -complexes.
STRENGTH OF LEWIS BASES

An acid-base interaction may, in general, be considered as follows:

\[
\text{B}^n + \text{AH}^m \quad \leftrightarrow \quad \text{B}^n \text{H}^{n+1} + \text{A}^{m-1}
\]

Base     Acid     Acid     Base

where 'n' and 'm' are charges on the acid and the base respectively. A base has the ability to form protonated species with a unit positive charge. Consequently, there is a difference between electronic structure of the base and its protonated form (conjugated acid). The base strength can be measured quantitatively, when a standard acid is used in an aqueous solution. The equilibrium for the uncharged bases can be represented as follows:

\[
\text{B} + \text{H}_2\text{O} \quad \leftrightarrow \quad \text{BH}^+ + \text{OH}^-
\]

So, the basicity constant, \( K_b \) in aqueous solution, can be used to represent the base strength:
\[
K_b = \frac{(BH^+)(OH^-)}{(B)} \quad \ldots (15)
\]

In equilibrium water being in excess, its concentration is included in the equilibrium constant, \( K_b \). If \( H_3O^+ \) is taken as standard acid, then equilibrium for uncharged base becomes

\[
B + H_3O^+ \rightleftharpoons BH^+ + H_2O \quad \ldots (16)
\]

So, that the dissociation constant \( K_a \) for the conjugate acid \( BH^+ \) can also be used to measure the base strength.

Thus

\[
K_a = \frac{(B)(H_3O^+)}{(BH^+)} \quad \ldots (17)
\]

The following simple relation exists between \( K_a, K_b \) and \( K_w \)

\[
K_a \times K_b = K_w
\]

where

\[
K_w = (H_3O^+)(OH^-) \quad \ldots (18)
\]

For weak bases, the value of \( K_b \) is too small to be determined experimentally and only \( K_a \) can be measured. Further Hammett \(^{78,79}\) led to the possibility of measuring \( K_a \) values for extremely weak bases. The basic assumption was to utilize the ratio of the activity co-efficient, \( \frac{f_B}{f_{BH^+}} \) for the base and protonated base. Therefore the value of \( K_a \)
can be expressed as follows:

\[ K_a = \frac{(B)}{(BH^+)} \cdot a_{H^+} \cdot \frac{f_B}{f_{BH^+}} \quad \ldots \ (19) \]

since \( a_{H^+} \cdot \frac{f_B}{f_{BH^+}} = h_0 \)

\( a_{H^+} \) denotes hydrogen ion activity and \( f \) denotes molar-concentration activity co-efficient where '\( h_0 \) is independent of the nature of the base used and interpreted as quantitative measure of the acidity of the medium, where

\[ H_o = -\log h_0 \]

\( h_0 \) may be defined for acidities. \( H_o \) is called acidity function for the uncharged base.

If \( H_o \) values are known, \( K_a \) value can be calculated from the following relationship:

\[ H_o = pK_a + \log \frac{(B)}{(BH^+)} \quad \ldots \ (20) \]

**TYPE OF ADDUCT FORMED IN SOLUTION**

The Lewis acids are electron pair acceptors while Lewis bases can donate electrons. Thus the interaction of a Lewis acid with a Lewis base, results in adduct formation. The spectroscopic and structural studies indicate that two
types of species\textsuperscript{81} can lead to adduct formation as given below.

1. \textbf{Anilinium Ion Type of Species}

Anilinium ions\textsuperscript{81} are formed when bases derived from aniline are protonated in aqueous acids. For an anilinium ion the lone pair present, on amino nitrogen, is involved in adduct formation. The anilinium ions show absorption at shorter wave-length side than do the parent bases\textsuperscript{82} and the adduct results from strong acid – strong base pair\textsuperscript{83}.

2. \textbf{Change Transfer Species}

The electron donor character of base and acceptor character of $Mx_n$ may lead to the formation of ion pairs ($B^+, \overline{Mx_n}$). The adduct results from weak acids with weak bases interactions. Woodward believed\textsuperscript{84} that complexes were formed through semi polar bond. Brackman suggested\textsuperscript{85} that:

\[
B + Mx_n \xrightarrow{\text{reaction}} (B, Mx_n), (B^+ \overline{Mx_n})
\]

complex existed in various canonical forms. The interaction between these canonical forms would contribute to the resonance energy, stabilizing the complex. The Mulliken\textsuperscript{86} presented 'quantum mechanical theory' for the interaction of electron acceptors and donors (Lewis acids and bases)
to form molecular compound ranging from loose complex to stable compounds. The complex formed can exist in two energy states.

a) **Ground State Complex**

In this state the binding between the components is mainly due to van der waals interactions, including dipole orientation, induced dipole, London dispersion and other effects. In addition, the stability of ground state complex is due to transfer of charge (electrons) from donor (Lewis base) to acceptor (Lewis acid). Thus the formation of \( (B^+ \overset{n}{M}x_n) \) would involve bonding which may be due to electrostatic, polarization and covalent interactions. The extent of charge transfer and the binding strength at ground state depends \(^{87}\) upon the ionization potential of Lewis base and electron affinity of Lewis acid.

b. **Excited State Complex**

There may be a complete transfer of electrons from the donor to the acceptor. Between the two states or energy (the ground state and excited state) optical transitions are allowed to give rise to absorption spectrum.

The weakening of acid-base pair favours charge transfer interaction \(^{83}\). The charge transfer occurs on new long wave-length absorption and new bands show charge transfer
spectra; therefore adduct formed is termed as charge transfer species, and forces which lead to complex formation are called charge transfer forces. The AlX₃ - benzene interactions and spectra have also been explained in this way. Mixture of stannic chloride with toluene, dichlorobenzene and other aromatic solvents show similar effects. For nitrogen bases, FeCl₃ - aniline system had already been studied by Shuba and Zenchelsky.

TYPES OF LEWIS ACID-BASE INTERACTIONS

Ingold has named the Lewis acid as 'nucleophile' as they are attracted to electron rich parts of the basic molecules. Similarly, the lewis bases are termed as 'electrophiles' as they are in need of electron-poor regions of acids with which they can react. Electrophiles are molecules where nucleus is poorly shielded by electron density. The Lewis acid-base reactions are described as nucleophilic attack on a base by an acid; or as an electrophilic attack on a base by an acid. The interaction, may in general, be represented by the following example:

\[ \text{H}_3\text{N} + \text{BF}_3 \rightarrow \text{H}_3\text{N} : \text{BF}_3 \]

The adduct formed is considered as a result of an electrophilic attack on the nitrogen atom by boron of the BF₃ molecule. It may be concluded that both the electrophili
and the nucleophilic reactions are complementary to each other. Many reactions result in the formation of a covalent bond and the rupture of a previously existing bond\textsuperscript{91}. The bond breaking reagent may either be an acid or a base. The types of such reactions are called displacement reactions as shown by the following generalised reactions.

(i) \[ \text{Nucleophilic displacement} \]

(ii) \[ \text{Electrophilic displacement} \]

The curved arrows indicate shift of electron density during the reactions. A specific example of such a nucleophilic displacement may be quoted as the attack on \( \text{H}_3\text{O}^+ \) by \( \text{OH}^- \) ions.

A typical electrophilic displacement is the reaction of water with sulphur trioxide:

Another type of displacement is a concerted displacemer...
reaction of boron trifluoride with aqueous hydrogen fluoride.

\[ \begin{align*}
H^{-}O^{+} : + H^{-}F : + B^{-}F & \rightarrow [H^{-}O^{-}H]^{+} + [F^{-}B^{-}F]^{-} \\
\end{align*} \]

The base (water) pushes at one end of hydrogen fluoride molecule while the acid (boron trifluoride) pulls at the other end of the hydrogen fluoride molecule. Such reactions generally involve attack by an atom or groups of atoms with an unpaired electron. These species are called radicals. Therefore, displacement involving breaking up of electron pairs are called 'Radical displacements'. An example of radical displacement reaction is given below:

\[ \begin{align*}
\cdot\ddot{F} : \dddot{H} :\dddot{Cl} : \quad \longrightarrow \quad \dddot{F} : \dddot{H} + \dddot{Cl} : \\
\end{align*} \]

Interactions of the metal halides of the type \((MX_n)\) as Lewis acids with different kinds of Lewis bases, e.g., aromatic hydrocarbons, ketones ethers and amines have already been studied\(^{92,93}\). From these studies two distinct spectral effects are observed as described follows:

a) An adduct spectrum is similar to the protonated base or that of the anilinium ion type.

b) Another type of spectrum of the adduct shows the characteristics of free radical ions, \((B^+, MX_n)\) and para
magnetism is expected for the formation of such species.

The interaction of metal halides as Lewis acids with Lewis bases can be summerized to give three different types of adducts (i) $B, MX_n$ (ii) $\tilde{B} - \tilde{MX}_n$ and (iii) $\tilde{B}, \tilde{MX}_n$.

1. $B, MX_n$: Type of Interaction

This type represents charge transfer interaction. The ground state shows non-bonded structure for the adduct of the type $B, MX_n$ along with the formation of the adduct of the type $\tilde{B} \tilde{MX}_n$ as well. The charge transfer transition is between the species and an excited state in which relative contribution of $B, MX_n$ and $\tilde{B} - \tilde{MX}_n$ adducts into the total wave function are reversed. The $B, MX_n$ type of adduct shows weaker interaction than $\tilde{B} \tilde{MX}_n$ or $\tilde{B}, \tilde{MX}_n$ type due to less electron transfer. The charge transfer is greatly influenced by the donors (Lewis bases) ionization potentials. The weak interaction can also be considered to be of the physical nature. For example, if mono functional solute is present in a solvent, it does not take part in a chemical reaction. There is another type of weak interaction which is of chemical nature, where a 'stable complex' is formed. In this case, the solute dissolved remains in the form of a complex in polar solvents. The chemical interaction between a solute and the solvent
may be classified\textsuperscript{96} into two types depending upon the energy involved in the interaction. Where the solute and the solvent are both polar, a stable complex is formed as a result of strong interaction. This interaction is usually of the donor-acceptor type; and in many cases, the interaction is of the hydrogen bonding type. The later type of interaction has been a subject of numerous investigations\textsuperscript{97}. Since the distance between the approaching group is less, therefore, such complexes show somewhat defined geometry. In general, the solvent and the solute molecules interact in stoichiometric ratios to form such complex molecules. In the formation of such complexes, a large interaction energy is involved which is roughly equal to the energy involved in the formation of the donor-acceptor bonds. As a result of such strong interactions, the characteristic vibrational band of the group involved, in complex formation, is generally broadened and a considerable shift towards low frequency is observed. This type of shift is called the dipolar interactions.

The second type of chemically weaker interaction can take place between polar solute and a non-polar or a weakly polar solvent. With the result weaker complexes are formed. Bellamy\textsuperscript{98} has concluded that weaker complexes are formed in non-polar solvents. The interaction of a solute and a
non-polar solvent may occur due to dipole-induced dipole interactions. The polar group can accommodate the solvent molecules and the weaker complexes so formed would show geometrical orientation to some extent. But there is no clear distinction between these two types of complexes.

In non-polar or slightly polar solvents, the existence of molecular interactions between A - H vibrators and the various donor molecules have been reported\textsuperscript{99} before. If there is a weak interaction with the non-polar solvent, the addition of a weaker or a stronger donor would disturb the solute-solvent equilibrium and the A - H - D complex will be formed. The strength of such an interaction will depend upon the basic strength of the donor involved. The reported\textsuperscript{99} study of alcohol-base interactions was used for assessing the hydrogen bond strength that was found to be in the following order:

\begin{center}
Ether > acetonitrile > chlorobenzene > benzene
\end{center}

Huong and Lacombe\textsuperscript{100} reported for the formation of such complexes between m-chlorophenol and different bases in carbon tetrachloride. While Ali Muhammad\textsuperscript{101} reported for phenol-acetone interaction in carbon tetrachloride.
2. \( \hat{B} - \overline{M}X_n \) Type Interaction

Interaction of Lewis acid with Lewis base results in complex formation along with partial charge transfer from electron donor component of the complex to electron acceptor component of the complex. Weiss\(^{102,103} \) suggested that the stability of the complex is due to the coulombic interaction. The adduct formed remains in solution in the form of ion-pairs by charge transfer. Woodward\(^{84} \) believed that the components of complex (ion pairs) are held together through semi-polar bond. Then Brügge\(^{104,105} \) gave an idea that only dipole-dipole, dipole-induced-dipole or dispersion interaction can explain the loose nature of such complexes. Mulliken\(^{86} \) concluded that the components or ion pairs are held together due to van der waals interaction, and bond formed is an intermolecular electron pair bond. Therefore the configuration for the \( \hat{B} - \overline{M}X_n \) is electrostatic, polarized, covalent bonding due to the donation and sharing of electron pairs. In terms of electronic changes, the adducts are similar to the protonation of a base and formation of an anilinium ion. In both cases similar spectral changes are observed. For stable compound\(^{86} \) like \( R_3N:BF_3 \), the dative bond structure \( R_3\hat{N} \rightarrow \overline{BF}_3 \) is accepted. Mulliken also stressed that the resonance occurs between no-bond configuration of \( B, MX_n \)
type and dative bond configuration of $\bar{B} - \bar{M}X_n$ type.

The $\bar{B} - \bar{M}X_n$ type of interactions are stronger than $B, MX_n$ type but weaker than $\bar{B}, \bar{M}X_n$ type of adducts. For example $N,N,N',N'$ - tetramethyl-p-phenylene diamine (TMPD) interacts with TCNE$^{106}$ as follows:

$$\text{TMPD} + \text{TCNE} \rightleftharpoons (\text{TMPD TCNE}) \rightleftharpoons \text{TMPD}^+ \text{TCNE}^- \rightleftharpoons \text{TMPD}^+ + \text{TCNE}^-$$

Weaker complex Ion pair Free ions

stronger complex

Basker$^{107}$ studied interaction between triaryl derivative of group V elements with iodine, in chloroform as solvent. It was observed that at first covalent (charge transfer) complex was formed which then changed into ionic species. Since triphenyl derivatives are strongly basic$^{108}$ in nature, the formation of covalent complexes would have been expected. Another example for the formation of iodine adducts with phosphine derivatives$^{109}$ is the study of such interactions in carbon tetrachloride as a solvent. The study involved the addition of phosphine derivatives to iodine solutions. Charge transfer interaction was not observed but spectral changes supported the formation of ionic species, similar to the base-iodine interactions$^{110,111,112,113}$ in polar non-aqueous media. Unlike triaryl derivatives of arsenic and antimony, triphenyl phosphines were known$^{107,114,115}$ to form ionic compounds with halogens. Whereas arsine
and stibine derivatives formed comparatively unstable molecular complexes. When the concentration of iodine exceeded the phosphine derivatives concentration, the adduct formed were in the form of "ion pair" and solution was observed to be non-conducting.

Similarly stannic halide adducts with aromatic amines in o-dichlorobenzene solvent and zinc halide adduct with aromatic amines in ether solvent have already been studied by Satchell and Wardell\textsuperscript{83,116}. The adducts formed are of the type, $\hat{B} - \bar{M}X_n$.

3. The $\hat{B}, \bar{M}X_n$-Type of Interaction

If the base and the acid or either of the two is very strong or the solvent is polar, the adducts of the type $\hat{B}, \bar{M}X_n$ may be formed. It represents free radical ion formation and indicates stronger type of interaction than $B, MX_n$ type or $\hat{B} - MX_n$ type. An example for such a type of interaction may be quoted\textsuperscript{117} here. Interaction of ketones with one ferric chloride molecule takes place with the formation of an intermediate complex. As a result of the transfer of an unshared electron pair from oxygen of the carbonyl group to the d-orbital of one of the iron atom in ferric chloride occurs. The ferric chloride molecule is polarized to such an extent that cleavage of Fe - Cl bond occurs and the $(FeCl_4)^-$ is eliminated as shown by the
The acid-base interaction could be influenced by a number of factors. Normally, an acid-base interaction results in the formation of a coordinate bond and the product formed may be stable or can undergo rearrangements or dissociation, which may occur as a result of the influencing factors which are described as follows.
1. **Solvent Effect**

The solvents play an important role on the acid-base interactions, because they possess varying properties in terms of polarity and dielectric constant. The acidity or basicity of a system consisting of an acid or a base dissolved in a solvent is greatly affected by the acid-base properties of the solvent. Thus in dilute solutions, in water, the strongest acidic species, that can be present is in the form of hydronium ion ($H_3O^+$) and most strongly basic species can be present is in the form of a hydroxide ion. Stronger acids than the hydronium ion are converted to the hydronium ion and their relative strength can not be distinguished. In amphoteric solvents, the strongest acid is the characteristic cation and the strongest base is the characteristic anion. Water being amphoteric solvent, it exerts a levelling effect on the strengths of Bronsted acids such as $HClO_4$, $BH_3$, $H_2SO_4$ and $HCl$, all of which are completely ionised and quantitatively converted to $H_3O^+$. Thus if medium of higher acidity is required, it is necessary to use solvent that is less basic than water e.g., acetic acid. It is observed that all those acids as mentioned above which are completely dissociated in water, form a series of decreasing strength in acetic acid solutions and even the strongest perchloric acid is only 50% ionized. However, such a solution has a much higher acidity than a solution of
perchloric acid of the same concentration in water because the conjugate acid of acetic acid is a much stronger proton donor than hydronium ion.

Since solvents can reduce the effective acidity of an acid by solvation of the acidic species, therefore, aprotic solvents are often preferred for reaction involving Lewis acids.

Solvents can directly effect the rate of reaction. For instance electrophilic substitution reaction is retarded by solvents \(^{120}\), such as nitro benzene and pyridine, which can co-ordinate with metal halides \(^{121,122,123}\), because the donor solvents have high polarity and can interact with the base to form adduct of the ionic nature. On the other hand, there are certain metal halides that enhance the rate of reaction. For example, the addition of aluminium chloride and stannic chloride to the ferric chloride - chlorobenzene system facilitated the reaction.

Solvents greatly affect the Friedel and Crafts type of reactions. For example acylation of naphthalene with acetyl chloride in solvent like ethylene chloride or carbon disulphide yields 1-acetylnaphthalene whereas in nitrobenzene or nitromesitylene, the product contains considerable amounts of two isomers. The formation of 2-acetylnaphthalene is due to excess of acylating agents.

Reasons for the attack at 2 position is due to steric
hindrance. Since solvent that favours this position forms bulky complexes with acylating agents\textsuperscript{124}. The effect of solvent on isomer ratio in substitution reactions is also observed in many other\textsuperscript{125} instances. For example when B-naphthol methyl ether is acylated with acetyl chloride in carbon disulphide or benzene solution, the product is 2-methoxyl-1-acetyl naphthalene\textsuperscript{126}. However, if reaction is carried out in nitrobenzene solution the product is 2-methoxy-6-acetylnaphthalene\textsuperscript{127}. The solvent can affect the isomer ratios obtained during acylation and alkylations. For example acylation of phenols in the presence of aluminium chloride catalyst is observed that para, ortho ratio was the lowest in carbon disulphide solution while highest in nitrobenzene solution\textsuperscript{128}. Similar observations with other acyl halide acylations have been reported\textsuperscript{129}.

Generally solvent effects are due to the fact that active acylating or alkylating species is solvated to certain extent to give rise to a bulkier substituting agent, with different steric effect.

The solvation of active substituting agent (acylium, nitronium or carbonium ion) may change\textsuperscript{130} its activity and influence not only the position, but also substrate selectivity.

Pepper\textsuperscript{131} has shown that the rate of degree of polymerization of styrene and methyl styrene by tin tetrachloride
is increased by an increase in the dielectric constant of the solvent. Presence of traces of moisture can reduce the rate of polymerization in solvents of high dielectric constant, but increase the rate in hydrocarbons is reported. Solutions of stannic chloride in solvents of high dielectric constants show conductivity in the presence of traces of moisture. The polymerization has an ionic mechanism, but in solvents of high dielectric constants, for example nitroparaffins, it does not show the hydrated ions.

It was found that solvent used has little effect on proportion of isomers but greatly affect the yields of the products of reactions. For example the yield of naphthoyl benzoic acid changes with change of solvents:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Yield%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>87-91</td>
</tr>
<tr>
<td>O-dichloro benzene</td>
<td>91</td>
</tr>
<tr>
<td>Tetra chloro ethane</td>
<td>43</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>28</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>15-18</td>
</tr>
</tbody>
</table>

2. The Temperature Effects

Generally the rate of a chemical reaction increases with rise in temperature. In some organic reactions e.g., sulphonation of naphthalene or related reactions change in temperature affect the orientation of the new substituent.
However, in many Friedel and Crafts reactions changes can take place if temperature is not controlled. Even moderate elevation in temperature can bring about secondary condensations. At very high temperature almost all Friedel-Crafts reaction mixtures can be converted to oily complexes having unknown compositions.

Aluminium chloride catalyzed reactions usually proceed at high temperature with the evolution of heat. In alkylation, acylations, and most addition reactions temperatures of 90-100°C are rarely needed, where as dehydrating and dehydrogenating condensations are carried out at high temperature in aluminium chloride – sodium chloride melts.

The Protonic acids, like sulphuric acid and anhydrous HF are also used at low temperatures due to (i) secondary decomposition which occurs when organic compounds are heated at elevated temperature with sulphuric acid (ii) due to volatility of anhydrous HF.

At elevated temperature some reactions can take place even in the absence of catalysts. While some reactions can occur at very low temperature but in the presence of catalysts for example benzoyl naphthalene is obtained in a Friedel-Crafts type ketone synthesis with AlCl₃ as catalyst in carbon disulphide as solvent at 0°C. At reflux temperature of the components (naphthalene, benzoylchloride)

-benzoynaphthalene was obtained in the absence of any
catalyst, even before Friedle-Crafts synthesis\textsuperscript{134}. Another example is that of meso-ketones which are obtained by Nenitzescu\textsuperscript{135} when the components were heated in refluxing nitrobenzene solution at about 200°C in the absence of catalysts. He also showed that when benzyl chloride is heated with such highly reactive aromatic compounds as biphenyl, naphthalene, anisole, and mesitylene, the expected diarylmethane derivatives are obtained in the absence of any catalyst.
EXPERIMENTAL
Solvents provide media for various reactions. In the present work, as Lewis acid-base interactions are investigated, therefore the choice of suitable solvent will greatly effect acid-base interactions\(^{136}\). The selection of a suitable solvent is important for the type of interactions investigated. The solvent should be non-aqueous as the Lewis acids are hydrolyzed in water and the adducts formed as a result of variety of acid-base interactions would also be hydrolysed and decomposed. Water has been recognized as a universal solvent. Ability of water to dissolve materials\(^{137}\) has led to the general assumption that water is unique in its solvent characteristic. No other solvent shows such a wide range in physical and chemical properties. In 1893, Ostwald was convinced\(^{138}\) that so far as its ability to form Electrolyte solutions or to bring about ionization was concerned, water stood in a class by itself, a position which is not even approximately compatible any other liquid. Although subsequent researches have demonstrated that differences among solvents are differences of a degree rather than of kind and that all the effects produced by any other solvent materials\(^{137}\) on the basis of properties of solvents may be grouped into three broad periods. When the use of water as a solvent had been established then attention was directed to other organic compounds such as alcohols esters and ketones as electrolytic
solvents for inorganic substances. The second period began with liquid ammonia studies by Cady\textsuperscript{139} in 1897, which were continued by Walden\textsuperscript{140}, Kraus\textsuperscript{141} and Franklin\textsuperscript{142} in 1898. The investigations of Walden\textsuperscript{143}, in 1899, on the solvent character of liquid sulphur dioxide may be regarded as introduction to the third period. During this period a variety of solvents have been investigated from both practical and theoretical point of view.

Solvents may be classified in number of ways\textsuperscript{144}. A more convenient basis for classification lies in the electrolytic characteristics of the solvent. Solvents which are themselves polar in nature show the following behaviour in general:

1. As ionizing solvents, either because of the attractions which such polar groups have for ions which already exist in solute or because of tendencies which such materials have to rupture polar covalent linkages present in non-ionic compounds such as hydrogen acids. In a very general way, the Electrolytic solvents with high dielectric constants behaving as better electrolytic solvents than those with lower dielectric constants\textsuperscript{143}. Solvents with high dielectric constants\textsuperscript{145} such as formic acid, nitromethane, hydrogen cyanide, acetonitrile, methyl thiocyanate, ammonia, ethylene glycol, methanol and water behave as ionizing solvents. Those with low dielectric
constants, such as hydrocarbons and halogenated hydrocarbons are the poorest.

The concept of leveling and differentiating solvents proved useful in combination with the Bronsted-Lowry theory which may be applied to electrolytic solvents in general.

2. Leveling solvents are those in which most soluble electrolytes appear strongly ionised; such solvents include the highly polar materials like water, ammonia and the lower alcohols.

3. Differentiating solvents are those in which electrolyte vary widely in ionisation strengths with changes in the solvents. For example less polar materials such as certain amines and halogenated hydrocarbons belong to this type of solvents.

4. Solvents can also be classified as protonic and aprotic solvents. The separation refers back to Bronsted's idea of acid-base behaviour.

a) Protonic solvents are those which provide hydrogen ions e.g., water and liquid ammonia:

\[ 2H_2O \rightleftharpoons H_3O^+ + OH^- \]

\[ 2NH_3 \rightleftharpoons NH_4^+ + NH_2^- \]

b) Aprotic solvents are those from which protons are not ordinarily obtained or they neither give up nor take up
protons to any considerable extent\textsuperscript{13}. Examples of these are paraffin hydrocarbons, benzene, ortho dichlorobenzene, ether and chloroform. Broadly speaking, organic solvents are included in this class of solvents.

**Purification of Solvent-Orthodichlorobenzene**

\textit{(1,2-dichlorobenzene)}

Ortho dichlorobenzene is an inert solvent\textsuperscript{147}. (Molecular weight 147.01). In general, 1,3-dichlorobenzene (Boiling Point 173\textdegree C)\textsuperscript{148}, 1,4-dichlorobenzene (Boiling Point 174\textdegree C)\textsuperscript{148} and moisture are present as impurities in orthodichlorobenzene. In the present work orthodichlorobenzene (Pure B.D.H. Grade) was taken in a one dm\textsuperscript{3} quick fit flask. Lithium aluminium hydride, a strong reducing agent, was added in small amounts into the solvent with occasional shaking from time to time. Shaking was continued till no more bubbles were evolved. The flask was fitted with a coil condenser. A calcium chloride tube was fitted at the open end of the condenser so as to exclude the possibility of moisture getting into the flask. The flask was refluxed for twelve hours. At the beginning, slow heating was started. The moisture present reacted with the added hydride and hydrogen gas was evolved in the form of bubbles. Heating was increased till the solvent started boiling, refluxing was continued to destroy the traces of moisture present in the solvent. After refluxing, the flask was stoppered and transferred into
a dry box. After cooling orthodichlorobenzene was filtered through a sintered funnel. The filtered solvent was distilled\textsuperscript{149}. The distillation flask was fitted with a still-head having a quick fit thermometer. A calcium chloride tube was fitted with the receiving bend in order to exclude traces of moisture. The first fraction coming over below the boiling point of orthodichlorobenzene was rejected so that low boiling impurities, i.e. 1,3-dichlorobenzene (Boiling Point 173°C)\textsuperscript{148} and 1,4-dichlorobenzene (Boiling Point 174°C)\textsuperscript{148} were distilled over in the first fraction. The middle fraction (Boiling Point 179°C-180°C)\textsuperscript{148} was collected in a clean dry flask.

The remaining few cm\textsuperscript{3} of the solvent was left undistilled. The middle cut fraction was removed, stoppered and shifted to the dry box for further use.

**PREPARATION OF GERMANIUM TETRACHLORIDE**

Germanium tetrachloride, GeCl\textsubscript{4} (Molecular weight 214.41) Germanium tetrachloride, used in the present work, was obtained from two sources:

1. Germanium tetrachloride was prepared by heating powdered germanium in a stream of dry chlorine at 500° - 600°C\textsuperscript{150}.

\[
\text{Ge} + 2\text{Cl}_2 \rightleftharpoons \text{GeCl}_4
\]
0.275 gm mole of germanium powder was taken in a china dish for washing so as to remove any adsorbed impurities on the surface of the powder. First germanium powder was thoroughly washed with distilled water three times. Then the powder was washed with ethyl alcohol and finally, washing with di ethylether was carried out. Thus the well washed germanium powder was placed in an oven at 110°C for about four hours. The dried germanium powder was then used for the preparation of germanium tetrachloride.

A boat with dried germanium powder was placed in a Pyrex tube and a stream of dry chlorine was passed over it. The germanium powder was heated. The final temperature ranged 500°C to 600°C. The reaction was started at much lower temperature. The tube was filled with broken crucible pieces on which germanium powder was spread so as to enhance the rate of reaction. The tube was tilted towards the exhaust end, which was connected with a gas trap by means of an adapter. The trap was cooled with an ice-salt mixture. The germanium tetrachloride formed in the reaction chamber vaporized and the vapours were condensed and collected as yellow coloured liquid. The presence of chlorine and other impurities imparted yellow colour to the product. The product was fractionated to remove chlorine. After removing chlorine, the flask was stoppered and shifted to a dry box for transferring the germanium tetrachloride into a distillation flask.
2. Germanium tetrachloride (B.D.H. Grade) was purchased in the form of ampoules. Each ampoule contained one gram germanium tetrachloride. The material was pure and before using, it was distilled by the same procedure as used for the germanium tetrachloride prepared in the laboratory. The method for purification is described as explained under.

**Purification of Germanium Tetrachloride**

A quick fit distillation assembly was fitted. Dry current of chlorine gas was passed through the apparatus during distillation to prevent the volatilization of traces of arsenic (present as impurity) as trichloride$^{151,152}$. This arsenic trichloride is high boiling liquid with a boiling point at $129^\circ$C$^{153}$. It remained in the distillation flask while germanium tetrachloride Boiling Point 83.1$^\circ$C$^{154}$ was distilled over. When a current of chlorine was passed through the apparatus during distillation, the distillate was found to be free from arsenic. When the temperature of the out coming vapours approached the boiling point of germanium tetrachloride, the distillate was collected. The distillate collected was then transferred into a semi-micro Claisen-Vigreux distillation flask$^{155}$. Some copper powder was added$^{156}$ in the distillation flask to remove the last traces of arsenic and was refluxed$^{156}$ for three hours so as to remove any absorbed chlorine. After refluxing, distillation was carried out. The temperature of vapours of germanium
tetrachloride passing on to the condenser was noted. The condenser was connected to a multiple receiver. Having distilled the first fraction the multiple bend was tilted to collect the next fraction in an other receiving flask. After collecting the middle cut fraction, the pure germanium tetrachloride was shifted to a dry box for further use. The last fraction of germanium tetrachloride (a few cm\(^3\)) was rejected. The boiling point of the purified germanium tetrachloride as observed during distillation was 83.0\(^\circ\)C, whereas, in the literature, its boiling Point 83.1\(^\circ\)C\(^{154}\) and 86.0\(^\circ\)C\(^{152}\) is also reported.

**Purification of Bases Used**

**The Nitrogen Bases**

Majority of the bases were obtained from different manufacturers for laboratory chemicals. Some of the bases were solids and others were liquids. Both solid and liquid bases were purified before use. The solid bases were purified by recrystallization\(^{157,158,159}\) of most of the bases, which dissolved and formed a fairly saturated solution at room temperature. Therefore, the alcohol needed, for recrystallization, was purified before use as follows.

**Purification of Alcohols**

For recrystallization of nitrogen bases from alcohols ethyl alcohol (E. Merck grade) was taken into a distillation
flask. Anhydrous calcium oxide \(^{160}\) (pre-heated in an oven and then cooled in a desiccator) was added to the flask containing ethyl alcohol. The mixture was refluxed \(^{83}\) for six hours. After refluxing, it was kept standing overnight. Ethyl alcohol was first heated slowly. When it started boiling, the distillate was collected in a clean and already dried receiver. First and last fractions of the distillate were rejected; only the middle cut fraction was preserved in a dry box for recrystallization of the bases as described below.

**Purification of Solid Bases**

Alcohol was used for recrystallization as mentioned above. Then filtered the solution through a sintered glass filter in a dry box. The filtrate was taken in a china dish and was concentrated on a water bath and then, the concentrated solution was cooled. Mostly, crystals of pure base separated out on cooling. Addition of petroleum ether also helped in throwing crystals out of solution. The crystals were filtered, washed with petroleum ether and finally dried on a vacuum line to remove the last traces of solvent and moisture if any. The purified solid nitrogen bases were characterized by running an IR spectrum in Nujol mull. The nitrogen bases showed absorptions Ca 3,550 to 3,250 cm\(^{-1}\) range as variable intensity absorptions, for the asymmetric and symmetric N-H stretching vibrations.
Further melting points of the solid bases were observed on a Gallen Kamp melting point apparatus.

**Purification of Liquid Bases**

Mini fractionating assembly, coil condenser, multichanne receivers and quick fit sample tubes were used for the purification of the liquid bases. Multichannel receiver was fitted with quick fit sample tubes. The liquid base was taken in a quick fit conical shaped distillation flask. After setting the apparatus, heating was slowly increased to boiling point of the base. A few drops were collected and then multiple-bend was tilted to recover the pure distillate into another receiving tube. The middle fraction was collected and the last fraction was rejected leaving behind an adequate quantity of the base undistilled. The observed boiling points of the liquid bases are given in table.

The physical properties of different nitrogen bases along with their melting points or boiling points (in case of liquids) are given in table 161 No.1

**Procedure for the Study of Germanium Tetrachloride - Base Interactions**

On both the Bronsted and Lewis concepts of acids and bases, a base includes molecules or ions having atoms with unshared electron pairs in their valence shells that can be donated to a proton or other electron-pair acceptors.
### TABLE 1

Physical Constants table of Nitrogen Bases

| Sr. No. | Name of Bases          | Molecular Weight | Density $\text{g} \text{m}^{-3}$ | Melting Point (Literature) $^\circ\text{C}$ | Melting Point (Observed) $^\circ\text{C}$ | Boiling Point (Literature) $^\circ\text{C}$ | Boiling Point (Observed) $^\circ\text{C}$ | PK  |
|---------|------------------------|------------------|----------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|------------------------|
| 1.      | 4-methyl, 3-nitro aniline | 214.43           |                                  | 117.00                                   | 117.00                                   |                                          |                                        | 2.90                   |
| 2.      | 2-methyl, 5-nitro       | 156.16           |                                  | 134.00                                   | 135.00                                   |                                          |                                        | 2.32                   |
| 3.      | 2-methyl, 4-nitro       | 152.15           |                                  | 108.00                                   | 107.00                                   |                                          |                                        | 0.94                   |
| 4.      | 2-methyl, 3-nitro       | 152.15           |                                  | 97.00                                    | 96.50                                    |                                          |                                        |           |
| 5.      | 2-nitro                 | 148.12           |                                  | 71.50                                    | 71.00                                    |                                          |                                        | -0.29                  |
| 6.      | 2-6 dinitro             | 183.12           |                                  | 142.00                                   | 142.00                                   |                                          |                                        |           |
| 7.      | 4-chloro, 2-nitro       | 172.57           |                                  | 117.00                                   | 117.00                                   |                                          |                                        | -0.94                  |
| 8.      | 2-chloro, 4-nitro       | 172.57           |                                  | 108.00                                   | 109.00                                   |                                          |                                        | -1.03                  |
| 9.      | 1,2-diaminobenzene      | 108.14           |                                  | 102-103                                  | 103.00                                   |                                          |                                        |           |
| 10.     | 1,4-diaminobenzene      | 108.14           |                                  | 139-141                                  | 140.00                                   |                                          |                                        |           |
| 11.     | 3,5-dinitro             | 183.12           |                                  |                                          |                                          |                                          |                                        | -0.22                  |
| 12.     | 4-methyl, 1-3 diamino benzene | 122.17     |                                  |                                          |                                          |                                          |                                        | 2.66                   |
| 13.     | 6,nitroquinoline        | 174.15           |                                  | 153-154                                   | 153.00                                   |                                          |                                        |           |
| 14.     | 2,2-Biquinoline         | 256.31           |                                  | 195-198                                   | 197.00                                   |                                          |                                        | 2.81                   |
| 15.     | 2-Aminopyridine         | 94.10            |                                  | 50-60                                    | 61.00                                    |                                          |                                        | 6.82                   |
| 16.     | 2,2' Bipyridine         | 156.19           |                                  | 69-71                                    | 70.00                                    |                                          |                                        | 4.35                   |
| 17.     | 4-nitroaniline          | 138.12           |                                  | 148.00                                   | 148.00                                   |                                          |                                        | 4.12                   |
| 18.     | Aniline                 | 93.12            | 1.0217                          |                                          |                                         | 182-184                                  | 184.10                   | 4.63                   |
| 19.     | 3-methyl aniline        | 107.16           | 0.9589                          |                                          |                                         | 82.30                                    | 81.00                   | 4.73                   |
| 20.     | Pyridine                | 79.10            | 1.5095                          |                                          |                                         | 114-116                                  | 115.00                   | 5.25                   |
| 21.     | N,N-dimethyl - naphthylamine | 171.23     | 1.0423                          |                                          |                                         | 139-140                                  | 134.00                   | 5.06                   |
| 22.     | 3-methyl pyridine       | 93.10            | 0.9548                          |                                          |                                         | 144.90                                   | 145.00                   | 5.68                   |

---

\[ a \]: 83

\[ b \]: 161

\[ c \]: Determined in present work.
According to Bronsted\(^1\), acids are proton donors but according to Lewis\(^3\) theory, they are electron pairs acceptors. The Lewis acid concept is much wider and such acids form a more general class of substances that include Bronsted acids as a special case. Although proton is an electron pair acceptor, it does not exist in free state in solution but it occurs in the solvated form, i.e., \(\text{H}_3\text{O}^+\) or as the unionized acid form; \(\text{HA}\). During neutralization process these species do not accept an electron pair to form a co-ordinate bond. A hydrogen bond is formed initially between the proton of the acid and the donor electron pair of the base but a covalent bond is only formed when the proton is transferred as shown below:

\[
\text{A} - \text{H}^+ : \text{B} \rightarrow \text{A} - \text{H} = \cdots = \text{B} \rightarrow \text{A}^+ \cdot \text{H} : \text{B} \quad \ldots \ (1)
\]

While the Lewis definition explains that a free proton may be properly regarded as an acid, so proton can be treated as Lewis acid as well, although it is a Bronsted acid. Moreover, the strengths of Bronsted acids and bases are more or less independent of the solvent. While for Lewis acids, relative strengths depend very much on the base with which they are interacting.

Germanium tetrachloride, having boiling point 86.5°C, and molecular weight 214.43, is a covalent monomeric compound.
having tetrahedral structure. Although the properties of germanium tetrachloride are known as Lewis acid. However, no investigations have been reported on the quantitative study of germanium tetrachloride as a Lewis acid. In the present work, germanium tetrachloride is used as a Lewis acid. The interaction of germanium tetrachloride with different types of nitrogen bases (as Lewis bases) in ortho dichlorobenzene as solvent are investigated.

All purified samples, the bases, the acid and the solvents were placed in a dry box. The manipulations involving germanium tetrachloride (including the filling of the spectrophotometer cells) were carried out in the dry box as well. Stock solutions were made by weight, solutions for optical measurements were made in 10 cm$^3$ or 5 cm$^3$ measuring flasks by taking the appropriate volumes of the stock solutions of the halide and the base. In all the interactions reported, in the present study, the stoichiometry base concentration was kept constant, and the halide (germanium tetrachloride) concentrations were varied.

**Spectroscopic Studies**

The acid-base interactions in the present work, have been studied by UV and Visible Spectrophotometry. The basic principles of the technique used in studies are as follows:
Basic Theory

There are two types of electronic spectra: Emission and Absorption spectra. Emission spectra is concerned with the analysis of the emitted light by a luminous source. While absorption spectra is obtained by spectroscopic analysis of the light transmitted by an absorbing medium, which is placed between the source of light and spectrophotometer. When a molecule absorbs radiation, its energy increases. This increase is equal to the energy of the photon absorbed as expressed by the relation

$$E = hv = \frac{hc}{\lambda}$$ ...

where $h$ is the plank's constant, $v$ and $\lambda$ are the frequency and wave-length of high radiation respectively and $c$ is the velocity of light. The change (or increase) in energy may be manifested in the form of changes in electronic, vibration or rotational energies of the molecule.

The electronic energy changes require greater amount of energy in the form of quanta, changes in vibration energy involve smaller quantities of energy and changes in rotational energy involve quantas even smaller than those required for the viberrational energy changes. Therefore electronic energy levels under normal conditions are called the ground states. The higher energy levels represent the first and second
excited states respectively. For each electronic level, there are ground and several possible excited states.

**Electronic Spectral Regions**

The visible and ultra-violet region \((3 \times 10^4 \text{–} 3 \times 10^7 \text{ Hz})\) extends from 1 \(\mu\text{m} \text{–} 10\) nm wave length. The 200 - 850 nm region form the basis of electronic spectroscopy. The visible region ranges between wave lengths 350 nm – 850 nm, and the region is sensitive to the human eye. The ultra-violet region may be sub-divided as (a) near ultra-violet region wave lengths 200 nm and 350 nm, and (b) Far Ultra violet or vacuum ultra violet region below 200 nm wave length.

**Spectrophotometry**

Beer and Lambert gave the law of light absorption which defines that the fraction of incident light absorbed is proportional to the number of molecules in the path, and if a substance dissolved in a solvent, the absorption of light is proportional to its molecular concentration, provided the solvent itself does not show any absorption in that particular region. The law can mathematically be stated as

\[
A = \log_{10} \left( \frac{I_0}{I_t} \right) = \epsilon \cdot C \cdot l.
\]

\(\epsilon\) = Absorption or extinction co-efficient

\(l\) = Path length in cm

\(C\) = Concentration expressed in gm moles/litre.
When 'C' is expressed in gm moles/litre and length in cm, then absorption co-efficient \( \epsilon \) becomes Molar Extinction Co-efficient. If the molecular weight of substance is known, the expression \( \frac{E_{1cm}}{1\%} \) is often used and can be related to by the following equation:

\[
E_{1cm} = \frac{\epsilon \times 10}{\text{Molecular weight}}
\]

such deviations may be due to:

1. Molecular association of the solute at high concentrations.
2. Ionization of solute in case of acids, bases and salts.
3. Fluorescence of the solute
4. Poor transmission of the solvent.

The intensity of absorbance for an electron transition at any wave length, is governed by the probability of the transition and the size of the absorbing molecule. The absorption maximum of a band corresponds to the most probable transition in that region of absorption. Therefore, the extinction co-efficient may be expressed as:

\[
\epsilon = K P a
\]

\( K = \text{Constant} \quad P = \text{Probability} \quad a = \text{Area of cross-section of molecule} \)
Measurements were made, using stoppered silica cells having one cm path length. The spectra were run on either SP8-400 UV/VIS PYE-UNICAM recording spectrophotometer or on 100-40 UV/VIS Hitachi spectrophotometer. For each concentration, fresh solution was made for recording the electronic spectra at 25°C. After recording the spectra, a suitable wave-length was selected for carrying on calculations.

Two types of spectral changes occurred. In most of the cases, the base absorbance band was knocked down by increasing concentrations of the acid and the adduct (if of the anilinium ion type) had its absorbance on the shorter wave-length side of the original base absorption. The other type of spectral change was observed where charge transfer band was obtained, as the new band came up on the longer wave-length side of the base bands. Whereas the original base absorption was knocked down correspondingly. After recording the spectra, a suitable wave-length was selected for carrying calculations. The equilibrium constant was determined by the formula as given below:

\[
\text{Acid} + \text{Base} \rightarrow \text{Adduct} \quad \ldots (25)
\]

\[
K = \frac{(\text{Adduct})_{\text{Eq}}}{(\text{Acid})_{\text{Eq}} (\text{Base})_{\text{Eq}}} \quad \ldots (26)
\]

\[
pK = -\log K = -\log \frac{1}{(\text{Acid})_{\text{Eq}} (\text{Base})_{\text{Eq}}} \quad \ldots (27)
\]
preparation of Germanium Tetrachloride Stock Solution

The stock solution of germanium tetrachloride was prepared by weighing ampoules. When an ampoule of germanium tetrachloride was used, the weight of germanium tetrachloride was determined by breaking the ampoule in a 25 cm$^3$ pre-weighed measuring flask containing about 10 cm$^3$ of ortho-dichlorobenzene solvent. The solvent was transferred into the flask in a dry box. The flask was stoppered and weighed again. The weight of germanium tetrachloride transferred into the flask was thus determined. Then by adding more solvent into the flask the volume was made up to the mark. The molarity of the stock solution of germanium tetrachloride was calculated as follows:

\[
\text{Molarity} = \frac{\text{Weight of Germanium Tetrachloride} \times 1000}{\text{Total volume made} \times \text{Molecular weight of germanium tetrachloride}}
\]

The stock solution of germanium tetrachloride, thus prepared, was used for making the various concentrations of the acid.

As an example, referring to the table (§)

1.05119 x 10$^{-2}$M stock solution of germanium tetrachloride was prepared by the procedure mentioned above for studying the acid-base interaction in ortho dichlorobenzene as a solvent. Since the concentration of the stock solution of germanium tetrachloride used was many fold greater than
the stoichiometric concentration of the base used (3-methyl aniline). Therefore, dilutions of the stock solution of germanium tetrachloride were prepared.

Preparation of the Base Stock Solution

A weighed quantity of the base under observation was taken in a 25 cm$^3$ flask. Then 10cm$^3$ ortho dichlorobenzene solvent was added into the measuring flask with the help of graduated pipette, and the solution was shaken well to dissolve the base completely. The volume was made up to the mark with the solvent. A known volume of the base stock solution was taken in a 10 cm$^3$ measuring flask; which was then diluted with the pure dry solvent and volume was made up to the mark. The base solution, thus prepared had the molarity in the $10^{-4}$ M range. Referring to table No. (8) 4.8525 x $10^{-3}$ M stock solution of 3-methyl aniline was prepared by dissolving 0.013 gms of the base in the solvent in a 25 cm$^3$ measuring flask and the volume was made up to the mark. Then 0.5 cm$^3$ stock solution of the base was diluted to 10 cm$^3$ with pure dry solvent, for spectroscopic measurements. The molarity of 3-methyl aniline base was calculated to be as 2.426 x $10^{-4}$ M. Thus stoichiometric concentration of the base was kept the same for each measurement.
Preparation of the Germanium Tetrachloride-Base Adduct Solution

For preparing the adduct solutions, the stoichiometric concentration of a base was kept constant and the stoichiometric concentrations of germanium tetrachloride were varied. In case of 3-methyl aniline base, eight 10 cm$^3$ clean dry measure flasks were taken. In each flask 0.5 cm$^3$ of the base stock solution ($4.8525 \times 10^{-3}$ M) was transferred. The volume of the first flask was completed without the addition of the Lewis acid. In the remaining (numbered flasks) varying stoichiometric concentrations of germanium tetrachloride were mixed and volumes were made with the solvent. The concentration of the acid was varied ($0.00 - 12.720 \times 10^{-4}$ M range, while the base concentration remains consistent in all the flasks.

Recording of Spectra

The solvent o-dichlorobenzene, was placed in 1 cm cell as reference and pure base solution No.1 was taken in another silica cell. The matched cells were filled and stoppered in a dry box. First of all pure base was run and then adduct solutions having varying stoichiometric concentrations of germanium tetrachloride were run in the visible region, 230-295 nm. The maximum absorbing wave-length ($\lambda_{\text{Max}}$) for the pure base was noted as 295 nm, and absorbance at 295 nm was observed ($A = 0.487$). Similarly
the absorbance of all other adduct solutions having varying concentrations of germanium tetrachloride were observed at 295 nm \( (\lambda_{\text{Max}}:). \) It was observed that as the stoichiometric concentration of the acid in adduct solutions increased, the absorbance decreased correspondingly. All the acid-base interactions were not alike. There were cases, where with solutions, the absorbance also increased correspondingly.

**Method for Calculation**

(Refering to table No.3 and figure No.10) Molarity of stock solution of 3-methyl aniline = \( 4.852 \times 10^{-3} \text{M} \).
Volume of the base taken in 10 cm\(^3\) flask = 0.5 cm\(^3\).

\[
(\text{Base})_{\text{Stoich}} = 2.426 \times 10^{-4} \text{M}
\]

\( \lambda_{\text{Max}}: \) for 3-methyl aniline base = 295 nm

Absorbance of pure base solution at 295 nm = 0.487.
So, molar extinction co-efficient \( (\epsilon) \), for the base can be determined as:

\[
\epsilon = \frac{A}{C}
\]

where 'A' is absorbance of the base at maximum wave-length 'C' is the stoichiometric concentration of the base. Therefore, molar extinction co-efficient for the 3-methyl aniline base was calculated ( \( \epsilon = 2007.419621 \)); then log of molar
extinction co-efficient was determined as (log $\epsilon = 3.30$).

The molar concentration of pure base present at equilibrium in any solution can be calculated:

$$\text{(Base)}_{\text{Eq}} = \frac{A}{\epsilon}$$

Thus molar concentrations of the base at equilibrium for adduct solutions, having different concentrations of the acid were determined at the respective maximum absorption values, which showed a decrease with increasing acid concentrations. The molar concentration of the adduct formed in solution at equilibrium, can be determined by subtracting the equilibrium concentration of the base from the stoichiometric concentrations or the base used. Thus knowing the equilibrium concentration of the adduct, the same was subtracted from the stoichiometric concentration of the acid in order to obtain the equilibrium concentration of the acid present at equilibrium.

Knowing the equilibrium concentration of the base and the adduct, the pK value for the interaction $\&$ was computed. 5-7 different concentrations of the acid were used. The pK values thus obtained, for each mixture, were averaged.

In case of 2-Aminopyridine-Germanium tetrachloride interaction in ODB, and 4-methyl, 3-nitro aniline in Ether, the absorbance of the adduct was increased with increasing
concentration of the solution. As far as the methods of preparation of germanium tetrachloride solution, base solution and adduct solutions are concerned, procedure adopted has already been discussed on the preceding pages, e.g., the base solution (of 2-Amino pyridine) thus prepared had the molarity in the $10^{-4}$M range. Referring to table No. [19], 1.700 x $10^{-4}$M stock solution of base was prepared. For the preparation of the adduct solutions the stoichiometric concentration of the acid was varied (1.071-52.60U)x $10^{-3}$M range, keeping the stoichiometric concentration of the base constant in all adduct solutions.

Spectra was recorded (in the same way as mentioned in the case of 3-methyl aniline) in the visible region 295 to 300 nm. The maximum absorbance of the pure base was observed at maximum wave-length (300 nm) as 0.540. The absorbance for all the adduct solutions having varying concentrations of acid were observed at 310 nm ($\lambda_{Max}$) as indicated in Fig. 2). The absorbance of the adduct solution increases with increasing concentration of germanium tetrachloride due to charge transfer. Therefore, calculations were different from previous ones.

Method for Calculation of $pK$ for 2-Amino pyridine interaction with Germanium tetrachloride solution in O.D.B. solution

Referring to table No. [19] and Fig. No. 21

Molarity of stock solution of 2-Amino pyridine = 4.00 x $10^{-3}$M.
(Base)_{Stoich \ used} = 1.7 \times 10^{-4} \text{M}

\lambda_{Max}: \text{for the adduct solution} = 310 \text{ nm}

Absorbance of pure base at 310 nm = 0.300

Molar Extinction Co-efficient \ (\epsilon) \ was determined
by finding the D Value graphically Fig. 22 and
equilibrium concentrations were determined. The ratio of
concentration of adduct/base at equilibrium was determined
from the spectra by the following equation (Table No. 19).

\[
\frac{(\text{Adduct})}{(\text{Base})} = \frac{D - D_0}{D_\infty - D}
\]

where 'D_0' is the minimum absorbance for the base. 'D_\infty' is the maximum absorbance on addition of germanium tetrachloride and 'D' is the absorbance of any mixed solution at the same chosen wave-length.

The pK value was calculated by two methods.

(i) By applying the formula:

\[
pK = -\log \frac{1}{(\text{Acid})_{Eq}} \cdot \frac{(\text{Acid})}{(\text{Base})}
\]

value of \((\text{Adduct})/(\text{Base})\) was taken from the spectra.

(ii) Graphical Method:

A graph was plotted Fig. 22 and table 19
between (Adduct)/(Base) ratio from the spectra and acid stoichiometric concentrations. A straight line was obtained and pK value was obtained.

It was found that pK values obtained by both the methods, agreed very closely.

**Measurement of pKₐ**

The pKₐ can be mathematically represented as

\[
pK_{BH^+} = \log \frac{C_{BH^+}}{C_B \cdot C_{H^+}} + \log \frac{[BH^+]}{[B] \cdot [H]} \quad \ldots \quad (29)
\]

For very dilute solutions in water, the value of activity coefficients are taken to be unity. Since base concentration is always extremely small, therefore, it is equivalent to the following expression:

\[
pK_{BH^+} = \lim_{C_A \to 0} e \left[ \log \frac{C_{BH^+}}{C_B} - \log C_{H^+} \right] \quad \ldots \quad (30)
\]

where 'Cₐ' is the molar concentration of a strong acid in water. For a strong acid, the concentration of the Bronsted acid, Cₜₐ can be calculated by the following relations:

\[
C_A = C_{H^+} + C_{BH^+} \quad \ldots \quad (31)
\]

assuming that a base is added in its uncharged form. Therefore
for a base whose ionization ratio can be directly measured in dilute aqueous solutions of strong acids, the $pK_a$ value can be calculated from the observed values of $C_A$ and $(C_{BH^+} / C_B)$. The expression:

$$\lim_{C_A \to 0} \left( \log \frac{C_{BH^+}}{C_B} - \log C_{H^+} \right)$$

varies with the concentration of the electrolyte up to at least 2 M concentration.

In general, the stock solutions of the bases were prepared by dissolving a known weight in a minimum quantity of ethanol and volume was made up with distilled water. The concentration of the stock solutions prepared had the concentration in the $1.0 \times 10^{-3}$ M range. The concentration was adjusted in accordance with the molar extinction coefficient values at the maximum absorbance. For the stock solution of the base $1.0 \text{ cm}^3$ was transferred into the number of $10 \text{ cm}^3$ flasks, and volume was made with distilled water.

For preparing 0.5 M solution of perchloric acid, exactly $40 \text{ cm}^3$ of $1.25 \text{ M}$ standardized acid (E. Merck Grade) was transferred into a $100 \text{ cm}^3$ measuring flask and made up the volume with distilled water. The stock solution of perchloric acid, thus prepared, was used for making various concentrations of the acid. For those bases which were insoluble
in water, ethyl alcohol was used as solvent. Therefore, that particular solvent which was used for the preparation of the base solution, was also used for preparing acid solution as well. For example stock of perchloric acid was prepared by taking 0.06 cm$^3$ of 6.5 M perchloric acid with the help of graduated pipette into a 25 cm$^3$ flask. Then by adding ethyl alcohol as a solvent into the flask, the volume was made up to the mark. Since the concentration of perchloric acid, thus prepared was much larger than the base concentration, therefore, further dilutions of stock solutions were carried out.

For the preparation of the adduct BH$^4$ solution, a fixed stoichiometric concentration of the base and varying stoichiometric concentrations of perchloric acid were mixed in 10 cm$^3$ measuring flasks. In case of 2,2-Biquinoline five 10 cm$^3$ (numbered) flasks were taken. In each flask 0.06 cm$^3$ of the base stock solution was added with the help of a graduated pipette. The volume was made with ethyl alcohol without adding perchloric acid in the flask. In the rest of the four flasks different stoichiometric concentrations of perchloric acid were transferred and volumes were made up to the mark with solvent. In each solution of the base, the perchloric acid concentration was varied from 0.00—$9.6000 \times 10^{-3}$ M. Whereas the base concentration was kept constant $0.28 \times 10^{-4}$ M. The more basic bases were
required the lesser was concentration of perchloric acid as compared with the less basic nitrogen donors with the successive increase in the acid concentration.

The solvent ethyl alcohol or ethanol-water mixture was used as reference in one cell and pure base solution prepared in the flask number I was transferred into the other cell and stoppered. Absorbance spectra were recorded in the 180 – 500 nm region. The spectral changes for the 2,2'-Bipyridine, N,N-dimethyl-2-naphthyl amine, 2,2'-Biquinoline and 4-methyl, 1,3-diaminobenzene, bases are shown in Fig. 1, 3, 5 and 7.

On addition of perchloric acid, the absorption spectra of the bases were observed to show a decrease in absorbance. As the base reacts with the acid, the formation of BH⁺ species takes place. The anilinium ions absorb on the short wave-length side of the base absorbance. Therefore, the absorption band of the free base was decreased with increasing perchloric acid concentration. The decreasing absorbance was considered to be the consequence of removal of base to form the BH⁺ species. At the maximum absorbance, wave-length of the base, the ratio of the protonated to unprotonated base were determined. For higher concentration of perchloric acid, formula\(^{\prime}\) \[ C_A = C_{H^+} + C_{BH^+} \] was employed. The Hammett's acidity function \( H_0 \) values were used as given in the literature.
For the more basic bases, where only a smaller concentration of perchloric acid was required for a complete conversion of the base into BH\(^+\) entity, equation:
\[
P^k_{BH^+} = \log \frac{C_{BH^+}}{C_B \cdot C_{H^+}} + 10q \frac{C_{H^+}}{C_{H^+}}
\]
was used. The \(pK_a\) values, thus obtained for each base, showed somewhat inconsistent behaviour. Therefore, graphical method of Mata, Leal and Garcia was followed. For each base, plots of perchloric acid concentration against
\[
\{ \log \frac{C_{BH^+}}{C_B} - \log C_{H^+} \}
\]
gave straight lines. The extrapolation of the straight lines gave \(pK_a\) values, where perchloric acid concentration is tending to be zero. These plots were shown in Fig. 2.4, 6 and 8. The values obtained by the intercepts on the \(pK_a\) co-ordinate are taken as exact and true value of \(pK_a\).
RESULTS

AND

DISCUSSION
DISCUSSION FOR pK_a VALUES

The pK_a Values of some Nitrogen Bases

The classical definition of a base, as given by Bronsted and Lowry, regarding bases as species which are capable of forming protonated entities, while Lewis considered basicity as an ability of an electron donor to donate an electron pair to form a covalent bond with an acceptor. Both concepts are equivalent as far as bases are concerned. The electron pairs donated by bases are indicated by unshared pair of electrons. In general, an acid-base interaction may be written as:

\[ \text{Acid}_1 + \text{Base}_2 \rightarrow \text{Base}_1 + \text{Acid}_2 \quad \ldots \quad (1) \]

\[ \text{H}^+ + \text{Base} \rightarrow \text{BH}^+ \quad \ldots \quad (35) \]

Proton Base

when the standard acid is water, the equilibrium for uncharged bases is reduced to the following equations:

\[ \text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^- \]

\[ K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad \ldots \quad (36) \]

where 'K_b' is the basicity constant. If H_3O^+ is taken as the standard acid, the equilibrium for uncharged bases becomes
\[ B + H_3O^+ \rightarrow BH^+ + H_2O \] \[ (37) \]

\[ K_a = \frac{[B][H_3O^+]}{[BH^+]} \] \[ (38) \]

'\( K_a \)' is also represented as \( K_{BH^+} \) which is the dissociation constant for the conjugate acid, \( BH^+ \) can be used to measure the basicity of the base. For weak bases, the value of \( K_B \) is negligible and only \( K_a \) quantity is measurable. Later on, Hammett measured the \( K_a \) values for extremely weak bases. His basic assumption was that the ratio of activity coefficients for bases and protonated base are equal for all the bases of the same charge, therefore,

\[ K_a = \frac{(B)}{(BH^+)} \cdot aH^+ \cdot \frac{f_B}{f_{BH^+}} \] \[ (39) \]

where

\[ a \cdot \frac{B}{BH^+} = h_0 \]

'\( aH^+ \)' denotes hydrogen ion activity and 's denotes molar concentration activity co-efficients. '\( h_0 \)' is a quantitative measure of acidity of the medium. It is related to \( H_0 \) by the following equation:

\[ H_0 = -\log h_0 \] \[ (40) \]

The '\( H_0 \)' is an acidity function. It is a quantitative measure of acidity conceived by Hammett and Deyrup. It is
derived from ionization equilibria of a particular class of indicators represented as:

\[ B + H^+ \longrightarrow BH^+ \] ...

and is defined by the following equation:

\[ H_0 = pK_a - \log \frac{C_{BH^+}}{C_B} \] ...

where \( C_{BH^+}/C_B \) is a concentration ratio of the base in its two forms, and the function \( H_0 \) is a measure of the extent to which the proton is transferred to an uncharged base in solution. The increase in negative values corresponding to the increase in acidity. Therefore, \( H_0 \) acidity scale is used for measuring the base strength of very weak uncharged bases.

The \( K_{BH^+} \) or \( K_a \) is the thermodynamic ionization constant of conjugate acid in terms of molar concentration in dilute aqueous solutions.

The nitrogen bases used in the present work varied greatly in their basic strengths. The bases, selected covered the range of \( pK_a = 6.82 \) for the most basic base and \( pK_a = -1.03 \) for the least basic base; as far as practically possible. The bases having \( pK_a \) values greater than 6.82 gave precipitation while studying their interaction with germanium tetrachloride in ortho dichlorobenzene or in ether. The \( pK_a \) values of most of the bases have already been given in the literature. But the \( pK_a \) values of
1,2-diaminobenzene, 1,4-diaminobenzene, 6-nitroquinoline, 2-methyl, 3-nitroaniline and 2,6-dinitroaniline are not available in the literature. In case of the base 2,2' -Bipyridine, the value of pK_a is checked to ascertain its more accurate value.

The spectra for these four bases are shown in Fig. 1 3 5 and 7. Extrapolation graphs are drawn in Fig. 2, 4, 6 and 8. The pK_a determinations are shown in table No. 3, 4, 5 and 6.

The pK_a values of the four nitrogen bases, as determined in present investigations, are shown below:

<table>
<thead>
<tr>
<th>Nitrogen Bases</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2,2'-Bipyridine</td>
<td>4.12</td>
</tr>
<tr>
<td>2. N,N'-Dimethyl-α-naphthylamine</td>
<td>3.71</td>
</tr>
<tr>
<td>3. 2,2'-Biquinoline</td>
<td>2.82</td>
</tr>
<tr>
<td>4. 4-Me, 1,3-diaminobenzene</td>
<td>2.66</td>
</tr>
</tbody>
</table>

These values indicate a quantitative comparison of the strengths of these bases towards a Bronsted acid. The already quoted pK_a value for 2,2'-Bipyridine (4.35) has been refined to be 4.12. This base seems to offer no steric hindrance to a proton, whereas the MX_n compounds case indicate significant hindrance towards the adduct formation as it is shown at a later stage in the present study.
However, in case of N,N-dimethyl-α-naphthylamine the value (3.71) differs from literature value (4.566).

In the case of bidentate donor bases, only the protonation of 1st donor centre has been studied. However, the second protonation equilibrium could have been obtained by an excessive use of the perchloric acid concentrations as given for the benzene disubstituted diamines. Since the bidentate donor bases for only 1:1 adducts with germanium tetrachloride. Therefore, for the sake of comparison, our interest was only to know the $pK_a$ values of such bases for their first protonation only. The $pK_a$ values of all the nitrogen bases used in the present work are shown in table 2 given on the next page.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Aniline derivatives</th>
<th>$pK_a$</th>
<th>Sr. No.</th>
<th>Nitrogen Bases</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3-methyl-</td>
<td>4.73$^b$</td>
<td>12.</td>
<td>2-Amino Pyridine</td>
<td>6.82$^b$</td>
</tr>
<tr>
<td>2.</td>
<td>Aniline</td>
<td>4.63$^b$</td>
<td>13.</td>
<td>Pyridine</td>
<td>5.52$^b$</td>
</tr>
<tr>
<td>3.</td>
<td>2-methyl,3-nitro-</td>
<td>-</td>
<td>14.</td>
<td>N,N'-dimethyl-α-naphthyl amine</td>
<td>4.566$^b$</td>
</tr>
<tr>
<td>4.</td>
<td>4-methyl,3-nitro-</td>
<td>2.90$^a$</td>
<td>15.</td>
<td>2,2',Bipyridine</td>
<td>4.35$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.12*</td>
</tr>
<tr>
<td>5.</td>
<td>2-methyl,5-nitro-</td>
<td>2.32$^a$</td>
<td>16.</td>
<td>2,2',Biquinolone</td>
<td>2.815*</td>
</tr>
<tr>
<td>6.</td>
<td>2-methyl,4-nitro-</td>
<td>0.94$^a$</td>
<td>17.</td>
<td>4-methyl,1-3 diamino benzene</td>
<td>2.66*</td>
</tr>
<tr>
<td>7.</td>
<td>2-nitro-</td>
<td>-0.29$^a$</td>
<td>18.</td>
<td>1,2-diaminobenzene</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>2,6-dinitro-</td>
<td>-</td>
<td>19.</td>
<td>1,4-diaminobenzene</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>2-chloro,4-nitro-</td>
<td>-0.94$^a$</td>
<td>20.</td>
<td>6-nitroquinolone</td>
<td>-</td>
</tr>
<tr>
<td>10.</td>
<td>4-chloro,2-nitro-</td>
<td>-1.03$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>3,5-dinitro-</td>
<td>0.22$^c$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a = .83$

$b = 161$

$c = 142$

$* =$ Determined in present work.
The bases selected are nitrogen donor type which may be classified as follows:

Type A     Aniline derivatives
Type B     Pyridine, Bipyridine, Quinoline and their derivatives
Type C     Diamines

Interaction of these three different types of nitrogen donor bases have been investigated with germanium tetrachloride in aprotic media. The media for study of such interactions being ortho dichlorobenzene and Ether as reported in the following pages.
TABLE 3

\[ \text{pK}_a \text{ determination of 2-2',Bipyridine in water at 25°C} \]

\[
\begin{align*}
\text{(Base)}_{\text{Stoich}} & = 0.2448 \times 10^{-4} M \\
\lambda_{\text{Max: for the base}} & = 290 \text{ nm} \\
\log \epsilon_{290} & = 4.21 \\
[\text{Perchloric acid}]_{\text{Stoich}} & = [0.040 - 0.100] \times 10^{-4} M
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Adduct]_{\text{Stoich}} Mx10^4</th>
<th>Absorbance at maximum wave-length at 290 nm</th>
<th>[Base]_{\text{Eq}} Mx10^4</th>
<th>[Adduct]_{\text{Eq}} Mx10^4</th>
<th>\log \frac{[\text{Adduct}]}{[\text{Base}]}</th>
<th>\text{pK}<em>a = \text{Lim}</em>{C_{\text{B}} \to 0} \left[ \log \frac{[\text{Adduct}]}{[\text{Base}]} \right]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.400</td>
<td>0.2448</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.040</td>
<td>0.370</td>
<td>0.2264</td>
<td>0.0184</td>
<td>-1.0900</td>
<td>4.31</td>
</tr>
<tr>
<td>3.</td>
<td>0.080</td>
<td>0.325</td>
<td>0.1989</td>
<td>0.0459</td>
<td>-0.6382</td>
<td>4.46</td>
</tr>
<tr>
<td>4.</td>
<td>0.100</td>
<td>0.278</td>
<td>0.1701</td>
<td>0.0747</td>
<td>-0.3574</td>
<td>4.64</td>
</tr>
</tbody>
</table>

Value of pK$_a$ from graph = 4.12

pK$_a$ value from plot of acid conc. Vs. pK$_a$ (Fig. 2) = 4.12
Fig. 1 Electronic spectra of 2,2'-Bipyridine (0.2448x10^{-4} M) containing different concentrations of Perchloric acid in water at (Mx10^{-4}) (1) 0.000, (2) 0.040, (3) 0.080, (4) 0.100
Fig. 2 A plot of 2,2'-bipyridine experimental $pK_a$ values Vs. hydrogen ion concentrations for extrapolating at infinite dilution.
TABLE 4

Determination of $pK_a$ value of N,N-Dimethyl-$\alpha$-naphthyl amine in water at 25°C

$\lambda_{\text{Max}}$ for the base = 300 nm

\[ \log \epsilon \approx 4.02 \]

(Base)\text{Stoich} = 0.642 \times 10^{-4} \text{M}

(Perchloric acid)\text{Stoich} = (0.04 - 8.00) \times 10^{-4} \text{M}

<table>
<thead>
<tr>
<th>Sr No</th>
<th>[Acid]\text{Stoich} Mx10^4</th>
<th>Absorbance of the base at 300 nm</th>
<th>[Base]\text{Eq} Mx10^4</th>
<th>[Adduct]\text{Eq} Mx10^4</th>
<th>$\log \left( \frac{\text{Adduct}}{\text{Base}} \right)$</th>
<th>$pK_{BH}^{+} = \lim_{C_A \to 0} \left( \frac{\text{Adduct}}{\text{Base}} \right)$</th>
<th>$-\log (\text{Acid})$ S</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>0.68</td>
<td>0.642</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.04</td>
<td>0.58</td>
<td>0.547</td>
<td>0.095</td>
<td>-0.7602</td>
<td>4.63</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>0.50</td>
<td>0.55</td>
<td>0.519</td>
<td>0.123</td>
<td>-0.6252</td>
<td>3.67</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>0.80</td>
<td>0.48</td>
<td>0.453</td>
<td>0.189</td>
<td>-0.3796</td>
<td>3.72</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2.00</td>
<td>0.40</td>
<td>0.377</td>
<td>0.265</td>
<td>-0.1531</td>
<td>3.54</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>3.00</td>
<td>0.34</td>
<td>0.321</td>
<td>0.321</td>
<td>0.0000</td>
<td>3.52</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>5.00</td>
<td>0.31</td>
<td>0.293</td>
<td>0.349</td>
<td>+0.0759</td>
<td>3.37</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>6.00</td>
<td>0.28</td>
<td>0.264</td>
<td>0.378</td>
<td>+0.1559</td>
<td>3.37</td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>8.00</td>
<td>0.28</td>
<td>0.264</td>
<td>0.378</td>
<td>+0.1559</td>
<td>3.25</td>
<td></td>
</tr>
</tbody>
</table>

$\ pK_a \ value \ from \ graph = 3.71$

$\ pK_a \ value \ from \ plot \ of \ acid \ conc. \ vs. \ pK_a \ (\text{Fig. 4}) = 3.71$
Fig. 3 Electronic spectra of N,N-dimethyl-η-naphthyl amine (0.642x10^{-4} M) containing different concentrations of perchloric acid in water at 25° (Mx10^{-4}) (1) 0.00, (2) 0.04, (3) 0.05, (4) 0.80, (5) 2.00, (6) 3.00, (7) 5.00, (8) 6.00, (9) 8.00
Fig. 4 A plot of N,N-dimethyl-α-naphthyl amine pKₐ values vs hydrogen ion concentrations for extrapolating at infinite dilution.
TABLE 5

Determination of $pK_a$ value for 2-2',Biquinoline in water at 25°C

$[\text{Base}]_{\text{Stoich}} = 0.234 \times 10^{-4} \text{M}$

$\lambda_{\text{Max}}$ for the base = 326 nm

$\log < 326 = 4.36$

$[\text{Perchloric Acid}]_{\text{Stoich}} = [3.600 - 9.600] \times 10^{-4} \text{M}$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>$[\text{Acid}]_{\text{Stoich}} \times 10^{-4}$</th>
<th>Absorbance of the base at 326 nm</th>
<th>$[\text{Base}]_{\text{Eq}} \times 10^{-4}$</th>
<th>$[\text{Adduct}]_{\text{Eq}} \times 10^{-4}$</th>
<th>$\log \left[\frac{\text{Adduct}}{[\text{Base}]}\right]_{A=p}$</th>
<th>$pK_a = \text{Lim}_{A \rightarrow p}$</th>
<th>$\log \left[\frac{\text{Adduct}}{[\text{Base}]}\right] - \log [\text{Acid}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.00</td>
<td>0.535</td>
<td>0.2340</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>3.60</td>
<td>0.410</td>
<td>0.1794</td>
<td>0.0547</td>
<td>-0.5158</td>
<td>2.928</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>6.00</td>
<td>0.315</td>
<td>0.1378</td>
<td>0.0962</td>
<td>-0.1559</td>
<td>3.066</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>8.40</td>
<td>0.230</td>
<td>0.1006</td>
<td>0.1334</td>
<td>+0.1226</td>
<td>3.198</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>9.60</td>
<td>0.190</td>
<td>0.0831</td>
<td>0.1509</td>
<td>+0.2591</td>
<td>3.277</td>
<td></td>
</tr>
</tbody>
</table>

Value of $pK_a$ from graph = 2.815

$pK_{\text{BH}}^+$ value from plot of acid conc. Vs. $pK_{\text{BH}}^+$ (Fig. 6) = 2.815
Fig. 5  Electronic spectra of 2,2'-Biquinoline (0.234x10^{-4} M) containing different concentrations of Perchloric acid in water at 25°(Mx10^{-4})

(1) 0.00, (2) 3.60, (3) 6.00, (4) 8.40, (5) 9.60
Fig. 6 A plot of 2,2'-biquinoline $pK_a$ value vs hydrogen ion concentrations for extrapolating at infinite dilution.
### TABLE 6

Determination of $\text{pK}_a$ value for 4-methyl, 1-3 diaminobenzene in water at 25°C

$$
\text{(Base)}_{\text{Stoich}} = 0.2946 \times 10^{-4} \text{M}
$$

$\lambda_{\text{Max}}$ for the base = 200 nm

$$
\log \xi_{200} = 4.53
$$

$$
[\text{Perchloric acid}]_{\text{Stoich}} = [1.00 \ 60.00] \times 10^{-4} \text{M}
$$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Acid $\text{Stoich}$ $\times 10^{-4}$</th>
<th>Absorbance of the base at 200 nm $\times 10^4$</th>
<th>Base $\text{Eq}$ $\times 10^4$</th>
<th>Adduct $\text{Eq}$ $\times 10^4$</th>
<th>log $\frac{\text{Adduct}}{(\text{Base})}$</th>
<th>$\text{pK}<em>{BH}^+ = \text{Lim}</em>{C_{\text{A}}\to 0} \left[ \log \frac{\text{Adduct}}{(\text{Base})} - \log(\text{Acid}) \right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.000</td>
<td>0.2946</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.000</td>
<td>0.890</td>
<td>0.2622</td>
<td>0.0324</td>
<td>-0.9081</td>
<td>3.09</td>
</tr>
<tr>
<td>3.</td>
<td>3.000</td>
<td>0.880</td>
<td>0.2592</td>
<td>0.0354</td>
<td>-0.8646</td>
<td>2.66</td>
</tr>
<tr>
<td>4.</td>
<td>5.000</td>
<td>0.835</td>
<td>0.2460</td>
<td>0.0486</td>
<td>-0.7042</td>
<td>2.60</td>
</tr>
<tr>
<td>5.</td>
<td>13.000</td>
<td>0.610</td>
<td>0.1797</td>
<td>0.1149</td>
<td>-0.1942</td>
<td>2.50</td>
</tr>
<tr>
<td>6.</td>
<td>50.000</td>
<td>0.265</td>
<td>0.0780</td>
<td>0.2166</td>
<td>+0.4435</td>
<td>2.74</td>
</tr>
<tr>
<td>7.</td>
<td>60.000</td>
<td>0.210</td>
<td>0.0618</td>
<td>0.2328</td>
<td>+0.5760</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Value of $\text{pK}_a$ from graph = 2.66

$\text{pK}_{BH}^+$ value from plot of acid conc. Vs. $\text{pK}_a$ (Fig. 8) = 2.66
Fig. 7  Electronic spectra of 4-methyl,1,3-diaminobenzene($0.2946 \times 10^{-4} \text{M}$) containing different concentrations of Perchloric acid in water at 25° ($M \times 10^{-4}$) (1) 0.00, (2) 1.00, (3) 3.00, (4) 5.00, (5) 13.00, (6) 50.00, (7) 60.00
Fig. 5: A plot of 4-methy-1,3-diamino benzene pKa value vs hydrogen ion concentrations for extrapolating at infinite dilution.
Interactions of Germanium tetrachloride with N-donor Bases in o-dichlorobenzene

Germanium tetrachloride shows interactions with different types of nitrogen bases. The bases chosen for this study may be placed in two different groups.

The group first included the derivatives of aniline bases. A number of substituents are varied on the benzene nucleus so as to reduce or enhance the basic character of NH₂ group in this group of bases. Thus aniline derivatives are selected in such a way that the largest basicity is studied with the Lewis acid as far as practically possible. The pKₐ values of this group of bases varied from 4.73 to -1.03 (Table 7). Therefore, the most basic aniline derivative, 3-methyl aniline having (pKₐ = 4.73), is 5.75×10¹ times more basic than the least basic 4-chloro, 2-nitro aniline having pKₐ value equal to -1.03.

All the bases; serial No.1-9 (Table 7) showed measureable interaction in ODB solvent. The electronic transitions of these bases show spectral changes on adduct formation with germanium tetrachloride.

Spectral Effects on Adduct Formation

The nitro anilines are thought⁹⁵ to owe their longer wave length absorption around 380-400 nm (in the visible region) to the charge transfer transition between the lone pair of electrons on the amino nitrogen atom to the oxygen
atoms of the nitro groups:

\[
\begin{align*}
&\text{NH}_2 \quad \text{N} \quad \text{O} \\
&\text{O} \quad \text{N} \quad \text{O} \\
&\text{NH}_2 \\
&\text{N} \quad \text{O}
\end{align*}
\]

In case of aniline and 3-methyl aniline, the lone pair of electrons would show \( \pi \rightarrow \pi^* \) transitions in the UV region. This transition is observed at 295 nm, for both the bases. The methyl substituent makes the 3-methyl aniline 1.26 times more basic than the aniline itself.

The aniline derivatives are known to have two types of spectral effects. The formation of the adduct may be strong or weak depending upon the basic strength of aniline derivatives or the acidic strength of the Lewis acid. Formation of a less stable adduct, \( B M X_n \); charge transfer adducts remove observable free base absorption, but give new absorption on the longer wave length side of the free base band.

This phenomenon has no parallel behaviour as observed for the aniline derivatives in aqueous protonic acids. When a more stable adduct is formed, the lone pair of electrons on the nitrogen atom of the amino group is completely engaged with the Lewis acid and it is no more available for the charge transfer transition. Such type of interaction has
been termed as anilinium ion type behaviour by Satchell and Wardell, because, when anilines are protonated in aqueous medium, the anilinium ions formed absorb at considerably shorter wave lengths, than do the parent bases.

In such interactions, the adduct absorption presumably lies on the short wave length side of the original base band.

In present work, germanium tetrachloride on interacting with aniline derivative bases shows spectral changes characteristic of the 'anilinium' type.

The absorption spectra of free bases showed a decrease in absorbance on addition of germanium tetrachloride and the decrease is corresponding with the increase in the concentrations of the Lewis acid. All the bases show the formation of strong germanium tetrachloride - base adducts. No charge transfer absorption is observed in any of the bases investigated in this group of nitrogen donors. From the previous experiences it is presumable that the adducts, formed in o-dichlorobenzene solution, have their 'anilinium' type of absorption of the UV side. The shorter wave length side, of the free bases, is not easy to follow the appearance of an 'anilinium' ion type of absorbance. The reason being that the Lewis acid, MXₙ, have their own absorption in UV region. Moreover, solvents are not all that transparent in this region. Therefore, the spectra are only recorded
in visible region.

In the case of 4-Me, 3-nitro aniline – germanium tetra chloride interaction, an isobestic point is observed at 335 nm; indicates 1:1 adduct formation. As the \( \lambda_{\text{Max}} \) positions varied from 300 – 400 nm, it was not possible to detect isobestic point in all these interactions. However, from the observed spectral changes, the adduct formed in solution can be represented as an equilibrium system.

\[
\begin{align*}
K \\
B + \text{GeCl}_4 & \underset{1:1}{\rightleftharpoons} B : \text{GeCl}_4 \\
\end{align*}
\]

where 'B' is an aniline derivative base. The equilibrium constants are computed for each of the interaction. The pK ( = \(-\log K\)) values are reported in Tables (7-17) for each base, consistent pK values are obtained indicating 1:1 adduct formation. No other species having complex stoichiometry is observed. The pK values indicate the strength of the interactions that takes place between the Lewis acid and variety of the bases chosen. Quantitatively as different bases interact with the same Lewis acid, therefore, the basic strength of these bases toward germanium tetrachloride is measured. The pK value for the strongest base (3-methyl aniline) is -3.46 and for the
Weakest base it is $-7.15$. The highest $\Delta^pK$ observed is $-3.46-(-2.15)=-1.31$. This means that 3-methyl aniline is 20.42 times more stronger base as compared with the least basic, 4-chloro, 2-nitroaniline. It is interesting to note that Lewis acidity is largely squashed as compared with the Bronsted acidity. These bases are found to follow almost the same order of basicity towards Bronsted acids ($pK_a$ values) as observed from the $pK$ values of the interactions with germanium tetrachloride. (See table 7). The $pK$ value for 2-methyl, 4-nitro aniline and 2-nitro aniline are greater than expected.

**Correlation of $pK$ and $pK_a$ Values**

It has been shown previously for similar interactions involving other metal halides there is a reasonably fair correlation between $pK$ and $pK_a$ values (where $K_a$ is the acid dissociation constant of $R\text{C}_6\text{H}_4\text{NH}_3^+$ in water at 25°C). For the present system, a plot of $pK$ Vs. $pK_a$ value is shown in Fig. 4.

The data fits well by the following equation:

$$pK = \gamma pK_a + (-2.518)$$  

The relationship is true for the unhindered bases. The slope of the line which relates $pK$ to $pK_a$ is found
to be \( pK = 0.370 \ (pK_a) + (-2.518) \) for Germanium tetrachloride in o-dichlorobenzene solution. The \( \Delta pK = pK_{\text{Exp}} - pK_{\text{Calc}} \) values are shown in table 7. It is observed that where substituents are present at ortho to the amino group, the adduct formation is hindered. Therefore, the \( \Delta pK \) values are significant.

The \( pK \) values obtained for germanium tetrachloride in o-dichlorobenzene show that this metal halide is a fairly strong Lewis acid. The \( pK \) values obtained for this acid are greater than the values reported by Satchell and Wardell for stannic chloride interactions with the corresponding bases in o-dichlorobenzene. Although slope of the \( pK \) vs. \( pK_a \) plot for stannic chloride will differ that of the germanium tetrachloride. But the \( pK \) values observed for germanium tetrachloride certainly indicate stronger Lewis acidity for the metal halide. So far stannic chloride has been considered to be the strongest acid in o-dichlorobenzene. The present study shows that germanium tetrachloride will be a better Lewis acid as compared with other metal halides studied in the aprotic media.

On the basis of this study better catalytic activity of this Lewis acid is predicted for any acid-base reaction.
TABLE 7

Equilibrium Constant for Germanium tetrachloride-aniline base adduct formation in O-dichlorobenzene at 25°C

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Aniline derivative</th>
<th>( \lambda_{\text{Max: for base}} )</th>
<th>( pK_a )</th>
<th>( pK_{(\text{Exp.})} )</th>
<th>( pK_{(\text{Calc.})} )</th>
<th>( pK = [pK_{\text{Exp.}} - pK_{\text{Calc.}}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3-methyl</td>
<td>295</td>
<td>4.73(^a)</td>
<td>-3.46</td>
<td>-4.27</td>
<td>0.81</td>
</tr>
<tr>
<td>2.</td>
<td>Aniline</td>
<td>295</td>
<td>4.63(^b)</td>
<td>-4.26</td>
<td>-4.23</td>
<td>-0.03</td>
</tr>
<tr>
<td>3.</td>
<td>2-methyl,3-aniline</td>
<td>350</td>
<td>-</td>
<td>-4.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>4-methyl,3-nitro</td>
<td>368</td>
<td>2.90(^a)</td>
<td>-3.51</td>
<td>-3.59</td>
<td>0.08</td>
</tr>
<tr>
<td>5.</td>
<td>2-methyl,5-nitro</td>
<td>366</td>
<td>2.32(^a)</td>
<td>-3.04</td>
<td>-3.37</td>
<td>0.33</td>
</tr>
<tr>
<td>6.</td>
<td>2-methyl,4-nitro</td>
<td>336</td>
<td>0.94(^a)</td>
<td>-3.54</td>
<td>-2.87</td>
<td>-0.67</td>
</tr>
<tr>
<td>7.</td>
<td>2-nitro</td>
<td>388</td>
<td>-0.29(^a)</td>
<td>-3.10</td>
<td>-2.41</td>
<td>-0.49</td>
</tr>
<tr>
<td>8.</td>
<td>2,6-dinitro</td>
<td>420</td>
<td>-</td>
<td>-2.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>2-chloro,4-nitro</td>
<td>348</td>
<td>-0.94(^a)</td>
<td>-2.46</td>
<td>-2.17</td>
<td>0.03</td>
</tr>
<tr>
<td>10.</td>
<td>4-chloro,2-nitro</td>
<td>404</td>
<td>-1.03(^a)</td>
<td>-2.15</td>
<td>-2.14</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

\( a = 83 \)

\( b = 161 \)
Fig. 9 Plot of pK vs. $pK_a$ values of germanium tetrachloride with aniline derivatives; in o-dichlorobenzene.

$$pK = -0.370 \ pK_a - 2.518$$
### Table 8

3-Methylanilene - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} & = 2.426 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max:}} \text{ for the base} & = 295 \text{ nm} \\
\log \varepsilon_{295} & = 3.30
\end{align*}
\]

\[
\text{Germanium tetrachloride}_{\text{Stoich}} = (0.339 - 12.720) \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid] _ \text{Stoich} _ MX10^-4</th>
<th>Absorbance of the base at 295 nm</th>
<th>[Base] _ \text{Eq} _ MX10^-4</th>
<th>[Acid] _ \text{Eq} _ MX10^-4</th>
<th>[Adduct] _ \text{Eq} _ MX10^-4</th>
<th>pK = -log \ \frac{[\text{Adduct}]}{[\text{Acid}] \cdot [\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.487</td>
<td>2.426</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.339</td>
<td>0.460</td>
<td>2.291</td>
<td>0.204</td>
<td>0.135</td>
<td>-3.46</td>
</tr>
<tr>
<td>3.</td>
<td>0.662</td>
<td>0.435</td>
<td>2.167</td>
<td>0.403</td>
<td>0.259</td>
<td>-3.47</td>
</tr>
<tr>
<td>4.</td>
<td>1.287</td>
<td>0.397</td>
<td>1.977</td>
<td>0.838</td>
<td>0.449</td>
<td>-3.43</td>
</tr>
<tr>
<td>5.</td>
<td>2.041</td>
<td>0.350</td>
<td>1.743</td>
<td>1.358</td>
<td>0.683</td>
<td>-3.46</td>
</tr>
<tr>
<td>6.</td>
<td>4.747</td>
<td>0.244</td>
<td>1.215</td>
<td>3.536</td>
<td>1.211</td>
<td>-3.45</td>
</tr>
<tr>
<td>7.</td>
<td>7.673</td>
<td>0.176</td>
<td>0.877</td>
<td>6.124</td>
<td>1.549</td>
<td>-3.46</td>
</tr>
<tr>
<td>8.</td>
<td>12.720</td>
<td>0.110</td>
<td>0.548</td>
<td>10.842</td>
<td>1.878</td>
<td>-3.50</td>
</tr>
</tbody>
</table>

\[ pK_a = 4.73 \]

Average pK = -3.46±0.04
Fig. 10 Electronic spectra of 3-methylaniline (2.426x10^{-4} M) containing different concentrations of germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10^{-4}) (1) 0.000, (2) 0.339, (3) 0.662, (4) 1.287, (5) 2.041 (6) 4.747, (7) 7.673, (8) 12.720.
### TABLE 9

Aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

**Stoichiometry**

\[
\begin{align*}
\text{(Base)}_{\text{Stoich}} &= 3.225 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max: for the base}} &= 295 \text{ nm} \\
\log \varepsilon_{295} &= 3.237
\end{align*}
\]

\[
\text{[Germanium tetrachloride]}_{\text{Stoich}} = [0.211 - 5.227] \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]$_{\text{Stoich}}$ x 10$^{-4}$</th>
<th>Absorbance of the base at 295 nm</th>
<th>[Base]$_{\text{Eq}}$ x 10$^{-4}$</th>
<th>[Acid]$_{\text{Eq}}$ x 10$^{-4}$</th>
<th>[Adduct]$_{\text{Eq}}$ x 10$^{-4}$</th>
<th>(pK_a) = -log (\frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.557</td>
<td>3.225</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.211</td>
<td>0.526</td>
<td>3.045</td>
<td>0.031</td>
<td>0.180</td>
<td>-4.28</td>
</tr>
<tr>
<td>3.</td>
<td>0.267</td>
<td>0.518</td>
<td>2.999</td>
<td>0.041</td>
<td>0.226</td>
<td>-4.26</td>
</tr>
<tr>
<td>4.</td>
<td>1.361</td>
<td>0.370</td>
<td>2.142</td>
<td>0.278</td>
<td>1.083</td>
<td>-4.26</td>
</tr>
<tr>
<td>5.</td>
<td>3.012</td>
<td>0.206</td>
<td>1.193</td>
<td>0.980</td>
<td>2.032</td>
<td>-4.24</td>
</tr>
<tr>
<td>6.</td>
<td>3.617</td>
<td>0.159</td>
<td>0.921</td>
<td>1.313</td>
<td>2.304</td>
<td>-4.28</td>
</tr>
<tr>
<td>7.</td>
<td>4.318</td>
<td>0.130</td>
<td>0.753</td>
<td>1.846</td>
<td>2.472</td>
<td>-4.25</td>
</tr>
<tr>
<td>8.</td>
<td>4.714</td>
<td>0.117</td>
<td>0.678</td>
<td>2.166</td>
<td>2.548</td>
<td>-4.26</td>
</tr>
<tr>
<td>9.</td>
<td>5.227</td>
<td>0.095</td>
<td>0.550</td>
<td>2.552</td>
<td>2.675</td>
<td>-4.28</td>
</tr>
</tbody>
</table>

\[pK_a = 4.63\]

Average \(pK\) = \(-4.26 \pm 0.02\)
Fig. 11 Electronic spectra of aniline (3.225x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution of 25°C (Mx10^{-4}), (1) 0.00, (2) 0.211, (3) 0.267, (4) 1.361, (5) 3.012, (6) 3.617, (7) 4.318, (8) 4.714, (9) 5.227.
TABLE 10

2-Methyl, 3-Nitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

(Base) \( _{\text{Stoich}} \) = \( 1.971 \times 10^{-4} \) M

\( \lambda_{\text{Max: for the base}} \) = 350 nm

\( \log \epsilon \text{ for } 350 \) = 3.24

\( [\text{Germanium tetrachloride}]_{\text{Stoich}} \) = \( [0.603 - 3.805] \times 10^{-4} \) M

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Acid ( _{\text{Stoich}} ) Mx10(^{-4} )</th>
<th>Absorbance of the base at 350 nm Mx10(^{-4} )</th>
<th>( [\text{Base}]_{\text{Eq}} ) Mx10(^{-4} )</th>
<th>( [\text{Acid}]_{\text{Eq}} ) Mx10(^{-4} )</th>
<th>( [\text{Adduct}]_{\text{Eq}} ) Mx10(^{-4} )</th>
<th>( pK = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.340</td>
<td>1.971</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.603</td>
<td>0.270</td>
<td>1.565</td>
<td>0.197</td>
<td>0.406</td>
<td>-4.12</td>
</tr>
<tr>
<td>3.</td>
<td>1.199</td>
<td>0.210</td>
<td>1.217</td>
<td>0.447</td>
<td>0.754</td>
<td>-4.14</td>
</tr>
<tr>
<td>4.</td>
<td>1.572</td>
<td>0.180</td>
<td>1.043</td>
<td>0.644</td>
<td>0.928</td>
<td>-4.14</td>
</tr>
<tr>
<td>5.</td>
<td>2.129</td>
<td>0.145</td>
<td>0.840</td>
<td>0.998</td>
<td>1.131</td>
<td>-4.13</td>
</tr>
<tr>
<td>6.</td>
<td>2.788</td>
<td>0.115</td>
<td>0.666</td>
<td>1.483</td>
<td>1.305</td>
<td>-4.12</td>
</tr>
<tr>
<td>7.</td>
<td>3.345</td>
<td>0.100</td>
<td>0.580</td>
<td>1.954</td>
<td>1.391</td>
<td>-4.09</td>
</tr>
<tr>
<td>8.</td>
<td>3.805</td>
<td>0.085</td>
<td>0.493</td>
<td>2.337</td>
<td>1.478</td>
<td>-4.11</td>
</tr>
</tbody>
</table>

Average \( pK = -4.12\pm0.03 \)
Fig. 12 Electronic spectra of 2-methyl, 3-nitroaniline (1.971x10^{-4} M) containing difference; of Germanium tetrachloride in o-dichloro benzene solution at 25°C (Mx10^{4}), (1) 0.00, (2) 0.603, (3) 1.199, (4) 1.572, (5) 2.129, (6) 2.788, (7) 3.345, (8) 3.805.
TABLE 11

4-methyl, 3-nitro aniline – Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

(Base)\text{Stoich} = 2.602 \times 10^{-4} \text{ M}

\lambda_{\text{Max: for the base}} = 368 \text{ nm}

\log \varepsilon = 3.37

\text{[Germanium tetrachloride]}_{\text{Stoich}} = [0.931 – 13.590] \times 10^{-4} \text{ M}

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{\text{Stoich}} M \times 10^4</th>
<th>Absorbance of the base at 268 nm</th>
<th>[Base]_{\text{Eq}} M \times 10^4</th>
<th>[Acid]_{\text{Eq}} M \times 10^4</th>
<th>[Adduct]_{\text{Eq}} M \times 10^4</th>
<th>pK_a = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.61</td>
<td>2.602</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.931</td>
<td>0.52</td>
<td>2.218</td>
<td>0.547</td>
<td>0.384</td>
<td>-3.50</td>
</tr>
<tr>
<td>3.</td>
<td>4.237</td>
<td>0.32</td>
<td>1.365</td>
<td>3.000</td>
<td>1.237</td>
<td>-3.48</td>
</tr>
<tr>
<td>4.</td>
<td>6.690</td>
<td>0.24</td>
<td>1.024</td>
<td>5.112</td>
<td>1.578</td>
<td>-3.48</td>
</tr>
<tr>
<td>5.</td>
<td>10.602</td>
<td>0.15</td>
<td>0.640</td>
<td>8.640</td>
<td>1.962</td>
<td>-3.55</td>
</tr>
<tr>
<td>6.</td>
<td>13.590</td>
<td>0.12</td>
<td>0.512</td>
<td>11.500</td>
<td>2.090</td>
<td>-3.55</td>
</tr>
</tbody>
</table>

pK_a = 2.90

Average pK = -3.51 \pm 0.05
Fig. 13 Electronic spectra of 4-methyl, 3-aniline (2.602x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25\(^\circ\) (Mx10^{-4}), (1) 0.00, (2) 0.931, (3) 4.237, (4) 6.690, (5) 10.602, (6) 13.590.
TABLE 12

2-methyl, 5-nitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
\text{[Base]} & \quad \text{Stoich} & = & & 2.366 \times 10^{-4} M \\
\lambda_{\text{Max:}} \text{ for the base} & = & 366 \text{ nm} \\
\log \varepsilon & = & 3.38 \\
\text{[Germanium tetrachloride]} \quad \text{Stoich} & = & [1.891 - 16.369] \times 10^{-4} M
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid] \text{Stoich} Mx10^4</th>
<th>[Absorbance of the base at 366 nm]</th>
<th>[Base] Eq Mx10^4</th>
<th>[Acid] Eq Mx10^4</th>
<th>[Adduct] Eq Mx10^4</th>
<th>pK = -log \frac{[Adduct]}{[Acid][Base]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.57</td>
<td>2.366</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.891</td>
<td>0.49</td>
<td>2.034</td>
<td>1.559</td>
<td>0.332</td>
<td>-3.02</td>
</tr>
<tr>
<td>3</td>
<td>3.416</td>
<td>0.43</td>
<td>1.785</td>
<td>2.835</td>
<td>0.581</td>
<td>3.06</td>
</tr>
<tr>
<td>4</td>
<td>5.645</td>
<td>0.37</td>
<td>1.536</td>
<td>4.816</td>
<td>0.830</td>
<td>-3.05</td>
</tr>
<tr>
<td>5</td>
<td>7.637</td>
<td>0.33</td>
<td>1.370</td>
<td>6.641</td>
<td>0.996</td>
<td>-3.04</td>
</tr>
<tr>
<td>6</td>
<td>11.374</td>
<td>0.27</td>
<td>1.121</td>
<td>10.129</td>
<td>1.245</td>
<td>-3.04</td>
</tr>
<tr>
<td>7</td>
<td>16.365</td>
<td>0.22</td>
<td>0.913</td>
<td>14.912</td>
<td>1.453</td>
<td>-3.03</td>
</tr>
</tbody>
</table>

\[ pK_a = 2.32 \]
\[ \text{Average } pK = -3.04 \pm 0.02 \]
Fig. 14 Electronic spectra of 2-methyl, 5-nitro aniline (2.366x10^{-4} M) containing different concentrations of Germanium tetrachloride in O-dichlorobenzene solution at 25°C (Mx10^{4}), (1) 0.00, (2) 1.89, (3) 3.416, (4) 5.645, (5) 7.637, (6) 11.374, (7) 16.365.
### TABLE 13

2-methyl, 4-nitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
&\text{(Base)}_{\text{Stoich}} = 0.789 \times 10^{-4} \text{ M} \\
&\lambda_{\text{Max: for the base}} = 336 \text{ nm} \\
&\log \varepsilon_{336} = 3.95 \\
&[\text{Germanium tetrachloride}]_{\text{Stoich}} = [0.453 - 4.537] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich} Mx10^4</th>
<th>Absorbance of the base at 336 nm</th>
<th>[Base]_{Eq} Mx10^4</th>
<th>[Acid]_{Eq} Mx10^4</th>
<th>[Adduct]_{Eq} Mx10^4</th>
<th>pK = -log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.70</td>
<td>0.789</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.453</td>
<td>0.62</td>
<td>0.699</td>
<td>0.363</td>
<td>0.090</td>
<td>-3.55</td>
</tr>
<tr>
<td>3.</td>
<td>1.287</td>
<td>0.51</td>
<td>0.575</td>
<td>1.073</td>
<td>0.214</td>
<td>-3.54</td>
</tr>
<tr>
<td>4.</td>
<td>1.745</td>
<td>0.46</td>
<td>0.518</td>
<td>1.474</td>
<td>0.271</td>
<td>-3.55</td>
</tr>
<tr>
<td>5.</td>
<td>2.464</td>
<td>0.41</td>
<td>0.462</td>
<td>2.137</td>
<td>0.327</td>
<td>-3.52</td>
</tr>
<tr>
<td>6.</td>
<td>4.537</td>
<td>0.29</td>
<td>0.327</td>
<td>4.075</td>
<td>0.462</td>
<td>-3.54</td>
</tr>
</tbody>
</table>

\[ pK_a = 0.94 \quad \text{Average } pK = -3.54 \pm 0.02 \]
Electronic spectra of 2-methyl, 4-nitro aniline (0.789x10⁻⁴ M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10⁻⁴), (1) 0.00, (2) 0.453, (3) 1.287, (4) 1.745, (5) 2.464, (6) 4.537.
2-nitro aniline - Germanium tetrachloride interaction in 0-dichlorobenzene solution at 25°C

(Base)\textsubscript{Stoich} = 0.753 \times 10^{-4} \text{M}

\( \lambda_{\text{Max}} \) for the base = 388 nm

\( \log \alpha \) 388 = 4.22

(\text{Germanium tetrachloride})\textsubscript{Stoich} = \{1.378 - 3.389\} \times 10^{-4} \text{M}

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]\textsubscript{Stoich} \times 10^4</th>
<th>Absorbance of the base at 388 nm</th>
<th>[Base]\textsubscript{Eq} \times 10^4</th>
<th>[Acid]\textsubscript{Eq} \times 10^4</th>
<th>[Adduct]\textsubscript{Eq} \times 10^4</th>
<th>pK = \text{-log} \left( \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]} \right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.26</td>
<td>0.753</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.378</td>
<td>1.08</td>
<td>0.645</td>
<td>1.270</td>
<td>0.108</td>
<td>-3.12</td>
</tr>
<tr>
<td>3.</td>
<td>2.713</td>
<td>0.95</td>
<td>0.568</td>
<td>2.528</td>
<td>0.185</td>
<td>-3.11</td>
</tr>
<tr>
<td>4.</td>
<td>3.003</td>
<td>0.92</td>
<td>0.550</td>
<td>2.800</td>
<td>0.203</td>
<td>-3.12</td>
</tr>
<tr>
<td>5.</td>
<td>3.345</td>
<td>0.91</td>
<td>0.544</td>
<td>3.136</td>
<td>0.209</td>
<td>-3.09</td>
</tr>
<tr>
<td>6.</td>
<td>3.389</td>
<td>0.90</td>
<td>0.538</td>
<td>3.174</td>
<td>0.215</td>
<td>-3.10</td>
</tr>
</tbody>
</table>

\( pK_a = -0.29 \)

Average \( pK = -3.108 \pm 0.018 \)
Fig. 16 Electronic spectra of 2-nitro aniline ($0.753 \times 10^{-4}$ M) containing different concentrations of Germanium tetrachloride at $25^\circ (M \times 10^{-4})$

(1) 0.00, (2) 1.376, (3) 2.713, (4) 3.003, (5) 3.245, (6) 3.369.
TABLE 15

2,6-dinitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

(Base)\textsubscript{Stoich} = 0.786 \times 10^{-4} \text{M}

λ\text{Max: for the base} = 420 \text{ nm}

\log \varepsilon_{420} = 4.029

[Germanium tetrachloride]\textsubscript{Stoich} = [0.809 - 2.998] \times 10^{-4} \text{M}

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Acid\textsubscript{Stoich} Mx10^4</th>
<th>Absorbance of the base at 420 nm</th>
<th>Base\textsubscript{Eq} Mx10^4</th>
<th>Acid\textsubscript{Eq} Mx10^4</th>
<th>Adduct\textsubscript{Eq} Mx10^4</th>
<th>pK = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.84</td>
<td>0.786</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>2.809</td>
<td>0.81</td>
<td>0.758</td>
<td>0.781</td>
<td>0.028</td>
<td>-2.675</td>
</tr>
<tr>
<td>3.</td>
<td>1.670</td>
<td>0.78</td>
<td>0.730</td>
<td>1.614</td>
<td>0.056</td>
<td>-2.676</td>
</tr>
<tr>
<td>4.</td>
<td>2.279</td>
<td>0.76</td>
<td>0.711</td>
<td>2.204</td>
<td>0.075</td>
<td>-2.680</td>
</tr>
<tr>
<td>5.</td>
<td>2.998</td>
<td>0.74</td>
<td>0.692</td>
<td>2.904</td>
<td>0.094</td>
<td>-2.670</td>
</tr>
</tbody>
</table>

Average pK = -2.675±0.005
Fig. 17 Electronic spectra of 2,6-dinitroaniline (0.786x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10^{-4}), (1) 0.00, (2) 2.809, (3) 1.670, (4) 2.219, (5) 2.998.
2-chloro, 4-nitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
\text{(Base)}_{\text{Stoich}} &= 0.788 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max}}: &\text{ for the base} = 348 \text{ nm} \\
\log \xi_{348} &= 4.19 \\
\end{align*}
\]

\[
[\text{Germanium tetrachloride}]_{\text{Stoich}} = [1.115 - 3.505] \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{\text{Stoich}} Mx10^4</th>
<th>Absorbance of the base at 348 nm</th>
<th>[Base]_{\text{Eq}} Mx10^4</th>
<th>[Acid]_{\text{Eq}} Mx10^4</th>
<th>[Adduct]_{\text{Eq}} Mx10^4</th>
<th>pK = -log [Adduct] / [Acid] * [Base]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.220</td>
<td>0.788</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.115</td>
<td>1.182</td>
<td>0.763</td>
<td>1.090</td>
<td>0.025</td>
<td>-2.48</td>
</tr>
<tr>
<td>3.</td>
<td>1.803</td>
<td>1.160</td>
<td>0.749</td>
<td>1.764</td>
<td>0.039</td>
<td>-2.47</td>
</tr>
<tr>
<td>4.</td>
<td>2.787</td>
<td>1.123</td>
<td>0.725</td>
<td>2.724</td>
<td>0.063</td>
<td>-2.50</td>
</tr>
<tr>
<td>5.</td>
<td>3.505</td>
<td>1.105</td>
<td>0.714</td>
<td>3.431</td>
<td>0.074</td>
<td>-2.48</td>
</tr>
</tbody>
</table>

\[ pK_a = -0.94 \quad \text{Average } pK = -2.49 \pm 0.02 \]
Fig. 18 Electronic spectra of 2-chloro, 4-nitro aniline (0.788x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10^{-4}), (1) 0.00, (2) 1.115, (3) 1.803, (4) 2.787, (5) 3.505.
TABLE 17

4-chloro, 2-nitro aniline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\frac{[\text{Base}]}{\text{Stoich}} = 1.970 \times 10^{-4} \text{M}
\]

\[
\lambda_{\text{Max: for the base}} = 404 \text{ nm}
\]

\[
\log \varepsilon_{404} = 3.73
\]

\[
[\text{Germanium tetrachloride}]_{\text{Stoich}} = [1.025 - 4.712] \times 10^{-4} \text{M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>([\text{Acid}]_{\text{Stoich}}) Mx10^4</th>
<th>Absorbance of the base at 404 nm</th>
<th>([\text{Base}]_{\text{Eq}}) Mx10^4</th>
<th>([\text{Acid}]_{\text{Eq}}) Mx10^4</th>
<th>([\text{Adduct}]_{\text{Eq}}) Mx10^4</th>
<th>(\text{pK} = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.065</td>
<td>1.970</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1.025</td>
<td>1.050</td>
<td>1.942</td>
<td>0.997</td>
<td>0.028</td>
<td>-2.16</td>
</tr>
<tr>
<td>3</td>
<td>1.778</td>
<td>1.040</td>
<td>1.924</td>
<td>1.732</td>
<td>0.046</td>
<td>-2.14</td>
</tr>
<tr>
<td>4</td>
<td>2.372</td>
<td>1.030</td>
<td>1.905</td>
<td>2.307</td>
<td>0.065</td>
<td>-2.17</td>
</tr>
<tr>
<td>5</td>
<td>3.346</td>
<td>1.020</td>
<td>1.887</td>
<td>3.263</td>
<td>0.083</td>
<td>-2.13</td>
</tr>
<tr>
<td>6</td>
<td>4.712</td>
<td>1.000</td>
<td>1.850</td>
<td>4.592</td>
<td>0.120</td>
<td>-2.15</td>
</tr>
</tbody>
</table>

\(\text{pK}_a = 1.03\)  
Average \(\text{pK} = -2.15 \pm 0.02\)
Fig. 19  Electronic spectra of 4-chloro,2-nitro aniline (1.970x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx:10^{-4}), (1) 0.00, (2) 1.025, (3) 1.778, (4) 2.372, (5) 3.346 and (6) 4.712.
The second group of bases are the heterocyclic nitrogen donors and some diamino benzene derivatives (Table 18).

The aniline derivatives show absorption bands due to intramolecular charge transfer as discussed in the preceding pages. Two diamino benzene derivatives are studied in ortho dichlorobenzene. They show one absorption band around 300 nm.

<table>
<thead>
<tr>
<th>Benzene derivatives</th>
<th>$\lambda_{\text{Max}}$ (Base)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-diaminobenzene</td>
<td>298 nm</td>
</tr>
<tr>
<td>4,Me-1,3-diaminobenzene</td>
<td>300 nm</td>
</tr>
</tbody>
</table>

These diamino bases do not carry a nitrogen group. Therefore the absorption cannot be attributed to charge transfer transition (in the excited state) from either of the two amino groups to the nitro group. Moreover, there is only one absorption band and two amino groups are present and one would expect two absorption if the NH$_2$ group are involved in the electronic transition. The appearance of one band must arise from involvement of a common donor centre which results from the two amino groups. Therefore, these transitions are assigned as the $\lambda \rightarrow \lambda^*$ transitions. The diamino derivatives are bidentate Ligands, therefore, both the amino groups may be involved in adduct formation with germanium tetrachloride. The interaction of germanium tetrachloride with 4-methyl,
1,3-diaminobenzene are observed to take place with disappearance of the free base absorbance with increasing concentrations of the acid. No new band on longer wave length side (so called charge transfer) is observed. This type of interaction is a strong and the spectral change is of the 'anilinium' type. The adduct band would presumably be on the shorter wave length side, which has not been studied due to absorptions of the solvent and the Lewis acid in the UV region. Nevertheless, the calculations supported the formation of 1:1 adducts with these two diamino benzenes. The pK values are constant and 1:1 stoichiometry is confirmed. As the adducts are 1:1, it follows amino groups in meta and ortho positions will form different types of adducts as compared with the ortho amino acids (c.f. the work of Wardell) for interaction of R SnCl₃ with diamino nitrobenzene derivatives. The possible co-ordinations may be represented as follows:

![Diagram](attachment:image.png)

The spectral changes are shown in Fig. 30 and 31.
In both cases, the free diamino absorption band is decreased and no visible absorption remains with excess of GeCl$_4$. This would favour the structure II and III for 1:1 adduct formation. Sterically it look somewhat odd for the o-amino groups to be involved in co-ordination, but keeping in mind the comparable, large size of GeCl$_4$, the adduct II is possibly formed and the possibility of structure I is less likely for the reason as discussed above. Formation of six-membered ring (structure-II) is supported by higher $pK$ ($= -4.98$) value observed for the interactions.

The heterocyclic bases included in this group are those having one or two donor nitrogen atoms in aromatic ring compounds. The simplest heterocyclic base used is pyridine.

The lone pair orbital energy is near that of the upper occupied $\pi^*$ orbitals. It is further predicted that because of greater nuclear charge on nitrogen, the $\pi^*$ -orbital degeneracy is removed and the energies of the most of the orbitals are lowered.
Molecular orbital diagram of pyridine $\bar{\Lambda}$-orbitals.

The $\bar{\Lambda}_3$ an $\eta$ (lone pair) orbitals are near by with an uncertainty of order.

For the reasons as discussed above, the absorption of pyridine will be drastically different from that of benzene. Therefore heterocyclic having nitrogen atom, as the heteroatom, will show $\eta$—$\bar{\Lambda}_4$ transitions. Pyridine is expected to show this transition somewhat in the UV region in ortho-dichlorobenzene solution (of this transition for pyridine in 95% ethanol around 260 nm). An addition of germanium tetrachloride solutions to the pyridine solution; a charge transfer type of absorption is observed on longer wave length side at 300 nm. Calculations of $pK$ values are carried out in two different ways and results are shown in Table 18—29. constant values confirm the 1:1 stoichiometry of the adduct formed. 2-Amino pyridine shows similar spectral changes Fig. 21 on addition of germanium tetrachloride. The adduct absorption is observed
at 310 nm. From the computed pK values Table 19 it is inferred that a 1:1 adduct is formed which may involve amino group or the hetero nitrogen atom or both.

2,2' bipyridine shows the $n \rightarrow \pi^*$ transition at 294 nm.

On adduct formation with germanium tetrachloride, a shoulder comes up on the longer wave length side which develops into an absorption peak at 316 nm (Fig. 26). Calculations of pK value are shown in Table 23,24 and from graph 29 The values obtained are remarkably close together and 1:1 base-GeCl$_4$ interaction is inferred for this system.

The behaviour of 2,2' biquinoline is similar to 2,2' bipyridine. However, an isobestic point at 350 nm is observed for the former base which indicates the presence of two kinds of entities i.e. free and complexed base. pK values are given in Table no. 25 to 26 and fairly consistent values confirm to a 1:1 adduct formations. Both the nitrogen atoms are involved in co-ordination with germanium tetrachloride.

The spectral effects observed in case of 6-nitro quinoline are quite different from the cases discussed above. The base has an absorption band at 298 nm and is knocked down by addition of germanium tetrachloride (Fig. 32). The base shows an anilinium type of spectral
effects because the free base absorbance is removed by interaction with germanium tetrachloride. The calculations for pK value are shown in Table 29 and constant value confirm the formation of 1:1 equilibrium.

N,N'-dimethyl-α-naphthyl amine shows spectral changes similar to the aniline derivatives as discussed in the preceding section. The base absorbance falls down and the adduct absorbance comes up on the UV side with a clear isobestic point at 295 nm (Fig. 25). The equilibrium constant values are shown in Table 22. Highly consistent values are remarkable and interaction is very strong in favour of the adduct formation. It is however, interesting to note that the two methyl groups offered little hindrance for adduct formation with germanium tetrachloride. Probably, the high electron density distorted the spectral orientation of the methyl groups on adduct formation with Lewis acid.

A comparison of the Lewis acidity of germanium tetrachloride towards the second group of Lewis bases is given in Table 18. Most of these bases are stronger than the aniline derivative bases. Like the aniline derivatives, the pK values seems to be related linearly with pK values determined in the present work. The plot of pK versus pKₐ values for these bases is shown in Fig. 20. Fairly reasonable straight line behaviour
is observed. GeCl₄ obeys

\[ pK = +0.461 (pK_a) + (-6.415). \]

equation for its interaction with the nitrogen donor bases. The \( pK \) \( [= pK_{(Exp)} - pK_{(Calc)}] \) values are given in the right hand column of the Table No. 18. The deviations are insignificant except for one or two cases. Therefore, the bases show similar trends for adduct formation towards Bronsted as well as Lewis acids. However, the Lewis acidity is levelled greatly as compared with the \( pK \) values. This conclusion is similar to the result already noticed in the case of germanium tetrachloride interaction with aniline derivative bases.
<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Nitrogen base</th>
<th>( \lambda_{\text{Max: for base}} ) nm</th>
<th>( \lambda_{\text{Max: for adduct}} ) nm</th>
<th>( pK_a )</th>
<th>( pK_{(\text{Exp})} )</th>
<th>( pK_{(\text{Calc.})} )</th>
<th>( pK=(pK_{\text{Exp}}-pK_{\text{Calc.}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2,N-methyl-pyridine</td>
<td>-</td>
<td>310</td>
<td>6.82(^a)</td>
<td>-3.570</td>
<td>-3.53</td>
<td>-0.040</td>
</tr>
<tr>
<td>2.</td>
<td>Pyridine</td>
<td>-</td>
<td>300</td>
<td>5.52(^a)</td>
<td>-4.079</td>
<td>-4.052</td>
<td>-0.027</td>
</tr>
<tr>
<td>3.</td>
<td>N,N-dimethyl-naphthyl amine</td>
<td>315</td>
<td>-</td>
<td>4.566(^a)</td>
<td>-4.54</td>
<td>-4.28</td>
<td>-0.260</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.710(^*)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>2,2'-Bipyridine</td>
<td>294</td>
<td>316</td>
<td>4.350(^a)</td>
<td>-4.836</td>
<td>-4.352</td>
<td>-0.484</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.120(^*)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>2,2',Biquinoline</td>
<td>322</td>
<td>356</td>
<td>2.815(^*)</td>
<td>-4.633</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>4-methyl,1-3 diaminebenzene</td>
<td>300</td>
<td>-</td>
<td>2.660(^*)</td>
<td>-4.980</td>
<td>-4.910</td>
<td>-0.0717</td>
</tr>
<tr>
<td>7.</td>
<td>1,2-diamino benzene</td>
<td>298</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-3.375</td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>6-nitro quinoline</td>
<td>298</td>
<td>-</td>
<td>-</td>
<td></td>
<td>-2.36</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) = 161

\(^*\) = determined in present work.

Equation for the linear relationship between \( pK \) vs. \( pK_a \) for GeCl\(_4\) interactions with nitrogen bases.

\[ pK = 0.461 \, pK_a - 6.415 \]
Fig 20 Plot of $pK$ vs. $pK_a$ values of germanium tetrachloride with nitrogen bases in o-dichlorobenzene.
TABLE 19

2-Aminopyridine - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C
(Graphical Method)

\[
\text{[Base]}_{\text{Stoich}} = 1.700 \times 10^{-4} \text{M}
\]

\[
\lambda_{\text{Max:}} \text{ for adduct} = 310 \text{ nm}
\]

\[
\log \epsilon_{310} = 3.72
\]

\[
\text{[Germanium tetrachloride]}_{\text{Stoich}} = [1.071 - 52.600] \times 10^{-4} \text{M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich} Mx10^4</th>
<th>Absorbance of the adduct at 310 nm</th>
<th>([\text{Adduct}]_{\text{Base}} = \frac{[D - D_e]}{D_e - D}) from spectra</th>
<th>([\text{Acid}]_{\text{Eq}} Mx10^4)</th>
<th>pK = -log\left(\frac{1}{[\text{Acid}]} - \frac{[\text{Adduct}]}{[\text{Base}]}\right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.300[D_o]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.071</td>
<td>0.375</td>
<td>0.144</td>
<td>0.359</td>
<td>-3.60</td>
</tr>
<tr>
<td>3.</td>
<td>2.260</td>
<td>0.500</td>
<td>0.506</td>
<td>1.310</td>
<td>-3.59</td>
</tr>
<tr>
<td>4.</td>
<td>3.705</td>
<td>0.600</td>
<td>1.017</td>
<td>2.565</td>
<td>-3.60</td>
</tr>
<tr>
<td>5.</td>
<td>6.601</td>
<td>0.700[D]</td>
<td>2.051</td>
<td>5.271</td>
<td>-3.59</td>
</tr>
<tr>
<td>6.</td>
<td>10.446</td>
<td>0.765</td>
<td>3.577</td>
<td>8.993</td>
<td>-3.60</td>
</tr>
<tr>
<td>7.</td>
<td>12.481</td>
<td>0.780</td>
<td>4.174</td>
<td>11.001</td>
<td>-3.58</td>
</tr>
<tr>
<td>8.</td>
<td>15.359</td>
<td>0.800</td>
<td>5.263</td>
<td>13.840</td>
<td>-3.58</td>
</tr>
<tr>
<td>9.</td>
<td>52.560</td>
<td>0.895[D_e]</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[pK_a = 6.82\] \hspace{1cm} \text{Average } pK = -3.59 \pm 0.02

\[pK \text{ from graph} = -3.57\]
Fig. 21 Electronic spectra of 2-aminopyridine (1.700x10^{-4} M) containing different concentration of germanium tetrachloride at 25° (Mx10^{-4})

(1) 0.00, (2) 1.071, (3) 2.160, (4) 3.765, (5) 6.601, (6) 10.446,
Fig. 22 A plot of $[\text{Adduct}] / [\text{Base}]$ against $[\text{Acid}]_{eq}$ for 2-Amino
TABLE 20

Pyridine - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

(Graphical Method)

\[
\begin{align*}
[\text{Base}]_{\text{Stoich}} & = 5.057 \times 10^{-4} \text{M} \\
\lambda_{\text{Max}} \text{ for the adduct} & = 300 \text{ nm} \\
\log \varepsilon_0 & = 2.575 \\
[\text{Germanium tetrachloride}]_{\text{Stoich}} & = [0.605 - 12.660] \times 10^{-4} \text{M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid] _ Stoich Mx10^4</th>
<th>Absorbance of the adduct at 300 nm</th>
<th>[\frac{[\text{Adduct}]}{[\text{Base}]} = \frac{D - D_0}{D_\infty - D} \text{ from spectra} ]</th>
<th>[Acid] _ Eq Mx10^4</th>
<th>pK = -log \left[ \frac{1}{[\text{Acid}]} - \frac{[\text{Adduct}]}{[\text{Base}]} \right]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.005 (D_∞)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.605</td>
<td>0.020</td>
<td>0.0882</td>
<td>0.073</td>
<td>-4.08</td>
</tr>
<tr>
<td>3</td>
<td>1.260</td>
<td>0.040</td>
<td>0.2333</td>
<td>0.195</td>
<td>-4.08</td>
</tr>
<tr>
<td>4</td>
<td>2.912</td>
<td>0.085 [D]</td>
<td>0.7619</td>
<td>0.650</td>
<td>-4.07</td>
</tr>
<tr>
<td>5</td>
<td>4.963</td>
<td>0.125</td>
<td>1.8461</td>
<td>1.616</td>
<td>-4.06</td>
</tr>
<tr>
<td>6</td>
<td>8.462</td>
<td>0.160</td>
<td>5.1666</td>
<td>4.204</td>
<td>-4.09</td>
</tr>
<tr>
<td>7</td>
<td>12.660</td>
<td>0.190 (D_∞)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

pK_a = 5.25

Average pK = -4.076±0.016
pK from table No. = -4.078±0.02
pK from Graph = -4.085
Mean pK = -4.079±0.006
TABLE 21

Pyridine - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\text{[Base]}_{\text{Stoich}} = 5.057 \times 10^{-4} \text{ M}
\]

\[
\lambda_{\text{Max: for the adduct}} = 300 \text{ nm}
\]

\[
\log \epsilon_{300} = 2.575
\]

\[
[\text{Germanium tetrachloride}]_{\text{Stoich}} = [0.605 - 12.660] \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich} Mx10^4</th>
<th>Absorbance of the adduct at 300 nm</th>
<th>[Base]_{Stoich} Mx10^4</th>
<th>[Acid]_{Eq} Mx10^4</th>
<th>[Adduct]_{Eq} Mx10^4</th>
<th>pK_a = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.605</td>
<td>0.020</td>
<td>4.525</td>
<td>0.073</td>
<td>0.532</td>
<td>4.06</td>
</tr>
<tr>
<td>3.</td>
<td>1.260</td>
<td>0.040</td>
<td>3.992</td>
<td>0.195</td>
<td>1.065</td>
<td>4.07</td>
</tr>
<tr>
<td>4.</td>
<td>2.912</td>
<td>0.085</td>
<td>2.795</td>
<td>0.650</td>
<td>2.262</td>
<td>4.09</td>
</tr>
<tr>
<td>5.</td>
<td>4.963</td>
<td>0.125</td>
<td>1.730</td>
<td>1.616</td>
<td>3.327</td>
<td>4.07</td>
</tr>
<tr>
<td>6.</td>
<td>8.462</td>
<td>0.160</td>
<td>0.799</td>
<td>4.204</td>
<td>4.258</td>
<td>4.10</td>
</tr>
<tr>
<td>7.</td>
<td>12.660</td>
<td>0.190</td>
<td>-</td>
<td>7.603</td>
<td>5.057</td>
<td>-</td>
</tr>
</tbody>
</table>

pK_a = 5.52

Average pK = -4.078 ± 0.022
Fig. 23 Electronic spectra of Pyridine (5.057×10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10^{-4}), (1) 0.00, (2) 0.605, (3) 1.260, (4) 2.112, (5) 4.963, (6) 8.462, (7) 12.660.
Fig. 24

A plot of \( \frac{[\text{Adduct}]}{[\text{Base}]} \) against \([\text{Acid}]_{eq} \times 10^{-4}\) for pyridin...
### TABLE 22

**N,N-Dimethylnaphthaliamine - Germanium tetrachloride interaction**

in o-dichlorobenzene solution at 25°C

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]&lt;sub&gt;Stoich&lt;/sub&gt; Mx10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>Absorbance of the base at 315 nm</th>
<th>[Base]&lt;sub&gt;Eq&lt;/sub&gt; Mx10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>[Acid]&lt;sub&gt;Eq&lt;/sub&gt; Mx10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>[Adduct]&lt;sub&gt;Eq&lt;/sub&gt; Mx10&lt;sup&gt;4&lt;/sup&gt;</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt; = -log $\frac{(Adduct)}{(Acid)(Base)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.960</td>
<td>1.869</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.089</td>
<td>0.920</td>
<td>1.790</td>
<td>0.012</td>
<td>0.077</td>
<td>-4.55</td>
</tr>
<tr>
<td>3.</td>
<td>0.076</td>
<td>0.715</td>
<td>1.391</td>
<td>0.099</td>
<td>0.477</td>
<td>-4.54</td>
</tr>
<tr>
<td>4.</td>
<td>0.068</td>
<td>0.675</td>
<td>1.313</td>
<td>0.125</td>
<td>0.555</td>
<td>-4.53</td>
</tr>
<tr>
<td>5.</td>
<td>0.082</td>
<td>0.495</td>
<td>0.963</td>
<td>0.277</td>
<td>0.905</td>
<td>-4.53</td>
</tr>
<tr>
<td>6.</td>
<td>0.141</td>
<td>0.420</td>
<td>0.817</td>
<td>0.363</td>
<td>1.052</td>
<td>-4.55</td>
</tr>
<tr>
<td>7.</td>
<td>3.140</td>
<td>0.150</td>
<td>0.291</td>
<td>1.563</td>
<td>1.577</td>
<td>-4.54</td>
</tr>
<tr>
<td>8.</td>
<td>3.456</td>
<td>0.130</td>
<td>0.253</td>
<td>1.841</td>
<td>1.616</td>
<td>-4.54</td>
</tr>
<tr>
<td>9.</td>
<td>4.108</td>
<td>0.100</td>
<td>0.194</td>
<td>2.432</td>
<td>1.675</td>
<td>-4.55</td>
</tr>
<tr>
<td>10.</td>
<td>4.548</td>
<td>0.090</td>
<td>0.175</td>
<td>2.855</td>
<td>1.694</td>
<td>-4.53</td>
</tr>
<tr>
<td>11.</td>
<td>5.398</td>
<td>0.070</td>
<td>0.136</td>
<td>3.665</td>
<td>1.733</td>
<td>-4.54</td>
</tr>
</tbody>
</table>

**pK<sub>a</sub> = 4.566**

**Average pK = -4.54±0.01**
Fig. 25 Absorbance changes at N,N-dimethyl-α-naphthyl amine \((1.668 \times 10^{-4})\) containing different concentrations of germanium tetrachloride in o-dichlorobenzene solution at 25°C (M = 10^-4), (1) 0.00, (2) 0.0090, (3) 0.576, (4) 0.616, (5) 1.102, (6) 1.445, (7) 3.140, (8) 3.458, (9) 4.106, (10) 4.548 and (11) 5.398 mol l^-1.
TABLE 23

2-2',Bipyridine - Germanium tetrachloride interaction in o-dichloro benzene solution at 25°C

(Graphical Method)

(Base) Stoich = 0.814 x 10^{-4} M

λ_max: for the adduct = 316 nm

log ε₃₁₆ = 4.15

(Germanium tetrachloride) Stoich = (0.126 - 5.066) x 10^{-4} M

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.01(D₀)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.126</td>
<td>0.15</td>
<td>0.139</td>
<td>0.021</td>
<td>-4.62</td>
</tr>
<tr>
<td>3.</td>
<td>0.325</td>
<td>0.37</td>
<td>0.455</td>
<td>0.065</td>
<td>-4.84</td>
</tr>
<tr>
<td>4.</td>
<td>0.399</td>
<td>0.44</td>
<td>0.597</td>
<td>0.090</td>
<td>-4.82</td>
</tr>
<tr>
<td>5.</td>
<td>0.645</td>
<td>0.66</td>
<td>[D]</td>
<td>1.300</td>
<td>0.182</td>
</tr>
<tr>
<td>6.</td>
<td>1.279</td>
<td>0.94</td>
<td>4.227</td>
<td>0.619</td>
<td>-4.83</td>
</tr>
<tr>
<td>7.</td>
<td>1.797</td>
<td>1.02</td>
<td>7.214</td>
<td>1.081</td>
<td>-4.82</td>
</tr>
<tr>
<td>8.</td>
<td>2.316</td>
<td>1.06</td>
<td>10.500</td>
<td>1.572</td>
<td>-4.82</td>
</tr>
<tr>
<td>9.</td>
<td>5.066</td>
<td>1.16(D∞)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

pKₐ = 4.35  

Average pK = -4.83±0.02

pK from table No = -4.84±0.02

pK from graph = -4.84

Mean pK = -4.83±0.004
TABLE 24

2-2', Bipyridine - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
\text{[Base]}_\text{Stoich} & = 0.814 \times 10^4 \text{ M} \\
\lambda_{\text{Max: for the adduct}} & = 316 \text{ nm} \\
\log \xi & = 4.15 \\
\text{[Germanium tetrachloride]}_\text{Stoich} & = [0.126-5.066] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr.</th>
<th>[Acid]_\text{Stoich} \times 10^4</th>
<th>Absorbance of the adduct at 316 nm</th>
<th>[Base]_\text{Eq} \times 10^4</th>
<th>[Acid]_\text{Eq} \times 10^4</th>
<th>[Adduct]_\text{Eq} \times 10^4</th>
<th>pK = -\log \left( \frac{\text{Adduct}}{(\text{Acid})(\text{Base})} \right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.01</td>
<td>0.814</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.126</td>
<td>0.15</td>
<td>0.705</td>
<td>0.021</td>
<td>0.105</td>
<td>-4.85</td>
</tr>
<tr>
<td>3.</td>
<td>0.325</td>
<td>0.37</td>
<td>0.554</td>
<td>0.065</td>
<td>0.260</td>
<td>-4.86</td>
</tr>
<tr>
<td>4.</td>
<td>0.399</td>
<td>0.44</td>
<td>0.565</td>
<td>0.090</td>
<td>0.309</td>
<td>-4.83</td>
</tr>
<tr>
<td>5.</td>
<td>0.645</td>
<td>0.66</td>
<td>0.351</td>
<td>0.182</td>
<td>0.463</td>
<td>-4.86</td>
</tr>
<tr>
<td>6.</td>
<td>1.279</td>
<td>0.94</td>
<td>0.154</td>
<td>0.619</td>
<td>0.660</td>
<td>-4.84</td>
</tr>
<tr>
<td>7.</td>
<td>1.797</td>
<td>1.02</td>
<td>0.898</td>
<td>1.081</td>
<td>0.716</td>
<td>-4.83</td>
</tr>
<tr>
<td>8.</td>
<td>2.316</td>
<td>1.06</td>
<td>0.070</td>
<td>1.572</td>
<td>0.744</td>
<td>-4.83</td>
</tr>
<tr>
<td>9.</td>
<td>5.066</td>
<td>1.16</td>
<td>-</td>
<td>4.252</td>
<td>0.814</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ pK_a = 4.35 \quad \text{Average } pK = -4.84 \pm 0.02 \]
Fig. 26  Electronic spectra of 2-2',Bipyridine (0.814x10^{-4} M) containing different concentrations Germanium tetrach in o-dichlorobenzene solution at 25°C (Mx10^{-4}), (1) 0. (2) 0.126, (3) 0.325, (4) 0.399, (5) 0.645, (6) 1.279 .797, (8) 2.316 and (9) 5.066.
A plot of [Adduct]/[Base] against [Acid]$_{Eq}$ for 2,2'-Bipyridine
TABLE 25

2-2', Biquinoline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

(Graphical Method)

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} &= 0.3995 \times 10^{-4} M \\
\lambda_{\text{Bax: for the adduct}} &= 356 \text{ nm} \\
\log \epsilon_{356} &= 4.39 \\
[\text{Germanium tetrachloride}]_{\text{Stoich}} &= (0.429 - 12.660) \times 10^{-4} M
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Acid ( \times 10^4 )</th>
<th>Stoich Absorbance at 356 nm</th>
<th>( \frac{\text{[Adduct]}}{\text{[Base]}} = \frac{D - D_0}{D_0 - D} ) from spectra</th>
<th>Acid ( \times 10^4 )</th>
<th>pK = (-\log\left(\frac{1}{(\text{Acid})} \cdot \frac{(\text{Adduct})}{(\text{Base})}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.01 (( D_0 ))</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.429</td>
<td>0.50</td>
<td>1.021</td>
<td>2.203</td>
<td>-4.65</td>
</tr>
<tr>
<td>3</td>
<td>0.501</td>
<td>0.45</td>
<td>1.204</td>
<td>0.220</td>
<td>-4.63</td>
</tr>
<tr>
<td>4</td>
<td>0.633</td>
<td>0.62</td>
<td>1.694</td>
<td>0.252</td>
<td>-4.65</td>
</tr>
<tr>
<td>5</td>
<td>0.905</td>
<td>0.71</td>
<td>2.592</td>
<td>0.289</td>
<td>-4.62</td>
</tr>
<tr>
<td>6</td>
<td>1.486</td>
<td>0.81</td>
<td>4.706</td>
<td>0.332</td>
<td>-4.61</td>
</tr>
<tr>
<td>7</td>
<td>2.685</td>
<td>0.89</td>
<td>9.800</td>
<td>0.362</td>
<td>-4.63</td>
</tr>
<tr>
<td>8</td>
<td>12.660</td>
<td>0.98 (( D ))</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ pK_a = 2.815^* \]

Average pK = -4.63±0.02

pK from table No. = -4.64±0.02

pK from graph = -4.63

Mean pK = -4.633±0.01
TABLE 26

2-2', Biquinoline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\text{(Base)}_{\text{Stoich}} = 0.3995 \times 10^{-4} \text{M} \\
\lambda_{\text{Max: for the adduct}} = 356 \text{ nm} \\
\log \varepsilon_{356} = 4.39 \\
[\text{Germanium tetrachloride}]_{\text{Stoich}} = [0.420 - 12.660] \times 10^{-4} \text{M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{\text{Stoich}} Mx10^4</th>
<th>Absorbance of the adduct at 356 nm</th>
<th>[Base]_{\text{Eq}} Mx10^4</th>
<th>[Acid]_{\text{Eq}} Mx10^4</th>
<th>[Adduct]_{\text{Eq}} Mx10^4</th>
<th>pK = -log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.429</td>
<td>0.50</td>
<td>0.196</td>
<td>0.226</td>
<td>0.203</td>
<td>-4.66</td>
</tr>
<tr>
<td>3.</td>
<td>0.501</td>
<td>0.54</td>
<td>0.179</td>
<td>0.281</td>
<td>0.220</td>
<td>-4.64</td>
</tr>
<tr>
<td>4.</td>
<td>0.633</td>
<td>0.62</td>
<td>0.147</td>
<td>0.381</td>
<td>0.252</td>
<td>-4.63</td>
</tr>
<tr>
<td>5.</td>
<td>0.905</td>
<td>0.71</td>
<td>0.110</td>
<td>0.616</td>
<td>0.289</td>
<td>-4.63</td>
</tr>
<tr>
<td>6.</td>
<td>1.486</td>
<td>0.81</td>
<td>0.069</td>
<td>1.154</td>
<td>0.332</td>
<td>-4.62</td>
</tr>
<tr>
<td>7.</td>
<td>2.655</td>
<td>0.89</td>
<td>0.037</td>
<td>2.293</td>
<td>0.362</td>
<td>-4.63</td>
</tr>
<tr>
<td>8.</td>
<td>12.660</td>
<td>0.98</td>
<td>-</td>
<td>12.261</td>
<td>0.399</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ pK_a = 2.815 \quad \text{Average } pK = -4.64 \pm 0.02 \]
Fig 28 Electronic spectra of 2-2', Biquinoline (0.3995x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25° (M x 10^{-4}) (1) 0.00, (2) 0.429, (3) 0.501, (4) 0.633, (5) 0.905, (6) 1.486, (7) 2.655 and (8) 12.600 mol. dm^{-1}. 
Fig 29 A plot of [Acid]/[Base] against [Acid]$_{eq}$ for 2,2'-Biquinol
TABLE 27

4-Methyl 1,3 phenylene diamine – Germanium tetrachloride interaction

in o-dichlorobenzene solution at 25°C

\[ [\text{Base}]_{\text{Stoich}} = 0.982 \times 10^{-4} \text{M} \]

\[ \lambda_{\text{Max}}: \text{for the base} = 300 \text{ nm} \]

\[ \log \varepsilon_{300} = 3.526 \]

\[ [\text{Germanium tetrachloride}]_{\text{Stoich}} = (0.151 - 5.537) \times 10^{-4} \text{M} \]

<table>
<thead>
<tr>
<th>Sr, [Acid] _Stoich _N x 10^4</th>
<th>Absorbance of the base at 300 nm</th>
<th>[Base] _Eq _M x 10^4</th>
<th>[Acid] _Eq _M x 10^4</th>
<th>[Adduct] _Eq _M x 10^4</th>
<th>pK = -log ( \frac{[\text{Adduct}]}{[\text{Acid}] \cdot [\text{Base}]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.000</td>
<td>0.330</td>
<td>0.982</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2. 0.151</td>
<td>0.285</td>
<td>0.848</td>
<td>0.017</td>
<td>0.134</td>
<td>-4.97</td>
</tr>
<tr>
<td>3. 0.390</td>
<td>0.220</td>
<td>0.645</td>
<td>0.053</td>
<td>0.337</td>
<td>-4.99</td>
</tr>
<tr>
<td>4. 0.670</td>
<td>0.147</td>
<td>0.437</td>
<td>0.125</td>
<td>0.545</td>
<td>-5.00</td>
</tr>
<tr>
<td>5. 0.998</td>
<td>0.092</td>
<td>0.274</td>
<td>0.290</td>
<td>0.708</td>
<td>-4.95</td>
</tr>
<tr>
<td>6. 3.328</td>
<td>0.015</td>
<td>0.044</td>
<td>2.392</td>
<td>0.938</td>
<td>-4.95</td>
</tr>
<tr>
<td>7. 4.199</td>
<td>0.010</td>
<td>0.030</td>
<td>3.247</td>
<td>0.952</td>
<td>-4.99</td>
</tr>
<tr>
<td>8. 5.537</td>
<td>0.007</td>
<td>0.021</td>
<td>4.576</td>
<td>0.961</td>
<td>-5.00</td>
</tr>
</tbody>
</table>

\[ pK_a = 2.66 \]

Average \[ pK = -4.98 \pm 0.03 \]
Fig. 30  Electronic spectra of 4-Me\textsubscript{2}\textsubscript{2}1,3-diamino benzene (0.982x10\textsuperscript{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25° (Mx10\textsuperscript{-4}) (1) 0.00, (2) 0.151, (3) 0.390, (4) 0.670, (5) 0.998, (6) 3.328, (7) 4.199, (8) 5.537, mol. dm\textsuperscript{-3}. 
TABLE 28

1,2-diamino benzene - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\begin{align*}
[\text{Base}]_{\text{Stoich}} & = 3.699 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max}} \text{ for the base} & = 298 \text{ nm} \\
\log \varepsilon & = 3.596 \\
[\text{Germanium tetrachloride}]_{\text{Stoich}} & = [0.738 - 14.734] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich}</th>
<th>Absorbance of the base at 315 nm</th>
<th>[Base]_{Eq}</th>
<th>[Acid]_{Eq}</th>
<th>[Adduct]_{Eq}</th>
<th>pK = -log \left( \frac{[\text{Adduct}]}{[\text{Acid}] \cdot [\text{Base}]} \right)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>1.460</td>
<td>3.699</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.738</td>
<td>1.330</td>
<td>3.369</td>
<td>0.408</td>
<td>0.332</td>
<td>-3.380</td>
</tr>
<tr>
<td>3</td>
<td>2.143</td>
<td>1.120</td>
<td>2.837</td>
<td>1.281</td>
<td>0.862</td>
<td>-3.375</td>
</tr>
<tr>
<td>4</td>
<td>3.398</td>
<td>0.970</td>
<td>2.457</td>
<td>2.156</td>
<td>1.242</td>
<td>-3.370</td>
</tr>
<tr>
<td>5</td>
<td>4.578</td>
<td>0.840</td>
<td>2.128</td>
<td>3.007</td>
<td>1.571</td>
<td>-3.390</td>
</tr>
<tr>
<td>6</td>
<td>6.022</td>
<td>0.740</td>
<td>1.875</td>
<td>4.198</td>
<td>1.824</td>
<td>-3.365</td>
</tr>
<tr>
<td>7</td>
<td>14.734</td>
<td>0.381</td>
<td>0.965</td>
<td>12.000</td>
<td>2.734</td>
<td>-3.373</td>
</tr>
</tbody>
</table>

Average pK = -3.375±0.015
Fig. 31 Absorbance spectra of 1,2-diaminobenzene (3.699x10^{-4} M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10^{-4}), (1) 0.000, (2) 0.738, (3) 2.143, (4) 3.398, (5) 4.576, (6) 6.022, (7) 14.734 mol dm^{-3}
TABLE 29

6-nitroquinoline - Germanium tetrachloride interaction in o-dichlorobenzene solution at 25°C

\[
\text{[Base]}_{\text{Stoich}} = 3.904 \times 10^{-3} \text{M}
\]

\[
\lambda_{\text{Max:}} \text{ of the base} = 298 \text{ nm}
\]

\[
\log \varepsilon_{298} = 3.60
\]

\[
\text{[Germanium tetrachloride]}_{\text{Stoich}} = (2.223 - 7.724) \times 10^{-4} \text{M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich}</th>
<th>Absorbance of the base at 298 nm</th>
<th>[Base]_{eq}</th>
<th>[Acid]_{eq}</th>
<th>[Adduct]_{eq}</th>
<th>pK = -log \frac{\text{[Adduct]}}{\text{[Acid][B]}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.56</td>
<td>3.904</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>2.223</td>
<td>1.49</td>
<td>3.729</td>
<td>2.048</td>
<td>0.175</td>
<td>-2.360</td>
</tr>
<tr>
<td>3.</td>
<td>4.713</td>
<td>1.42</td>
<td>3.553</td>
<td>4.362</td>
<td>0.351</td>
<td>-2.354</td>
</tr>
<tr>
<td>4.</td>
<td>6.192</td>
<td>1.38</td>
<td>3.453</td>
<td>5.741</td>
<td>0.451</td>
<td>-2.356</td>
</tr>
<tr>
<td>5.</td>
<td>6.931</td>
<td>1.36</td>
<td>3.403</td>
<td>6.430</td>
<td>0.501</td>
<td>-2.360</td>
</tr>
<tr>
<td>6.</td>
<td>7.724</td>
<td>1.34</td>
<td>3.353</td>
<td>7.173</td>
<td>0.551</td>
<td>-2.360</td>
</tr>
</tbody>
</table>

Average pK = -2.36±0.006
Fig. 32  Electronic spectra of 6-nitroquinoline (3.904x10⁻⁴ M) containing different concentrations of Germanium tetrachloride in o-dichlorobenzene solution at 25°C (Mx10⁻⁴) (1) 0.00, (2) 2.223, (3) 4.713, (4) 6.192, (5) 6.931, (6) 7.724
EXPERIMENTAL

The preparation and purification of the chemicals were carried out by the same procedures as followed for the work reported in o-dichlorobenzene. The same experimental techniques and similar method for computing equilibrium constant are adopted for the work in ether as solvent. The same UV visible spectrophotometers were used for recording the electronic spectra.

Selection of Ether as medium for the Acid-Base interactions

Ortho dichlorobenzene is an organic solvent having feeble polarity. Its dipole moment is 2.50. (cf. that of water as 1.85). It is comparatively an inert solvent. Organic compounds and other covalent compounds of the type (MX_n) are quite soluble in o-dichlorobenzene. The solvent solute interactions are insignificant. Therefore, the species formed in ortho dichlorobenzene, as a result of Lewis acid-base interactions predominantly exists as strong adduct (anilinium type) or as weakly bonded adduct of charge transfer type. Such types of interactions have already been discussed in the preceding discussion.

Ether as solvent, for studying such interactions, has been selected for the following reasons:
1. It is polar, non-aqueous co-ordinating solvent.
2. Its dipole moment is 1.15
3. It could be made anhydrous easily.
4. Its properties, as a solvent for the bases, germanium tetrachloride and the adduct formed are experimentally favourable.
5. Most of the data on quantitative aspect of Lewis acidity, is available in ether. Therefore for comparison's sake, the present work is carried out in ether as solvent as well.

However, I faced quite a bit of difficulty in persuading this investigation as solvent is highly volatile. All the work reported in ether was performed in winter seasons. The solvent was purified and dried in the following manner:

**Purification of Ether**
*(Diethyl Ether)*

\[(C_2H_5)_2O\]  (Molecular weight 74.12)
Boiling Point 34.6°C

The main impurities, in commercial ether, are moisture and ethanol. For this work, diethyl ether (E Merck Grade) was taken in "dm"³ quick fit flask. A strong reducing agent, Lithium aluminium hydride, was added in small fractions into the solvent with continuous
shaking. Shaking was continued till no more bubbles of hydrogen were evolved. The solvent was refluxed for six hours. After refluxing, the solvent was filtered through sintered filter in a clean dried receiver. Sodium wire was introduced into the ether container with the aid of a press; the container was held beneath the die, and the plunger was slowly lowered. The whole sodium was pressed into wire passing into the distilled ether. The container was then kept closed by a quick fit calcium chloride guard tube to exclude moisture and to permit the escape of hydrogen if produced. The ether was allowed to stand over sodium wire for about twenty four hours. The next day the sodium wire for about twenty four hours. The next day the sodium wire was checked for brightness, the bright surface indicated that no hydrogen bubbles had evolved from sodium in ether. The ether was then transferred to a quick fit distillation flask fitted with calcium chloride tube and a still head having a quick fit thermometer. On distillation, the first fraction coming over, around the boiling point of ether, was rejected. The middle fraction (Boiling Point 35°C) was collected in another quick fit dried receiving flask. The flask containing pure ether, was then removed from the distillation assembly, stoppered and shifted to the dry box for further use.
RESULTS AND DISCUSSIONS IN ETHER

Interactions of germanium tetrachloride with aromatic amines in ether solution

Two types of bases were selected for studying their interactions with germanium tetrachloride in ether.

A. Aromatic amines, including aniline derivatives, diamines and N,N-dimethyl-α-naphthyl amine.

B. Aromatic heterocyclic nitrogen donor bases.

Interaction of germanium tetrachloride with class 'A' type of bases

Germanium tetrachloride being an acceptor, dissolves in the polar solvent to form a solution where the acid is solvated.

GeCl₄ + n Et₂O → GeCl₄(Et₂O)ₙ

93 Modie has studied the interactions of BF₃ with oxygen donor ketones in ether. The Lewis bases completed with the co-ordinated ether at Lewis acid.

BF₃ Et₂O + L₁ → BF₃L₁ + Et₂O

where 'L₁' is a solute base. In other studies by 172 Ali Muhammad and Satchell, the degree of solvation of the
acid and the adduct is assured to be unknown. The solvent being in excess, therefore, its concentration was not included while calculating the equilibrium constant values.

Germanium tetrachloride on interaction with a donor, produced the following equilibrium:

\[
\begin{align*}
\text{GeCl}_4 \cdot n\text{Et}_2\text{O} + L & \rightleftharpoons K \quad \text{GeCl}_4 \cdot L(\text{Et}_2\text{O})_{n-1} \cdot (n-1)\text{Et}_2\text{O} \\
\end{align*}
\]

The aniline derivatives have characteristic absorption bands in visible region. As the acid concentration is increased, the absorption band of the free base is knocked down and all these bases show similar spectral changes. The interactions are of the anilinium ion type. The new wave length for the adduct exists in the UV region. In the case of 4-methyl, 3-nitro aniline the adduct band occurs at 320 nm. The calculations for the pK values are made at wave length for the maximum absorption of free base except for 4-methyl, 3-nitro aniline where graphical method is adopted at the new adduct absorptions at 320 nm. The pK results obtained for these interactions are summerized in Table No. 30

For each system the pK values, computed from a number of sets of experiments performed for each interaction, gave constant values. This confirms the
assumed 1:1 stoichiometry. The spectral changes are shown in Fig. 34 — 44 and the calculated pK values for each system are given in Table 30.

The pK values observed provide an interesting comparison amongst the strength of bases studied. As observed earlier during the interactions of these bases in o-dichlorobenzene, the Lewis acidity squashed in ether as compared with the Bronsted acidity (ef. the pK values with pKₐ). The Bronsted acidity varies $3.24 \times 10^4$ times from base 1-7 whereas Lewis acidity differ 36.31 times for the same set of bases. The pK values determined in ether are significantly less than the values determined for the corresponding system in ortho dichlorobenzene. The effect of ether co-ordination on the acidity of germanium tetrachloride is clearly visible from the corresponding pK values in ether and o-dichlorobenzene. Ortho dichlorobenzene is considered as non co-ordinating solvent.

**Bronsted and Lewis basicities of the nitrogen donors towards germanium tetrachloride in ether**

A plot of pK values against pKₐ values of the bases in water is shown in Fig. 33. It is clear that similar factor effects both the Bronsted and Lewis basicities.
The bases number 3 and 7 are deviated from the linear relationship. The base No.3, being other than an aniline derivative, is not expected to fall in line with the other nitrogen bases. Moreover, N,N-dimethyl group substantially reduces its Lewis basicity due to steric eff
The base number 7 is very much reduced in its basicity due to the presence of two nitro groups. Nevertheless, these bases 1,2,4,6 obey a linear relationship of the equation:

\[ \text{pK} = 0.083 \ \text{pK}_a - 4.016 \]

The \( \Delta \text{pK} \) figures are shown in the left hand column of the Table 3°. The deviations lie within experimental errors. Effects of same type are reported with \( \text{ZnX}_2 \)
in ether and cadmium iodide in acetone. However, the discrepant \( K \) values are too large.

For sterically unhindered nitrogen base equilibria in ether, the accumulated data indicate that the acidities of the acids studied are in the order:

\[
\text{GeCl}_4 > \text{SnCl}_4 \sim \text{GaBr}_3 \sim \text{AlCl}_3 > \text{SnBr}_4 > \\
\text{ZnCl}_2 \sim \text{ZnBr}_2 \sim \text{ZnI}_2
\]

Thus the present study reveals that germanium tetrachloride shows strong acidic behaviour in ether towards the aniline
derivative bases.

The interaction with diamino bases is very strong. Calculations support the 1:1 stoichiometry of the adducts. But the pK value obtained for 1:4 diamino benzene is found to be rather very odd. The calculations as expected for a 1:2 adduct failed to give constant pK values. The spectral changes are not very regular at lower concentrations. But the almost constant pK values (as shown in Table 4) clearly support the 1:1 adduct formation. However, the structure of the adduct formed remains undecided.
Equilibrium constant of Germanium tetrachloride - aniline base adducts in Ether solution

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Aniline derivative</th>
<th>$\lambda_{\text{Max:}}$ for base nm</th>
<th>$\lambda_{\text{Max:}}$ for adduct nm</th>
<th>$pK_a$</th>
<th>$pK_{(\text{Exp})}$</th>
<th>$pK_{(\text{Calc})}$</th>
<th>$pK = [pK_{(\text{Exp})} - pK_a]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-methyl-</td>
<td>295</td>
<td>4.73$^b$</td>
<td>-3.57</td>
<td>-3.62</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Aniline</td>
<td>295</td>
<td>4.63</td>
<td>-3.83</td>
<td>-3.63</td>
<td>-0.20</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>N,N'-dimethyl-</td>
<td>310</td>
<td>4.566$^a$</td>
<td>-2.27</td>
<td>-3.64</td>
<td>-1.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Naphthyl amine-</td>
<td></td>
<td>3.71*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4-methyl, 3-nitro-</td>
<td>370</td>
<td>320</td>
<td>2.90$^a$</td>
<td>-3.83</td>
<td>-3.77</td>
<td>-0.06</td>
</tr>
<tr>
<td>5</td>
<td>2-methyl, 3-nitro-</td>
<td>355</td>
<td></td>
<td></td>
<td>-2.774</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2-methyl, 4-nitro-</td>
<td>355</td>
<td>0.94$^a$</td>
<td>-3.97</td>
<td>-3.94</td>
<td>-0.03</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3,5-dinitro-</td>
<td>390</td>
<td>0.22$^c$</td>
<td>-1.96</td>
<td>-3.998</td>
<td>2.038</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2,6-dinitro-</td>
<td>420</td>
<td></td>
<td></td>
<td>-1.778</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1,2-diaminobenzene</td>
<td>295</td>
<td></td>
<td></td>
<td>-3.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1,4-diaminobenzene</td>
<td>295</td>
<td></td>
<td></td>
<td>-3.575</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2-methyl, 5-nitro-</td>
<td></td>
<td>2.32$^a$</td>
<td>No interaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2-nitro-</td>
<td></td>
<td></td>
<td>No interaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2-chloro, 4-nitro-</td>
<td></td>
<td></td>
<td>No interaction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>4-chloro, 2-nitro-</td>
<td></td>
<td></td>
<td>No interaction</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a = 83$

$b = 161$

$c = 162$

* = Determined in present work.

Equation for the linear relationship between $pK$ Vs. $pK_a$ for GeCl$_4$ interactions with aniline bases.

$$pK = 0.083 \times pK_a - 4.016$$
Fig. 33: Plot of $PK$ vs. $pK_a$ values of $\text{Catecholammonium}$ tallow chloride with aniline base adduct in ether.

$pK = 0.083 \quad pK_a = 4.016$
TABLE 31

3. Methyl aniline - Germanium tetrachloride interaction in Ether at 25°C

\[
\begin{align*}
[B]_{\text{Stoich}} &= 1.6 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max: for the base}} &= 295 \text{ nm} \\
\log 295 &= 3.53 \\
[B]_{\text{Germanium tetrachloride}}^{\text{Stoich}} &= [0.601 - 27.858] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{\text{Stoich}}</th>
<th>Absorbance of the base at 245 nm</th>
<th>[Base]_{\text{Eq}}</th>
<th>[Acid]_{\text{Eq}}</th>
<th>[Adduct]_{\text{Eq}}</th>
<th>pK_a = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.540</td>
<td>1.600</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.601</td>
<td>0.470</td>
<td>1.392</td>
<td>0.393</td>
<td>0.208</td>
<td>-3.58</td>
</tr>
<tr>
<td>3.</td>
<td>1.889</td>
<td>0.357</td>
<td>1.058</td>
<td>1.347</td>
<td>0.542</td>
<td>-3.58</td>
</tr>
<tr>
<td>4.</td>
<td>2.591</td>
<td>0.315</td>
<td>0.933</td>
<td>1.924</td>
<td>0.667</td>
<td>-3.57</td>
</tr>
<tr>
<td>5.</td>
<td>3.832</td>
<td>0.256</td>
<td>0.758</td>
<td>2.990</td>
<td>0.842</td>
<td>-3.57</td>
</tr>
<tr>
<td>6.</td>
<td>5.498</td>
<td>0.205</td>
<td>0.607</td>
<td>4.505</td>
<td>0.993</td>
<td>-3.56</td>
</tr>
<tr>
<td>7.</td>
<td>7.679</td>
<td>0.155</td>
<td>0.459</td>
<td>6.538</td>
<td>1.141</td>
<td>-3.58</td>
</tr>
<tr>
<td>8.</td>
<td>12.704</td>
<td>0.105</td>
<td>0.311</td>
<td>4.415</td>
<td>1.289</td>
<td>-3.56</td>
</tr>
<tr>
<td>9.</td>
<td>18.474</td>
<td>0.075</td>
<td>0.222</td>
<td>17.096</td>
<td>1.378</td>
<td>-3.56</td>
</tr>
<tr>
<td>10.</td>
<td>27.858</td>
<td>0.050</td>
<td>0.148</td>
<td>26.406</td>
<td>1.452</td>
<td>-3.57</td>
</tr>
</tbody>
</table>

\[pK_a = 4.73\] 

Average \[pK = -3.57 \pm 0.01\]
Fig. 34  Electronic spectra of 3-methyl aniline (1.6x10^{-4} M) containing different concentrations of \( \text{C}_{4}\text{H}_{9}\text{K} \) at 25°C (Mx10^{-4}) (1) 0.000, (2) 0.601, (3) 1 (4) 2.591, (5) 3.832, (6) 5.498, (7) 7.679, (8) 12.704, (9) 18.474, (10) 27.858, in ether.
TABLE 32

Aniline - Germanium tetrachloride interaction in Ether at 25°C

\[
[\text{Base}]_{\text{Stoich}} = 2.580 \times 10^{-4} \text{ M}
\]

\(\lambda_{\text{Max}}\) for the base = 295 nm

\[
\log \varepsilon_{295} = 3.42
\]

\[
[\text{Germanium tetrachloride}]_{\text{Stoich}} = (0.0601 - 3.3594) \times 10^{-4} \text{ M}
\]

| Sr. (Acid) No. | [Base] Eq | [Acid] Eq | [Adduct] Eq | Absorbance of the base at 295 nm | pK = -log \[
\frac{[\text{Adduct}]}{[\text{Acid}] [\text{Base}]}\]
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.000</td>
<td>0.680</td>
<td>2.5805</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2. 0.060</td>
<td>0.670</td>
<td>2.5425</td>
<td>0.022</td>
<td>0.0380</td>
<td>-3.83</td>
</tr>
<tr>
<td>3. 0.496</td>
<td>0.600</td>
<td>2.2769</td>
<td>0.127</td>
<td>0.0360</td>
<td>-3.84</td>
</tr>
<tr>
<td>4. 0.843</td>
<td>0.550</td>
<td>2.0872</td>
<td>0.3496</td>
<td>0.4933</td>
<td>-3.83</td>
</tr>
<tr>
<td>5. 1.524</td>
<td>0.464</td>
<td>1.7608</td>
<td>0.7046</td>
<td>0.8197</td>
<td>-3.82</td>
</tr>
<tr>
<td>6. 2.268</td>
<td>0.380</td>
<td>1.4420</td>
<td>1.1295</td>
<td>1.1385</td>
<td>-3.84</td>
</tr>
<tr>
<td>7. 2.832</td>
<td>0.335</td>
<td>1.2713</td>
<td>1.5232</td>
<td>1.3092</td>
<td>-3.83</td>
</tr>
<tr>
<td>8. 3.359</td>
<td>0.300</td>
<td>1.1384</td>
<td>1.9173</td>
<td>1.4421</td>
<td>-3.82</td>
</tr>
</tbody>
</table>

\(pK_a = 4.63\) \quad \text{Average} \ pK = -3.83 \pm 0.01
Fig. 35 Electronic spectra of aniline ($2.5805 \times 10^{-4} \text{M}$) containing different concentrations in ether at ($M \times 10^{-4}$) (1) 0.000, (2) 0.0601, (3) 0.45, (4) 0.8429, (5) 1.5243, (6) 2.2680, (7) 2.8324, (8) 3.3594 mol dm$^{-3}$. 
TABLE 33

N,N-Dimethyl-α-naphthyl amine - Germanium tetrachloride interaction
in Ether at 25°C

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} & = 0.934 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max}}: & \quad \text{for the base} \\
\log C & = 310 \\
\text{[Germanium tetrachloride]}_{\text{Stoich}} & = [2.506 - 37.050] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Acid $_{\text{Stoich}}$ $\times 10^4$</th>
<th>Absorbance of the base at 310 nm</th>
<th>[Base] $\times 10^4$</th>
<th>[Acid] $\times 10^4$</th>
<th>[Adduct] $\times 10^4$</th>
<th>pK$^a$ = -log $\frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.880</td>
<td>0.934</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>2.506</td>
<td>0.841</td>
<td>0.893</td>
<td>2.465</td>
<td>0.041</td>
<td>-2.27</td>
</tr>
<tr>
<td>3.</td>
<td>5.219</td>
<td>0.800</td>
<td>0.849</td>
<td>5.134</td>
<td>0.085</td>
<td>-2.29</td>
</tr>
<tr>
<td>4.</td>
<td>7.141</td>
<td>0.780</td>
<td>0.828</td>
<td>7.035</td>
<td>0.106</td>
<td>-2.26</td>
</tr>
<tr>
<td>5.</td>
<td>12.350</td>
<td>0.712</td>
<td>0.756</td>
<td>12.172</td>
<td>0.178</td>
<td>-2.28</td>
</tr>
<tr>
<td>6.</td>
<td>15.366</td>
<td>0.690</td>
<td>0.732</td>
<td>12.164</td>
<td>0.202</td>
<td>-2.26</td>
</tr>
<tr>
<td>7.</td>
<td>24.700</td>
<td>0.595</td>
<td>0.632</td>
<td>24.398</td>
<td>0.302</td>
<td>-2.29</td>
</tr>
<tr>
<td>8.</td>
<td>37.050</td>
<td>0.520</td>
<td>0.552</td>
<td>36.680</td>
<td>0.382</td>
<td>-2.27</td>
</tr>
</tbody>
</table>

pK$^a$ = 4.566

Average pK$^a$ = -2.27±0.02
Fig. 36  Electronic spectra of dimethyl-α-naphthyl amine \((0.934 \times 10^{-4} \text{ M})\) containing different concentrations of \(\text{CH}_3\text{CH}_2\) at \((4 \times 10^{-4})\) 
(1) 0.000, (2) 2.506, (3) 5.219, (4) 7.141, (5) 12.350, (6) 15.366, (7) 24.700, (8) 37.050 in ether
TABLE 34

4-Methyl, 3-nitro aniline – Germanium tetrachloride interaction in Ether at 25°C

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} &= 1.577 \times 10^{-4} M \\
\lambda_{\text{Max}}: & \text{for the adduct} = 320 \text{ nm} \\
\log \varepsilon_{320} &= 3.786 \\
\text{[Germanium tetrachloride]}_{\text{Stoich}} &= [1.029 \text{ to } 22.680] \times 10^{-4} M
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr.</th>
<th>[Acid] (_{\text{Stoich}}^\text{Mx10}^4)</th>
<th>Absorbance of the adduct at 320 nm</th>
<th>(\frac{[\text{Adduct}]}{[\text{Base}]} = \frac{D - D_0}{D_K - D})</th>
<th>(\text{Eq pK} = -\log \frac{1}{[\text{Adduct}] / [\text{Acid}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.115 (D_0)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>1.029</td>
<td>0.324</td>
<td>0.326</td>
<td>0.500</td>
</tr>
<tr>
<td>3.</td>
<td>1.701</td>
<td>1.458</td>
<td>0.676</td>
<td>0.953</td>
</tr>
<tr>
<td>4.</td>
<td>2.315</td>
<td>0.535</td>
<td>0.977</td>
<td>1.441</td>
</tr>
<tr>
<td>5.</td>
<td>3.499</td>
<td>0.655 D</td>
<td>1.742</td>
<td>2.429</td>
</tr>
<tr>
<td>6.</td>
<td>8.970</td>
<td>0.830</td>
<td>-5.296</td>
<td>7.614</td>
</tr>
<tr>
<td>7.</td>
<td>16.250</td>
<td>0.890</td>
<td>10.333</td>
<td>14.796</td>
</tr>
<tr>
<td>8.</td>
<td>22.680</td>
<td>0.965 (D)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(pK_a = 2.90\) \hspace{2cm} \text{Average } pK = -3.836

pK value from graph = -3.84

Mean pK = -3.838
Fig 37. Electron spectra of 4-methyl, 2-nitro anilines (1.57 x 1
containing different concentrations of Grunionium tetrachlorid at 1
(0.10 M) 1, 0.00, 2, 1.029, 3, 1.701, 4, 2.315, 5, 3.499, 6, 8.1
7, 16.250, 8, 22.680
Fig. 38

A plot of [Adduct]/[amine] against [Acid]_eq for 4-methyl, 2-nitroaniline
TABLE 35

2-methyl, 3-nitro aniline - Germanium tetrachloride interaction in Ether at 25°C

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} &= 1.971 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max}} &\text{ for the base} = 355 \text{ nm} \\
\log \varepsilon &\text{ at 355} = 3.22 \\
\text{[Germanium tetrachloride]}_{\text{Stoich}} &= [0.472-4.856] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.328</td>
<td>1.971</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.472</td>
<td>0.320</td>
<td>1.923</td>
<td>0.424</td>
<td>0.048</td>
<td>-2.77</td>
</tr>
<tr>
<td>3.</td>
<td>1.323</td>
<td>0.306</td>
<td>1.839</td>
<td>1.191</td>
<td>0.132</td>
<td>-2.78</td>
</tr>
<tr>
<td>4.</td>
<td>2.411</td>
<td>0.290</td>
<td>1.742</td>
<td>2.182</td>
<td>0.229</td>
<td>-2.78</td>
</tr>
<tr>
<td>5.</td>
<td>3.589</td>
<td>0.275</td>
<td>1.652</td>
<td>3.270</td>
<td>0.319</td>
<td>-2.77</td>
</tr>
<tr>
<td>6.</td>
<td>4.856</td>
<td>0.260</td>
<td>1.562</td>
<td>4.447</td>
<td>0.409</td>
<td>-2.77</td>
</tr>
</tbody>
</table>

Average pK = -2.77±0.006
Fig. 39 Electronic spectra of 2-methyl, 3-nitroaniline (1.971x10^{-4} M) containing \text{GdCl}_4^\text{−} different concentrations in ether at 25º (Mx10^{-4}) (1)0.000 (2)0.472, (3) 1.323, (4) 2.411, (5) 3.589, (6) 4.856.
### 2-methyl, 4-nitro aniline - Germanium tetrachloride interaction in Ether at 25°C

\[
\text{[Base]}_{\text{Stoich}} = 0.236 \times 10^{-4} \text{ M}
\]

\[
\lambda_{\text{Max: for the base}} = 355 \text{ nm}
\]

\[
\log \epsilon_{335} = 4.472
\]

\[
\text{[Germanium tetrachloride]}_{\text{Stoich}} = (0.162 - 0.353) \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr.</th>
<th>[Acid] (_{\text{Stoich}}) (\times 10^4)</th>
<th>Absorbance of the base at 355 nm (\times 10^4)</th>
<th>[Base] (_{\text{Eq}}) (\times 10^4)</th>
<th>[Acid] (_{\text{Eq}}) (\times 10^4)</th>
<th>[Adduct] (_{\text{Eq}}) (\times 10^4)</th>
<th>pK = (-\log) (\frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.700</td>
<td>0.236</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.162</td>
<td>0.620</td>
<td>0.209</td>
<td>0.135</td>
<td>0.027</td>
<td>-3.98</td>
</tr>
<tr>
<td>3.</td>
<td>0.214</td>
<td>0.600</td>
<td>0.202</td>
<td>0.180</td>
<td>0.034</td>
<td>-3.97</td>
</tr>
<tr>
<td>4.</td>
<td>0.263</td>
<td>0.575</td>
<td>0.194</td>
<td>0.226</td>
<td>0.042</td>
<td>-3.98</td>
</tr>
<tr>
<td>5.</td>
<td>0.353</td>
<td>0.550</td>
<td>0.185</td>
<td>0.302</td>
<td>0.051</td>
<td>-3.96</td>
</tr>
</tbody>
</table>

\[
pK_a = 0.94
\]

Average pK = -3.97±0.01
Fig. 40 Electronic spectra of 2-methyl, 4-nitro aniline \( (0.236 \times 10^{-4} \text{ M}) \) containing \( \text{CdCl}_2 \) at different concentrations in ether at 25°C \( (M \times 10^{-4}) \): (1) 0.000, (2) 0.162, (3) 0.214, (4) 0.258, (5) 0.353.
TABLE 37

3,5-dinitro aniline - Germanium tetrachloride interaction in Ether at 25°C

\[
\begin{align*}
\text{[Base]}_{\text{Stoich}} &= 1.966 \times 10^{-4} \text{ M} \\
\lambda_{\text{Max: for the base}} &= 390 \text{ nm} \\
\log \varepsilon_{390} &= 3.62 \\
\text{[Germanium tetrachloride]}_{\text{Stoich}} &= [5.722 - 10.340] \times 10^{-4} \text{ M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid] Eq Mx10^4</th>
<th>Absorbance at 390 nm</th>
<th>[Base] Eq Mx10^4</th>
<th>[Acid] Eq Mx10^4</th>
<th>[Adduct] Eq Mx10^4</th>
<th>pK = -log \frac{[Adduct]}{[Acid][Base]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.830</td>
<td>1.966</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>5.722</td>
<td>0.790</td>
<td>1.871</td>
<td>5.575</td>
<td>0.095</td>
<td>-1.96</td>
</tr>
<tr>
<td>3</td>
<td>10.340</td>
<td>0.760</td>
<td>1.800</td>
<td>10.174</td>
<td>0.166</td>
<td>-1.96</td>
</tr>
</tbody>
</table>

\[ pK_a = 0.22 \]

Average pK = -1.96
Fig. 41  Electronic spectra of 3-5,dinitro aniline \((1.966 \times 10^{-4} \text{M})\) containing GeCl₄ in ether at 25°C \((M \times 10^{-4})\) (1) 0.000, (2) 5.722, (3) 10.340
TABLE 38

2,6-dinitro aniline - Germanium tetrachloride interaction in ether at 25°C

\[ \text{[Base]}_{\text{Stoich}} = 0.3932 \times 10^{-4} \text{ M} \]

\[ \chi_{\text{Max}} \text{ for the base} = 420 \text{ nm} \]

\[ \log \varepsilon_{420} = 4.02 \]

\[ \text{[Germanium tetrachloride]}_{\text{Stoich}} = (5.670 - 14.743) \times 10^{-4} \text{ M} \]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{\text{Stoich}} \times 10^4</th>
<th>Absorbance of the base at 295 nm \times 10^4</th>
<th>[Base]_{\text{Eq}} \times 10^4</th>
<th>[Acid]_{\text{Eq}} \times 10^4</th>
<th>[Adduct]_{\text{Eq}} \times 10^4</th>
<th>pK = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.000</td>
<td>0.414</td>
<td>0.393</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>5.670</td>
<td>0.400</td>
<td>0.380</td>
<td>5.657</td>
<td>0.013</td>
<td>-1.778</td>
</tr>
<tr>
<td>3</td>
<td>11.340</td>
<td>0.380</td>
<td>0.361</td>
<td>14.711</td>
<td>0.032</td>
<td>-1.778</td>
</tr>
</tbody>
</table>

Average pK = -1.778±0.00
Fig. 42  Electronic spectra of 2-6, dinitro aniline (0.3932x10^{-4}M) containing different concentrations of ether at 25°C (Mx10^{-4}) (1) 0.000, (2) 5.670, (3) 11.340
TABLE 39

1-2, diamine benzene - Germanium tetrachloride interaction in ether at 25°C

\[
\text{[Base]}_{\text{Stoich}} = 1.849 \times 10^{-4} \text{ M}
\]

\[
\lambda_{\text{Max}} \text{ for the base} = 295 \text{ nm}
\]

\[
\log \in 295 = 3.697
\]

\[
\text{[Germanium tetrachloride]}_{\text{Stoich}} = [0.261 - 9.993] \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid] \times 10^4</th>
<th>Absorbance of the base at 295 nm</th>
<th>[Base] \times 10^4</th>
<th>[Acid] \times 10^4</th>
<th>[Adduct] \times 10^4</th>
<th>pK = -\log \frac{[Adduct]}{[Acid][Base]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.920</td>
<td>1.849</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.261</td>
<td>0.860</td>
<td>1.728</td>
<td>0.140</td>
<td>0.121</td>
<td>-3.70</td>
</tr>
<tr>
<td>3.</td>
<td>0.351</td>
<td>0.840</td>
<td>1.688</td>
<td>0.190</td>
<td>0.161</td>
<td>-3.70</td>
</tr>
<tr>
<td>4.</td>
<td>0.625</td>
<td>0.780</td>
<td>1.567</td>
<td>0.343</td>
<td>0.282</td>
<td>-3.72</td>
</tr>
<tr>
<td>5.</td>
<td>0.9-3</td>
<td>0.722</td>
<td>1.451</td>
<td>0.535</td>
<td>0.398</td>
<td>-3.71</td>
</tr>
<tr>
<td>6.</td>
<td>1.157</td>
<td>0.680</td>
<td>1.566</td>
<td>0.674</td>
<td>0.483</td>
<td>-3.72</td>
</tr>
<tr>
<td>7.</td>
<td>2.408</td>
<td>0.500</td>
<td>1.005</td>
<td>1.564</td>
<td>0.844</td>
<td>-3.73</td>
</tr>
<tr>
<td>8.</td>
<td>5.463</td>
<td>0.275</td>
<td>0.553</td>
<td>4.167</td>
<td>1.296</td>
<td>-3.75</td>
</tr>
<tr>
<td>9.</td>
<td>9.993</td>
<td>0.160</td>
<td>0.321</td>
<td>8.465</td>
<td>1.528</td>
<td>-3.75</td>
</tr>
</tbody>
</table>

Average pK = -3.72±0.03
**TABLE 40**

1,4-diamino benzene – Germanium tetrachloride interaction in ether at 25°C

\[
\begin{align*}
\text{[Base]} & \text{ Stoich} = 2.219 \times 10^{-4} \text{M} \\
\lambda_{\text{Max}} \text{ for the base} & = 325 \text{ nm} \\
\log \varepsilon_{325} & = 3.38 \\
\text{[Germanium tetrachloride]} & \text{ Stoich} = [0.162 - 19.566] \times 10^{-4} \text{M}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sr.</th>
<th>[Acid] Stoich ( \times 10^4 )</th>
<th>Absorbance of the base ( \text{at 325 nm} )</th>
<th>[Base] ( \text{Eq} \times 10^4 )</th>
<th>[Acid] ( \text{Eq} \times 10^4 )</th>
<th>[Adduct] ( \text{Eq} \times 10^4 )</th>
<th>pK = -log ( \frac{[\text{Adduct}]}{[\text{Acid}] [\text{Base}]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>0.532</td>
<td>2.219</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.162</td>
<td>0.515</td>
<td>2.148</td>
<td>0.091</td>
<td>0.071</td>
<td>-3.56</td>
</tr>
<tr>
<td>3.</td>
<td>0.914</td>
<td>0.442</td>
<td>1.847</td>
<td>0.542</td>
<td>0.372</td>
<td>-3.57</td>
</tr>
<tr>
<td>4.</td>
<td>1.201</td>
<td>0.420</td>
<td>1.752</td>
<td>0.734</td>
<td>0.467</td>
<td>-3.56</td>
</tr>
<tr>
<td>5.</td>
<td>2.049</td>
<td>0.355</td>
<td>1.481</td>
<td>1.311</td>
<td>0.738</td>
<td>-3.58</td>
</tr>
<tr>
<td>6.</td>
<td>3.705</td>
<td>0.265</td>
<td>1.105</td>
<td>2.591</td>
<td>1.114</td>
<td>-3.59</td>
</tr>
<tr>
<td>7.</td>
<td>6.481</td>
<td>0.185</td>
<td>0.772</td>
<td>4.984</td>
<td>1.497</td>
<td>-3.59</td>
</tr>
<tr>
<td>8.</td>
<td>9.573</td>
<td>0.135</td>
<td>0.563</td>
<td>7.917</td>
<td>1.656</td>
<td>-3.57</td>
</tr>
<tr>
<td>9.</td>
<td>17.923</td>
<td>0.075</td>
<td>0.313</td>
<td>16.017</td>
<td>1.906</td>
<td>-3.58</td>
</tr>
<tr>
<td>10.</td>
<td>19.566</td>
<td>0.069</td>
<td>0.288</td>
<td>17.635</td>
<td>1.931</td>
<td>-3.58</td>
</tr>
</tbody>
</table>

Average pK = -3.575±0.015
Fig. 44  Electronic spectra of 1,4-diaminobenzene (2.219x10^-4 M) containing GdCl₄ in ether at 25°C (Mx10^-4) (1) 0.000, (2) 0.162, (3) 0.914, (4) 1.201, (5) 2.049, (6) 3.705, (7) 6.481, (8) 9.573, (9) 17.923, (10) 19.566.
Interaction of Germanium tetrachloride with aromatic heterocyclic nitrogen bases

Four bases; 2-aminopyridine, pyridine, 2,2'-bipyridine and 2,2'-biquinoline are studied in ether solutions. These compounds are highly basic as compared with the aniline derivatives as discussed under bases of class A type. In order to check their Bronsted basicity, $pK_a$ values of 2,2'-bipyridine is determined (Fig. 4, 2, Table 3) to be 4.12 (cf. of the literature value of 4.35). Except pyridine, the other nitrogen donors are bidentate and favourable for 1:1 interactions with germanium tetrachlorid

Graddon and Rana used pyridine and bipyridine for studying their interactions with organosilicon isocyanates in acetonitrile which behave as Lewis acids. The stability of the adduct with bipyridine is reported to be low enough for measurement of the formation constant. No evidence of chelation has been reported with bipyridine. The base being the weakest in the present group is undoubte gave adduct formation with a weak electron acceptor. Pyridine forms a stronger adduct formation as shown by enthalpy of formation.

The electronic spectra of the heterocyclic nitrogen bases have already been explained in the work performed in ortho dichlorobenzene. The free bases in ether, show absorption bands in the wave length range 250 - 340 nm.
On increasing germanium tetrachloride concentrations, the free base absorption decreases for all these cases correspondingly. There is an indication that the adducts formed have their characteristic absorption on the shorter wave length side of the free base absorption. The spectral effects observed are of the 'anilinium ion'type as noted for the substituted anilines in ether. However, no new charge transfer, longer wave length, absorption is found with these bases. (cf. some of the substituted aniline base gave charge transfer absorption on adduct formation).

The spectral changes for these interactions are shown in Fig. 46, 47, 48 and 49. Pyridine shows major absorption at 250 nm with a shoulder at 257 nm. On adduct formation with germanium tetrachloride, the shoulder developed into the major absorption and the originally major peak is observed to be reduced to a shoulder. This indicates the existence of more than one kind of pyridine species in solution. The bipyridine and biquinoline show more than one absorption bands; which were knocked down on adduct formation with germanium tetrachloride.

The adduct solutions were clear and no precipitation was observed in any of these solution. The pK values, as calculated for 1:1 interactions, are shown in Table No. 42, 43, 44 and 45. The pK values indicate quite a strong strong interaction for the acid-base equilibria.
Although the formation constants for these bases are remarkable less than for their corresponding interactions in ortho dichlorobenzene. Ether seems to quench the Lewis acidity of germanium tetrachloride and bases having a larger Bronsted basicity difference levelled by the presence of ether as solvent. The consistent pK results support the 1:1 stoichiometry for these adducts. The adducts are presumed to have structures of the following type:

\[
\begin{align*}
\text{N} \quad \text{GeCl}_4 \\
\text{N} \quad \text{GeCl}_4 \\
\text{N} \quad \text{GeCl}_4 \\
\end{align*}
\]

The observed spectral effects show the complete involvement of the donor centers.

However, the solvent, having \(\alpha\) polar and co-ordinati character, may give rise to secondary effects on the initially adducts formed in solution. As a result of the transfer of unshared electron pair from oxygen of ether to an orbital on germanium in germanium tetrachloride, the latter may get polarised to such an extent that Ge—Cl bonds might break to form ions in solution:
Similar effects have been predicted for the ferric chloride interactions with oxygen donors in benzene solution. However, conductometric measurements are required to throw light on such side reaction possibilities.

Although the Lewis basicity is compounded, but there is a linear relationship between pK and pK_a values for these bases. A straight line behaviour is shown in Fig. 45. The $\Delta^{pK}$ (difference between the experimental and calculated pK values) values are insignificant deviations from the linear relationship which lies well within the experimental errors. For germanium tetrachloride

$$pK = -0.086 \cdot pK_a + 3.077$$
TABLE 41

Equilibrium constant of Germanium tetrachloride - hetero cyclic nitrogen bases in Ether at 25°C

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Hetero cyclic nitrogen bases</th>
<th>λ Max: for the base in nm</th>
<th>pK_a</th>
<th>pK_(Exp)</th>
<th>pK_(Calc)</th>
<th>pK = (pK_(Exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2-Amino pyridine</td>
<td>296</td>
<td>6.82a</td>
<td>-3.63</td>
<td>-3.66</td>
<td>+0.03</td>
</tr>
<tr>
<td>2.</td>
<td>Pyridine</td>
<td>250</td>
<td>5.52a</td>
<td>-3.32</td>
<td>-3.55</td>
<td>-0.23</td>
</tr>
<tr>
<td>3.</td>
<td>2,2'-Bipyridine</td>
<td>230</td>
<td>4.35a</td>
<td>-3.69</td>
<td>-3.45</td>
<td>-0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>280</td>
<td>4.12*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>2,1'-Squarimidine</td>
<td>310</td>
<td>2.815*</td>
<td>-3.35</td>
<td>-3.32</td>
<td>-0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>325</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a = 161

* = Determined in present work.

Equation for the linear relationship between pK vs. pK_a for GeCl_4 interactions with heterocyclic nitrogen bases:

\[ pK = -0.086 \times pK_a - 3.077 \]
Fig. 45 Plot of $pK$ vs. $pK_a$ values of Germanium tetrachloride with tetro cyclic bases in ether

$pK = -0.086$  $pK_a = 3.077$
2-Amino pyridine - Germanium tetrachloride interaction in Ether at 25°C

\[
\frac{[\text{Base}]}{\text{Stoich}} = 1.530 \times 10^{-4} \text{ M}
\]

\[\lambda_{\text{Max: for the base}} = 296 \text{ nm}\]

\[\log \langle 296 \rangle = 3.97\]

\[\frac{[\text{Germanium tetrachloride}]}{\text{Stoich}} = (0.223 - 20.674) \times 10^{-4} \text{ M}\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]\text{Stoich}</th>
<th>Absorbance of the base at 296 nm</th>
<th>[Base]_{\text{Eq}} \times 10^4</th>
<th>[Acid]_{\text{Eq}} \times 10^4</th>
<th>[Adduct]_{\text{Eq}} \times 10^4</th>
<th>pK_{a} = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.44</td>
<td>1.530</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.223</td>
<td>1.36</td>
<td>1.445</td>
<td>0.138</td>
<td>0.058</td>
<td>-3.62</td>
</tr>
<tr>
<td>3.</td>
<td>0.865</td>
<td>1.16</td>
<td>1.232</td>
<td>0.567</td>
<td>0.298</td>
<td>-3.63</td>
</tr>
<tr>
<td>4.</td>
<td>1.245</td>
<td>1.06</td>
<td>1.126</td>
<td>0.841</td>
<td>0.404</td>
<td>-3.63</td>
</tr>
<tr>
<td>5.</td>
<td>2.175</td>
<td>0.87</td>
<td>0.924</td>
<td>1.573</td>
<td>0.606</td>
<td>-3.62</td>
</tr>
<tr>
<td>6.</td>
<td>3.015</td>
<td>0.74</td>
<td>0.786</td>
<td>2.271</td>
<td>0.744</td>
<td>-3.62</td>
</tr>
<tr>
<td>7.</td>
<td>6.452</td>
<td>0.43</td>
<td>0.457</td>
<td>5.379</td>
<td>1.073</td>
<td>-3.64</td>
</tr>
<tr>
<td>8.</td>
<td>15.236</td>
<td>0.20</td>
<td>0.212</td>
<td>13.918</td>
<td>1.318</td>
<td>-3.65</td>
</tr>
<tr>
<td>9.</td>
<td>20.674</td>
<td>0.15</td>
<td>0.159</td>
<td>19.303</td>
<td>1.371</td>
<td>-3.65</td>
</tr>
</tbody>
</table>

\[pK_{a} = 6.82\] 

Average \[pK = -3.63 \pm 0.02\]
Fig 46  Electronic spectra of 2-Amino pyridine ($1.530 \times 10^{-4}\text{M}$) containing GeCl₄, different concentration in ether at 25°C ($M \times 10^{-4}$), (1) 0.009, (2) 0.223, (3) 0.865, (4) 1.245, (5) 2.175, (6) 3.015, (7) 6.452, (8) 15.236, (9) 20.674.
TABLE 43

Pyridine - Germanium tetrachloride interaction in Ether at 85°C

\[
\text{[Base]}_{\text{Stoich}} = 2.022 \times 10^{-4} \text{ M}
\]

\[
\lambda_{\text{Max}}: \text{for the base} = 250 \text{ nm}
\]

\[
\log \varepsilon_{250} = 3.96
\]

\[
[\text{Germanium tetrachloride}]_{\text{Stoich}} = [0.690 \quad 10.728] \times 10^{-4} \text{ M}
\]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich} Mx10^4</th>
<th>Absorbance of the base at 250 nm Mx10^4</th>
<th>[Base]_{Eq} Mx10^4</th>
<th>[Acid]_{Eq} Mx10^4</th>
<th>[Adduct]_{Eq} Mx10^4</th>
<th>pK = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.87</td>
<td>2.022</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.690</td>
<td>1.69</td>
<td>1.837</td>
<td>0.515</td>
<td>0.185</td>
<td>-3.30</td>
</tr>
<tr>
<td>3.</td>
<td>1.654</td>
<td>1.48</td>
<td>1.609</td>
<td>1.241</td>
<td>0.413</td>
<td>-3.31</td>
</tr>
<tr>
<td>4.</td>
<td>2.363</td>
<td>1.36</td>
<td>2.363</td>
<td>1.797</td>
<td>0.566</td>
<td>-3.33</td>
</tr>
<tr>
<td>5.</td>
<td>3.545</td>
<td>1.18</td>
<td>3.545</td>
<td>2.806</td>
<td>0.739</td>
<td>-3.31</td>
</tr>
<tr>
<td>6.</td>
<td>4.727</td>
<td>1.02</td>
<td>4.727</td>
<td>3.814</td>
<td>0.913</td>
<td>-3.33</td>
</tr>
<tr>
<td>7.</td>
<td>5.908</td>
<td>0.92</td>
<td>5.908</td>
<td>4.886</td>
<td>1.022</td>
<td>-3.32</td>
</tr>
<tr>
<td>8.</td>
<td>7.649</td>
<td>0.78</td>
<td>7.649</td>
<td>6.475</td>
<td>1.174</td>
<td>-3.33</td>
</tr>
<tr>
<td>9.</td>
<td>10.728</td>
<td>0.61</td>
<td>10.728</td>
<td>9.369</td>
<td>1.359</td>
<td>-3.34</td>
</tr>
</tbody>
</table>

\[pK_a = 5.52\]  \hspace{2cm} \text{Average } pK = -3.32 \pm 0.02
Fig. 47 Electronic spectra of Pyridine (2.0 × 10⁻⁴ M) containing GeCl₄ in different concentrations of ether at 25°C (Mx10⁻⁴) (1) 0.000, (2) 0.690, (3) 1.654, (4) 2.363, (5) 3.545, (6) 4.727, (7) 5.908, (8) 7.649, (9) 10.728.
TABLE 44

*2,2'-Bipyridine - Germanium tetrachloride interaction in Ether

at 25°C

<table>
<thead>
<tr>
<th>[Base]_{Stoich}</th>
<th>= 0.816 x 10^{-4} M</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{\text{MAX}} ) for the base</td>
<td>= 280 nm</td>
</tr>
<tr>
<td>( \log \varepsilon_{280} )</td>
<td>= 4.23</td>
</tr>
<tr>
<td>[Germanium tetrachloride]_{Stoich}</td>
<td>= [0.236 - 19.262] x 10^{-4} M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich} Mx10^4</th>
<th>Absorbance of the base at 280 nm Mx10^4</th>
<th>[Base]_{Eq} Mx10^4</th>
<th>[Acid]_{Eq} Mx10^4</th>
<th>[Adduct]_{Eq} Mx10^4</th>
<th>( pK = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.40</td>
<td>0.816</td>
<td>0.000</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.236</td>
<td>1.29</td>
<td>0.752</td>
<td>0.172</td>
<td>0.064</td>
<td>-3.69</td>
</tr>
<tr>
<td>3.</td>
<td>0.449</td>
<td>1.20</td>
<td>0.699</td>
<td>0.332</td>
<td>0.117</td>
<td>-3.70</td>
</tr>
<tr>
<td>4.</td>
<td>1.587</td>
<td>0.88</td>
<td>0.513</td>
<td>1.274</td>
<td>0.313</td>
<td>-3.68</td>
</tr>
<tr>
<td>5.</td>
<td>2.773</td>
<td>0.66</td>
<td>0.385</td>
<td>2.342</td>
<td>0.431</td>
<td>-3.68</td>
</tr>
<tr>
<td>6.</td>
<td>4.924</td>
<td>0.44</td>
<td>0.256</td>
<td>4.364</td>
<td>0.560</td>
<td>-3.70</td>
</tr>
<tr>
<td>7.</td>
<td>9.454</td>
<td>0.26</td>
<td>0.151</td>
<td>8.789</td>
<td>0.665</td>
<td>-3.70</td>
</tr>
<tr>
<td>8.</td>
<td>19.262</td>
<td>0.14</td>
<td>0.081</td>
<td>18.527</td>
<td>0.735</td>
<td>-3.69</td>
</tr>
</tbody>
</table>

\( pK^a = 4.35 \)
\( 4.12^* \)

\( a = 161 \)

* = Determined in present work.

Average \( pK = -3.69 \pm 0.01 \)
Fig. 48  Electronic spectra of 2-2',Bipyridine \((0.816\times10^{-4}\text{ M})\) containing GeC different concentrations in ether at \((\text{Mx10}^{-4})\), (1) 0.000, (2) 0.236, (3) 0.446, (4) 1.567, (5) 2.773, (6) 4.924, (7) 9.454, (8) 19.262.
TABLE 45

2-2', Biquinoline - Germanium tetrachloride interaction in Ether at 25°C

\[ [\text{Base}]_{\text{Stoich}} = 0.406 \times 10^{-4} \text{ M} \]
\[ \lambda_{\text{Max}}, \text{ for the base} = 325 \text{ nm} \]
\[ \log \varepsilon_{325} = 4.41 \]

\[ [\text{Germanium tetrachloride}]_{\text{Stoich}} = \{0.298-1.601\} \times 10^{-4} \text{ M} \]

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>[Acid]_{Stoich}</th>
<th>Absorbance of the base at 325 nm</th>
<th>[Base]_{Eq}</th>
<th>[Acid]_{Eq}</th>
<th>[Adduct]_{Eq}</th>
<th>( pK_a = -\log \frac{[\text{Adduct}]}{[\text{Acid}][\text{Base}]_{\text{Stoich}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>0.000</td>
<td>1.04</td>
<td>0.406</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>0.298</td>
<td>0.98</td>
<td>0.382</td>
<td>0.274</td>
<td>0.024</td>
<td>-3.36</td>
</tr>
<tr>
<td>3.</td>
<td>0.739</td>
<td>0.90</td>
<td>0.351</td>
<td>0.684</td>
<td>0.055</td>
<td>-3.36</td>
</tr>
<tr>
<td>4.</td>
<td>0.883</td>
<td>0.88</td>
<td>0.343</td>
<td>0.820</td>
<td>0.063</td>
<td>-3.35</td>
</tr>
<tr>
<td>5.</td>
<td>1.212</td>
<td>0.83</td>
<td>0.324</td>
<td>1.120</td>
<td>0.082</td>
<td>-3.35</td>
</tr>
<tr>
<td>6.</td>
<td>1.601</td>
<td>0.78</td>
<td>0.304</td>
<td>1.499</td>
<td>0.102</td>
<td>-3.35</td>
</tr>
</tbody>
</table>

\( pK_a = 2.815 \) \quad \text{Average } pK = -3.35 \pm 0.01
Fig. 49 Electronic spectra of 2-2',Biquinoline (0.406x10^{-4} M) containing 6 different concentrations in ether at (Mx10^{-4}) (1) 0.000, (2) 0.298, (3) 0.739, (4) 0.582, (5) 1.212, (6) 1.601
QUANTITATIVE COMPARISON OF LEWIS ACIDITY

The present investigations involved measurements of the quantitative strength of germanium tetrachloride interaction with nitrogen donor bases. For the sake of comparison, studies are carried out in ortho dichlorobenzene and ether. The results obtained in the form of pK values are compared in both these solvents. These results are shown in Table 46 and 47, for the two solvent systems. The pK values for other Lewis acids as determined previously against the same set of bases and the solvent are also collected from the literature.

On looking at the two tables, the following conclusions can obviously be drawn:

1) Germanium tetrachloride has come out to be a Lewis acid in both the solvents.

2) The pK values are greater in ortho dichlorobenzene as compared with the corresponding value in ether. This is a similar phenomenon as observed with other Lewis acids.

3) Levelling effects on Lewis acidity are note-worth. In general, the comparison of Bronsted acidity (i.e. $pK_a$ values) with the Lewis acidity (i.e. pK values) shows that in protonic medium the Bronsted acidity is largely expanded
but, in non-aqueous media, the pK values are observed to show a compressed scale. These values are further squashed as the polar and co-ordination properties of the aprotic solvent are enhanced.

**Correlation of pK with pK\(_a\)**

Linear relationships are observed, in both the solvents, between the pK and pK\(_a\) values for a large number and types of nitrogen bases. Although there are exceptions where steric conditions forbid the formation of a stable adduct. Otherwise, the unhindered bases show normal expected behaviour.

For similar interactions, it has previously been shown\(^{167,176}\) that there exists a fair correlation between pK and pK\(_a\) values. In the present system, the data are filled by:

\[
\begin{align*}
  \text{pK} &= -0.370 \, \text{pK}\(_a\) - 2.518 & \text{for aniline derivatives in o-dichlorobenzene} \\
  \text{pK} &= 0.083 \, \text{pK}\(_a\) - 4.016 & \text{for aniline derivatives in ether} \\
  \text{pK} &= 0.461 \, \text{pK}\(_a\) - 6.415 & \text{for heterocyclic nitrogen bases in o-dichlorobenzene} \\
  \text{pK} &= -0.086 \, \text{pK}\(_a\) - 3.077 & \text{for heterocyclic nitrogen bases in ether.}
\end{align*}
\]

The slope for similar interactions in different solvents
are different. In general, the slopes for $pK - pK_a$ plots differ for different Lewis acids. It depends upon the base chosen.

$\text{GeCl}_4$ is found to be the strongest Lewis acid among all the other Lewis acids investigated and reported in the literature. The studies in ODB and Ether clearly show its position at the top of the acidities ever known before. However, the acidity in ether is much less as compared with the results obtained in ODB. The $pK$ values as determined in ODB are shown in Table (46). Most of the bases studied show 'anilinium ion' type of spectral changes but in a few cases (e.g. nitro aniline) charge transfer complex formation is detected. In the later cases, the stability of the adducts formed is not high. (Such a phenomenon is not observed when ether is used as medium for the same set of bases). Keeping in mind the order of acidity in ether solution as given in the following paragraph, the Lewis acid strength for the $\text{MX}_n$ type of compounds in ODB are given as follows:

$$\text{GeCl}_4 > \text{SnCl}_4 > \text{SnBr}_4 > \text{ZnBr}_2$$

While comparing the interactions of $\text{GeCl}_4$ in ether with 4-methyl, 2-nitro aniline, 2-methyl, 4-nitroaniline, 3,5-dinitro aniline and 2-chloro, 4-nitro aniline, the
### TABLE 46

Comparison of pK values of bases with different Lewis acids in ortho dichlorobenzene

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Aniline Bases</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
<th>Germanium tetrachloride</th>
<th>Stannic chloride</th>
<th>Stannic Bromide</th>
<th>Zinc Bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>4-methyl,3-nitro-</td>
<td>2.90</td>
<td>-3.51</td>
<td>-3.60&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-1.55</td>
</tr>
<tr>
<td>2.</td>
<td>2-methyl,4-nitro-</td>
<td>0.94</td>
<td>-3.54</td>
<td>-2.38&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-0.05&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>3,5-dinitro-</td>
<td>0.22&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>-2.37&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>2-nitro-</td>
<td>-0.29</td>
<td>-3.10</td>
<td>-2.30&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>2-chloro,4-nitro-</td>
<td>-0.94</td>
<td>-2.48</td>
<td>-0.70&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>4-chloro,2-nitro-</td>
<td>-1.03</td>
<td>-2.15</td>
<td>-0.70&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ a = 83 \]
\[ b = 177 \]
\[ c = 386 \]
values for equilibrium constants $^1 K$ are shown in Table (47). The various Lewis acids are arranged in the decreasing order of acidity in the table. The covalent or predominant metal halides of the type, $MX_n$, possess much higher acidic strength than the alkyl or aryl substituted $R_m MX_{n-m}$ type of compounds. Thus the presence of an alkyl or an aryl group quenches the acidity of the metal halide. Further, the electron with drawing group substituted in R directly reduce the acidity of $R_m MX_{n-m}$ compounds. Considering the data in ether solutions, the order of acidity for $MX_n$ type of Lewis acids can be shown as follows:

$$\text{GeCl}_4 > \text{BF}_3 < \text{GaBr}_3 < \text{GaCl}_3 > \text{AlBr}_3 < \text{AlCl}_3 > \text{SnCl}_4$$

$$\text{SnBr}_4 > \text{ZnCl}_2 > \text{ZnBr}_2 > \text{ZnI}_2 > \text{SbCl}_3$$

The levelling behaviour has already been known where highly ionizable protonic acids show similar acidic strength in water. The same system exhibit different acidic strength in a solvent like acetic acid. In a non-aqueous medium, Ali Muhammad and Satchell have clearly shown that the nature of a solvent has a definit effect on $K$ values with the present investigations, it may be generalized that it is a widely spread phenomenon for the $MX_n$ type of Lewis acid equilibria with donor nitrogen
TABLE 47

Comparison of pK values of bases with different Lewis acids in ether

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Lewis Acids</th>
<th>4-methyl 2-nitro aniline</th>
<th>2-methyl 4-nitro aniline</th>
<th>3,5-dinitro 4-nitro aniline</th>
<th>2-chloro 4-nitro aniline</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Germanium tetrachloride</td>
<td>-3.83*</td>
<td>-3.94*</td>
<td>-1.96*</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>Stannic Chloride</td>
<td>-2.70*</td>
<td>-</td>
<td>-0.90*</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>Boron trifluoride</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>Aluminium chloride</td>
<td>-</td>
<td>-1.76h</td>
<td>-</td>
<td>-0.05i</td>
</tr>
<tr>
<td>5.</td>
<td>Gallium tribromide</td>
<td>-3.03h</td>
<td>-0.83</td>
<td>-0.27h</td>
<td>-</td>
</tr>
<tr>
<td>6.</td>
<td>Gallium trichloride</td>
<td>-2.83h</td>
<td>-0.80h</td>
<td>-0.27h</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>Stannic Bromide</td>
<td>-2.27c</td>
<td>+0.38c</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>Zinc Bromide</td>
<td>-1.55b</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9.</td>
<td>Zinc</td>
<td>-1.30b</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10.</td>
<td>p-CH₃-C₆H₄-Stannic chloride</td>
<td>-0.70b</td>
<td>+0.62d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11.</td>
<td>Zinc chloride</td>
<td>-</td>
<td>0.75b</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12.</td>
<td>Ph.Stannic Bromide</td>
<td>-2.27c</td>
<td>0.38c</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>13.</td>
<td>p-ClC₆H₄-Stannic chloride</td>
<td>-1.10d</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14.</td>
<td>Me-Stannic chloride</td>
<td>-0.33d</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>15.</td>
<td>p-Ph.C₆H₄-Stannic chloride</td>
<td>+0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16.</td>
<td>n-Bu-Stannic chloride</td>
<td>+0.10d</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17.</td>
<td>Antimony trichloride</td>
<td>-</td>
<td>-1.76h</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[
pK values of the bases \\
\begin{align*}
\alpha &= 168 \\
b &= 116 \\
c &= 116 \\
d &= 179 \\
e &= 162 \\
f &= 171 \\
g &= 178 \\
\end{align*}
\]

\[
h &= 167 \\
i &= 174
\]
bases. In order to account for the levelling effects, in non-aqueous solvents (moreover in polar donating solvents one would think of the involvement of the solvent with the $MX_n$ interaction. Thus Lewis acid is entrapped among the solvent molecules.

$$MX_n + n\text{Et}_2\text{O} \xrightarrow{} MX_n \text{Et}_2\text{O}$$

Therefore, the $K$ values must be reduced as compared with a system, where the solvent is only non-polar or negligibly co-ordinating, the increasing polarity of the medium may result in ionization of the $MX_n$ compounds or of the adducts formed as a result of the primary 1:1 interactions. Such complications have been pointed out for ferric chloride interaction with donors in polar solvents.

In the present system, we assume, the adducts are covalently bonded and their strengths vary according to the N-metal bond in adducts. If strongly bonded 'anilinium' type of spectral changes take place, or otherwise weakly bonded adducts showed charge transfer new absorptions on the longer wave length side of the free base absorption bands.

However, for the heterocyclic nitrogen base interactic with germanium tetrachloride might provoke the formation
of ionic species. The stoichiometry remains 1:1 for the systems as well. From the present study, germanium tetrachloride has come out to be the best electron acceptor in ortho dichlorobenzene. Ether levels its acidity down but it still remains the best Lewis acid in ether as well. Due to its excellent acceptor properties germanium tetrachloride is predicted to possess attracting catalysing properties for some systems which might have some industrial importance.
The Lewis acids are an important class of compounds due to their catalytic activities. Normally covalent or predominantly covalent compound having general formula, \( MX_n \) (where \( X \) = halogen or electronegative group) fall into this class of compounds. Such compounds show their acidic properties by interactions with donor molecules. A large number of solid products are reported in the literature. Regarding the electron accepting strength of these compounds the acid base interactions have been followed in non-aqueous media.

\[
\text{B:} + MX_n \xrightleftharpoons{} \text{B : MX}_n
\]

The determination of equilibrium constant values provides us a measure to what extent the interactions have taken place. The \( pK_a \) data have been determined and compared for a number of Lewis acid in non-aqueous solvents. No such studies are reported in the quantitative strength of \( \text{GeCl}_4 \) as Lewis acid. In the present work, its interactions with a variety of N-donor bases are investigated spectrophotometrically in ODB and Ether as solvents. The experimental data computed from these interactions are shown in table (48). The bases used had a wider spread of their \( pK_a \) values. Aniline derivatives and pyridine
derivative basermet the above requirement.

On adduct formation, two types of spectral effects are observed. In most of the cases, a new absorption band appeared on the shorter wave length side of the free base absorptions. This spectral change has been called as the 'anilinium' type adduct absorption. For a few bases in ODB, a new absorption band appeared on the longer wave-length side of the free base absorption. This is the charge transfer transition. No such behaviour is observed in ether. Therefore, the acid-base adducts formed in ODB solution may be of two types where as all the adducts formed in ether are of the same type.

Whatever the spectral changes are observed, the equilibrium constant data are determined from these changes. The $pK$ values enable us to come to the following conclusions:

1) GeCl$_4$ has shown its superior acidic character towards the bases studied in the present work. No other acid studied so far is found comparable in strength with this metal halide.

2) In both the solvents (ODB & Ether), the acidity of GeCl$_4$ is noticed to be at the top of the acidity scale.

3) Levelling effects on Lewis acidity are observed. The Bronsted acidity is widely spread out whereas the Lewis
acidity (represented by the pK values) is suppressed in ODB solutions. It is further squashed in polar solvent like ether. However, the order of the pK values remains the same irrespective of the solvent chosen or the base used as reference.

4) Linear relationships are found between the pK_a values and the pK values in either of the solvents. Nevertheless the sterically hindered bases or least basic donors showed deviations from this type of the behaviour.

5) The Germanium tetrachloride-base adducts formed in solution are inferred to be having 1:1 stoichiometry irrespective of the fact that some of the bases used were bidentate. In such systems, the donor groups lie adjacent to each other. The composition of the adducts is supported by the consistent pK values and in some cases by observing nice isobestic points (e.g. 2,2'-Biquinoline).

6) Due to the excellent Lewis acidity, as shown by the interactions investigated in the present work, Germanium tetrachloride is predicted to have attractive catalytic properties. For some systems where Germanium tetrachloride may act as a catalyst, its industrial application will be beneficial.
## TABLE 4C

Values of $pK_a$ and $pK$ in ether and o-dichlorobenzene in different bases

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<td>1.</td>
<td>3-methyl aniline</td>
<td>4.73</td>
<td>-3.46</td>
<td>-3.57</td>
<td>11.</td>
<td>4-chloro,2-nitro</td>
<td>1.03</td>
<td>2.15</td>
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<td></td>
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<td></td>
<td></td>
<td>1-aniline</td>
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<td></td>
<td></td>
<td>benzene</td>
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<tr>
<td>3.</td>
<td>2-methyl,3-nitro</td>
<td>-</td>
<td>-4.12</td>
<td>-2.77</td>
<td>13.</td>
<td>1,4-diaminobenzene</td>
<td>-</td>
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<tr>
<td></td>
<td>aniline</td>
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<tr>
<td>4.</td>
<td>4-methyl,3-nitro</td>
<td>-</td>
<td>-3.51</td>
<td>-3.83</td>
<td>14.</td>
<td>4-methyl,1,2-dia</td>
<td>2.66</td>
<td>-4.98</td>
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<td></td>
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<td>5.</td>
<td>2-methyl,5-nitro</td>
<td>2.32</td>
<td>-3.04</td>
<td>-</td>
<td>15.</td>
<td>2-Amino pyridine</td>
<td>6.82</td>
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<tr>
<td>6.</td>
<td>2-methyl,4-nitro</td>
<td>-</td>
<td>-3.54</td>
<td>-3.97</td>
<td>16.</td>
<td>Pyridine</td>
<td>5.52</td>
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<td>7.</td>
<td>3,5-dinitro</td>
<td>0.22</td>
<td>-</td>
<td>-1.96</td>
<td>17.</td>
<td>N,N-dimethyl</td>
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<td>-4.56</td>
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<td>naphthyl amine</td>
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<td>2-nitro</td>
<td>-0.29</td>
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<td>-</td>
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<td>2,2'-bipyridine</td>
<td>4.35</td>
<td>-4.84</td>
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<td>4.12</td>
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<td>9.</td>
<td>2,6-dinitro</td>
<td>-</td>
<td>-2.675</td>
<td>-1.778</td>
<td>19.</td>
<td>2,2'-biquinoline</td>
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<tr>
<td>10.</td>
<td>2-chloro,4-nitro</td>
<td>-2.90</td>
<td>-2.48</td>
<td>-</td>
<td>20.</td>
<td>6-nitroquinoline</td>
<td>-</td>
<td>-2.36</td>
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<tr>
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$a = 161$

$* = $ Determined in present work

$c = 146$
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148. \( \text{C} \cdot \text{N} \cdot \text{R} \cdot \text{R} \cdot \text{O} \cdot \text{Q} \) with ultraviolet and visible spectroscopy.


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