Acid-Base Concept
For the proper understanding of the acid-base neutralisation reactions in ethylacetate, which are being discussed in this thesis, a few words about the acid-base concept in general, and the acids and bases in the solvo system ethylacetate in particular, will be most appropriate at this moment. Earlier definitions of acids and bases were based on their empirical properties rather than on their theoretical interpretation. William Lewis (1746) defined an acid as a substance which had a sour taste and produced effervescence with chalk and bases were characterised by their negative properties of destroying or reversing the effects caused by acids. Later on Lavoisier's idea of oxygen being the major constituent of acids held for some time. But the discovery of hydrobromic, hydroiodic and hydrocyanic acids cast doubt about the oxygen theory of acids.

Davy, at first, was the opinion that acidity does not depend upon any particular elementary substance but on the peculiar arrangement of various atoms in the compound. But later on he recognised replaceable hydrogen as an essential constituent of the acids. Bases were regarded as substances which react with acids to form salts.

With the advent of Arrhenius theory of electrolytic dissociation, an acid was defined as the substance which dissociated in solution to give hydrogen ions and base as the substance
which produced hydroxyl ions in solution. The degree of
dissociation or more precisely the dissociation constant of
an acid or a base was considered to be a fairly good measure
of its strength. With the discovery of basic properties of
substances such as pyridine, ketones, amides, etc., it was
realised that the presence of hydroxyl ions was not a criterion
for a base while an ionisable hydrogen was still regarded as
an essential criterion for a substance to act as an acid.

Bronsted (82,83) and Lowry (84) in 1923, independently
of each other, proposed the protonic theory of acids and bases
and defined an acid as a substance which could donate a proton
and a base as a substance which could accept the proton. This
definition of an acid includes certain anions and cations such
as \( \text{HSO}_4^- \), \( \text{H}_2\text{PO}_4^- \), \( \text{NH}_4^+ \), etc., besides the usual protonic acids,
as illustrated below:

\[
\text{HCl} \quad \overset{\rightarrow}{\longrightarrow} \quad \text{H}^+ + \text{Cl}^- \quad \ldots \quad (i)
\]
(neutral molecule)

\[
\text{NH}_4^+ \quad \overset{\rightarrow}{\longrightarrow} \quad \text{H}^+ + \text{NH}_3 \quad \ldots \quad (ii)
\]
(cation)

\[
\text{HSO}_4^- \quad \overset{\rightarrow}{\longrightarrow} \quad \text{H}^+ + \text{SO}_4^{2-} \quad \ldots \quad (iii)
\]
(anion)

It may be observed that an acid after donating a proton
becomes an acceptor of proton and behaves as a base and conversely,
a base on accepting a proton would behave as an acid. The acid
and base thus related are called a conjugate acid-base system.

\[ A \rightarrow B + H^+ \]

where A and B are termed as conjugate acid-base pair. For example,

\[
\text{O} = \text{C} + H^+ \rightarrow \text{O} = \text{C} - \text{O-H}
\]

carbonate is a conjugate base of bicarbonate and bicarbonate
is a conjugate acid of carbonate.

It is to be expected that a substance dissolved in
a particular solvent may behave as an acid or as a base
depending upon whether the solvent is a proton acceptor or
a proton donor. Urea behaves as an acid when dissolved in
liquid ammonia and as a base when dissolved in formic acid.
No doubt, this theory recognises the existence of a wide
variety of bases such as hydroxyl ions, amide ions, pyridine,
ketones, etc., but by restricting the term acids to proton
donors only, it excludes certain compounds like tin(IV) chloride,
aluminium(III) chloride, sulphur(VI) oxide, etc., which act as
acids in non-protonic solvents.

Franklin (loc. cit) was the first to propose the solvent
system theory and has shown that just as water ionises to
hydronium and hydroxyl ions, liquid ammonia ionises to produce
ammonium and amide ions;
and it was found that just as acids dissociate in water to produce hydronium ions, substances like ammonium chloride which furnish ammonium ions may act as acids in liquid ammonia. Substances like sodamide which furnish amide ions may similarly act as bases. These neutralise each other in liquid ammonia just as in aqueous solutions the corresponding compounds, hydrochloric acid and sodium hydroxide, neutralise each other.

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

\[ (\text{acid}) \quad (\text{base}) \quad (\text{salt}) \quad (\text{solvent}) \]

The solution of ammonium salts in liquid ammonia dissolves metals with the evolution of hydrogen.

\[ 2\text{NH}_4^+ + \text{Mg} \rightarrow \text{Mg}^{2+} + \text{H}_2 + 2\text{NH}_3 \]

In this and other similar cases, the transfer of a proton is involved. However, the workers have gone further and have extended the solvent theory to non-protonic solvents as well. Thus Jander and his co-workers (85) who have made extensive study of the acid-base reactions in liquid sulphur dioxide have shown it to ionise as :

\[ 2\text{SO}_2 \rightarrow \text{SO}^{2+} + \text{SO}_3^{2-} \]
Thionyl compounds act as acids and metal sulphites as bases when dissolved in this solvent and neutralisation reaction between the two has been confirmed by conductometric titrations and appear to support the view. The overall reaction may be visualised as:

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

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

\[ 2\text{Cs}^+ + \text{SO}_3^{2-} + \text{SO}^{2+} + 2\text{Cl}^- \longrightarrow 2\text{CsCl} + 2\text{SO}_2 \]

But it was later found that when thionyl chloride with labelled \( ^{33}\text{S} \), is dissolved in liquid sulphur dioxide exchange is very slow which would not be the case if the solvent and thionyl chloride both gave \( \text{SO}^{2+} \) ions. The dissolved thionyl compound may, therefore, ionise as \( \text{SOCl}^+ + \text{Cl}^- \), which is inherently more probable. When either tetramethyl ammonium chloride or rubidium chloride is added to a solution of thionyl chloride in tagged sulphur dioxide, sulphur exchange occurs readily. This can be explained by the conversion of \( \text{SO}^{2+} \) ion formed by sulphur dioxide to \( \text{SOCl}^+ \), as a result of the presence of excess of chloride ions. Similarly, acetic anhydride (86) ionises into acetylum ions and acetate ions. Substances like acetyl chloride and acetonitrile which increase the concentration of acetylum ions behave as acids and metallic acetates which increase the concentration of acetate ions behave as bases in acetic anhydride and the neutralisation reaction can be
Solvent system theory has rendered valuable service as it has stimulated work in many more aqueous solvents. However, the main limitations of the solvent theory is that it only accounts for the acidic and basic behaviour of substances in solutions.

Cady and Elsey (87) simplified the definition of acids and bases on the basis of the solvo system theory and defined acids as the solutes which give rise to the cations characteristic of the solvent and the bases as the solutes which give rise to the anions characteristic of the solvent. However, it has been shown that acid-base reactions can also take place in the vapour state, i.e., without any solvent (88). Moreover, the ionisation of the solvent is not a pre-requisite for acid-base reactions since typical acid-base reactions have been carried out in non-polar solvents such as carbon tetrachloride and benzene (89).

Lewis (90) put forward the electronic theory of acids and bases to broaden this concept and defined a base as a substance which has a pair of electrons which it can donate to
establish a coordinate bond and an acid as a substance which may accept an electron pair to form such a bond. The neutralisation reaction thus involves the union of two such molecules resulting in the formation of a coordinate bond. A neutralisation reaction between pyridine and aluminium bromide may serve as an example:

\[ \text{Br} \\text{N} : + \text{Al} : \text{Br} \rightarrow \text{Br} \\text{N} : \text{Al} : \text{Br} \]

The first type of Lewis acids includes the molecules having less than a full octet of electrons, i.e., boron(III) fluoride, e.g.,

\[ \text{H} \quad \text{F} \quad \text{H} \quad \text{F} \quad \text{H} \quad : \text{N} : + \text{B} : \text{F} \rightarrow \text{H} : \text{N} : \text{B} : \text{F} \quad \text{H} \quad \text{F} \quad \text{H} \quad \text{F} \]

The second type of Lewis acids includes the heavy metal ions with incomplete stable orbits, i.e., silver ion,

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

The third type of Lewis acids includes those compounds which contain double bond except \( \text{C} = \text{C} \) bond, i.e., carbon dioxide with water is a typical acid base reaction:

\[ \text{:C} : + \text{H} : \text{O} : \text{H} \rightarrow \text{C} : \text{O} : \text{H} \quad \text{:O} : \text{H} \]
But the major drawback of Lewis theory is that it completely ignores the role played by the solvent. The Arrhenius and Bronsted-Lowry theories are credited with the fact that they provide a reasonable quantitative estimate of the relative strengths of acids and bases but in the case of Lewis concept, quantitative treatment of relative strength is not applicable.

Smith (91) has correlated the theories of Lewis and Franklin. According to him, a solute is an acid when its molecules (neutral or charged) are electron pair acceptors towards the molecules or ions of the solvent while a solute is a base when its molecules (neutral or charged) are electron pair donors towards molecules or ions of the polar solvent. Thus the reaction between an acid and a base shall take place through the agency of the solvent, which reacts with the solute either as such or in the form of ions. Hence when a Lewis acid reacts with a basic solvent, the concentration of the cations is increased. Similar arguments can be advanced for bases. Thus the strength of the acids and bases depends upon the extent of their reaction with the solvent to form solvo acids and solvo bases respectively which may subsequently undergo ionisation. Therefore, neutralisation reaction is essentially an exchange reaction between the ions which already exist in the solution of the polar solvent. A typical acid-base neutralisation reaction between tin(IV)chloride and
pyridine in selenyl chloride has been explained by Smith as follows:

$$2\text{SeOCl}_2 \rightarrow \text{SeOCl}_2 \cdot \text{SeOCl}^+ + \text{Cl}^-$$

(ionisation of the solvent)

$$\text{SnCl}_4 + 2\text{SeOCl}_2 \rightarrow \text{SnCl}_4 \cdot 2\text{SeOCl}_2 \rightarrow 2\text{SeOCl}^+ + \text{SnCl}_6^{2-}$$

(formation and ionisation of the solvo acid)

$$2\text{C}_5\text{H}_5\text{N} + 2\text{SeOCl}_2 \rightarrow 2\text{C}_5\text{H}_5\text{N} \cdot \text{SeOCl}_2 \rightarrow 2\text{C}_5\text{H}_5\text{N} \cdot \text{SeOCl}^+ + 2\text{Cl}^-$$

(formation and ionisation of the solvo base)

$$2\text{C}_5\text{H}_5\text{N} \cdot \text{SeOCl}^+ + 2\text{Cl}^- + 2\text{SeOCl}^+ + \text{SnCl}_6^{2-} \rightarrow$$

$$(\text{C}_5\text{H}_5\text{N} \cdot \text{SeOCl})_2 \text{SnCl}_6 + 2\text{SeOCl}_2$$

(neutralisation reaction)

Similarly, neutralisation reactions in phosphoryl chloride (92), nitrosyl chloride (93), acetyl chloride (94) and benzoyl chloride (95) have been explained. The above mechanism holds good in the case of solvents which are basic enough to combine with an acid or acidic enough to combine with a base and may not be applicable to solvents which are relatively inert.

Jander and his co-workers (96) have obtained quite interesting results even with diethyl ether as a solvent which is slightly basic in character. According to them, ether ionises as:

$$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_5^+ + \text{OC}_2\text{H}_5^-$$
and a new type of acids such as Li AlH₄ have been discussed which react with diethyl ether and acetone to give compounds of the type Li Al [(C₂H₅)OH]₄ and Li Al [(CH₃)₂CH]₄ respectively and these complexes have been confirmed conductometrically.

A comprehensive study of acid-base reactions has been made by Usanovich (97) and he has evolved a more general theory. He has defined an acid as any substance which forms salts with bases through neutralisation, gives up cations or combines with anions or electrons. Similarly he has defined a base as a substance which neutralises acids, gives up anions or electrons or combines with cations. Although the underlying concept is that of the salt formation but its scope is very wide and embraces every example of acid-base behaviour explained by any of the theories so far considered. It also embodies in it the oxidation reduction processes as representatives of acid-base neutralisation reaction. This theory has classified all examples of acidity and basicity but it has too wide a scope and includes even reactions which are better considered from other points of view as oxidation reduction phenomenon.

The acid-base behaviour is long recognised in oxide system and it is a well known fact that no protons are involved in this system. Lux (98) suggested that for such systems an acid is a substance which gains oxide ions and a
base is a substance which gives up oxide ions as represented below:

\[
\text{Base} \xrightarrow{\text{acid + oxide ion}} \text{acid} + \text{oxide ion}
\]

\[
\text{CaO} \xrightarrow{-2+} \text{Ca}^{2+} + \text{O}^{2-}
\]

\[
\text{SO}_4^{2-} \xrightarrow{-2} \text{SO}_3 + \text{O}^{2-}
\]

The strength of acids and bases can be measured from the relative magnitude of the equilibrium constants. The application of this theory is very limited and it can be reduced to be a part of the more general theories.

Quite recently an alternative to solvent theory has been suggested by Meek and Drago (99) who have carried out spectroscopic studies of the solutions of iron(III)chloride in phosphorus oxychloride and triethylphosphate and have found that the two solutions are similar in behaviour and both have shown the presence of tetrachloro ferrate ion, \((\text{FeCl}_4^-)\) suggesting similar behaviour of iron(III) chloride in both the solvents as: \(2\text{FeCl}_3 \xrightarrow{\text{at}} \text{FeCl}_2^+ + \text{FeCl}_4^-\) and it has been pointed out that it is not all necessary to obtain chloride ions from the autoionisation of the solvent which is contrary to Gutmans discussion of the problem based upon the autoionisation of the solvent as:

\[
\text{POCl}_3 \xrightarrow{-2} \text{POCl}_2^+ + \text{Cl}^-
\]

But Hubeeb (100) has combined the two concepts by interrelating the two. It is found that both the interpretations appear to
differ widely but actually they are quite similar and his explanation can be summed up as follows:

\[
\text{AB} \xrightarrow{+} \text{A}^+ + \text{B}^-
\]

and he is of the opinion that there is nothing special about the term characteristic about the acid \( \text{A}^+ \) or base \( \text{B}^- \) which can exist in appreciable concentrations in the solvent \( \text{AB} \) and a stronger acid \( \text{C}^+ \) reacts with the solvent as:

\[
\text{C}^+ + \text{AB} \xrightarrow{-} \text{CB} + \text{A}^+
\]

and similar behaviour can be shown by a stronger base \( \text{D}^- \) and he further points out that solvent system concept merely points to strongest possible acid-base pair and their neutralisation reactions may form solvent molecules. It is just possible a further equilibrium may be set up in phosphorus oxychloride as:

\[
\text{POCl}_2^+ + \text{FeCl}_3 \xrightarrow{-} \text{POCl}_3 + \text{FeCl}_2^+
\]

The direction of the reaction will depend upon the relative strengths of acids \( \text{POCl}_2^+ \) and \( \text{FeCl}_2^+ \). If the latter is stronger, it will accept a chloride ion from the solvent and if it is weaker, it will solvolyse to form only a limited amount of dichlorophosphoryl (\( \text{POCl}_2^+ \)) cation and shall, therefore, act as a typical weak acid and if the solvent is such that chloride ion transfer cannot take place (e.g., triethylphosphate), the iron must be contented with a less basic species.

From the above discussion, one concludes that, in fact, no single theory is yet adequate to explain satisfactorily all
types of acid-base behaviour and each theory has applications in its special field. The difference between the solvent system concept and the Lewis theory is not that they are different ways of explaining acid-base phenomenon but they are different ways of looking at this phenomenon. The Lewis theory can explain certain phenomenon and this concept is more comprehensive but this cannot be the sole criterion of usefulness.

In the present discussion the modified solvent theory of Smith has been applied in order to understand the acid-base reactions in ethylacetate. Since it has been proved that it ionises into acetylium ions (CH$_3$CO)$^+$ and ethoxy ions (OC$_2$H$_5$)$^-$, those substances which increase the concentrations of acetylium ions would act as acids and those which increase the concentration of ethoxy ions would act as bases. It is found that Lewis acids like tin(IV)chloride, antimony(V)chloride, aluminium (III)chloride would act as solvo acids in ethylacetate since their adduct with ethylacetate ionises to give acetylium ions.

$$\text{SnCl}_4 + 2\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{SnCl}_4\cdot 2\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow 2\text{CH}_3\text{CO}^+ + [\text{SnCl}_4(\text{OC}_2\text{H}_5)_2]^{2-}$$

$$\text{SbCl}_5 + \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{SbCl}_5\cdot \text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CO}^+ + [\text{SbCl}_5(\text{OC}_2\text{H}_5)]^-$$

and organic tertiary bases such as pyridine, quinoline, etc., would act as solvo bases as these would increase the concentration...
of ethoxy ions as:

\[ B + CH_3COOC_2H_5 \rightarrow B\cdot CH_3COOC_2H_5 \rightarrow BCH_3CO^+ + (OC_2H_5)^- \]

Acetyl chloride and acetic anhydride could act as acids in ethylacetate but their degree of ionisation is very low, hence the complexes of Lewis acids with acetic anhydride and acetyl chloride, whose degree of ionisation is fairly high, act as ansolvo acids in ethylacetate as:

\[ SnCl_4 \cdot 2CH_3COCl \rightleftharpoons 2CH_3CO^+ + SnCl_6^{2-} \]

\[ SbCl_5 \cdot CH_3COCl \rightleftharpoons CH_3CO^+ + SbCl_6^- \]